Nanoabrasives retention and removal mechanisms in polyurethane pads for copper CMP

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Nanoabrasives Retention and Removal Mechanisms in Polyurethane Pads for Cu CMP

by

Iftikhar Ul-hasen

A Dissertation
Submitted to the University at Albany, State University of New York
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Iftikhar Ul-hasen

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ABSTRACT

The continued reduction in integrated circuit (IC) feature size requires similar reductions in surface defectivity. A key source of surface defects in IC fabrication processes stems from nanoabrasives used in chemical-mechanical planarization (CMP) processing. During CMP processing, polished surfaces are more vulnerable to defects including scratching, nanoabrasive particle adhesion and nanoabrasive agglomerate adhesion. The removal of these nano-sized particles is a priority for the IC fabrication industry and is reflected in the 2008 ITRS defect budget. However, there is insufficient technical understanding regarding the retention of residual nanoabrasives on the surfaces of the CMP pad following a CMP process and how they can be removed. Particularly, there are no systematic quantitative studies regarding nanoabrasive transport - specifically, nanoabrasive retention, agglomeration and removal mechanisms at pad surfaces (including micro-pores and asperities) that have been exposed (or not exposed) to polishing.

In this dissertation research regarding the residual nanoabrasive transport in IC1000/SubaIV polyurethane pads following a Cu CMP process is presented. Removal mechanisms of residual nanoabrasive resident at CMP pad pores and asperities via a diamond pad conditioning disk is investigated for a range of conditioning parameters, nanoabrasive particles, and slurry formulations. Qualitative and quantitative analysis of nanoabrasive retention was carried out via conventional and environmental scanning electron microscopy (SEM and ESEM), x-ray photoelectron spectroscopy (XPS) and
SEM-based energy dispersion spectroscopy (SEM-EDS). To quantitatively describe the spectroscopic nanoabrasive retention data a semi-empirical model was developed. Quantitative spectroscopic and microscopic analyses on IC1000 CMP pads revealed considerable CMP slurry nanoabrasive retention at pad asperities and open pores that contacted the wafer during Cu CMP. Some of this residual nanoabrasive particle retention was found in individual and other in agglomeration form on the surface of the pad. Distinctive removal mechanisms related to retention of post CMP residual nanoabrasive on polyurethane CMP pad surface had been observed in terms of conditioning parameters, slurries chemistries, nanoabrasive composition, and pad surface location (asperity and open pores). A non-linear nanoabrasive removal model based on a time-dependent removal efficiency best described the nanoabrasive retention data.
ACKNOWLEDGEMENTS

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To my daughters, Nimrah and Rafiya

&

To the memory of my grandfathers, Ismail and Inayat
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6.1 Conclusions

6.2 Future Directions
1.1: CMP: Role in IC Fabrication – Introduction for Al RIE BEOL Processing and Adaptation to Cu Damascene Processing

The semiconductor industry has advanced rapidly in the last two decades. In the ultra-large-scale integration (ULSI) era, the number of transistors on a chip exceeded 40 million and it is expected that this number will increase to more than a billion in the very near future. This has been achieved through continued miniaturization of the device dimensions, introduction of new, higher performance materials on the chip, and novel integration and design schemes for both devices and interconnects. The need to connect an increasing number of devices has driven the utilization of multilevel interconnection schemes which require planarized surfaces (levels) to maintain manufacturability. One critical process technology required by manufacturers to continue both cost and performance improvement of integrated circuits (ICs) is chemical mechanical polishing/planarization (CMP). CMP was introduced into IC manufacturing almost two and half decades ago and has emerged as a leading edge fabrication technology adopted worldwide by the semiconductor industry. CMP processes for Si-based IC fabrication are used for global planarization, film removal, or a combination of both. Traditional CMP applications in CMOS technology are polishing/planarization of copper (integrated with or without low-k dielectric), polysilicon, STI (shallow trench isolation), tungsten plugs and oxide (ILD, pre-metal dielectric, etc.). CMP is still evolving for CMOS manufacturing and new applications are also being developed such as gate stack
engineering, 3D IC’s, advanced packaging, magnetic materials, phase change memory materials, MEMS, advanced substrates, and integrated optics. New applications for CMP are expected to emerge at a rapid rate due to the established capability of CMP technology to planarize surfaces and fabricate embedded submicron structures.7

Historically, the introduction of multilevel metallization schemes, in which different levels of metal line interconnections are isolated within an ILD (interlevel dielectric) and are connected by vertical vias through the ILD, were essential in advancing IC performance.4, 8 But a rough surface topography resulted from multilevel interconnect processing as the number of interconnect levels increased (Fig. 1.1 (a)). This irregular surface created an obstruction in conformal coating of photoresist and inhibited efficient lithographic pattern transfer.9 It became necessary to develop processes to restore global and local planarity to build multilayer structures.10 The need for surface planarity increased as the number of metallization layers grew and geometrical dimensions shrank.11 Planarization in IC manufacturing enabled numerous benefits such as higher photolithography and dry etch yields, minimization of prior level defects, elimination of step coverage concerns, elimination of contact interruption (undesired contacts and electro-migration effects), reduction of high contact resistance and inhomogeneous metallization layer thickness, and limitation in the stacking height of metallization layers.9 The depth of focus in photolithography also diminishes as the critical dimension of the device shrinks.1 When the critical dimension dropped below 350 µm, planarity requirements driven by depth-of-focus limitations outpaced available planarization techniques. Therefore, driven by necessity, an effective planarization process, known as CMP, was investigated, developed and implemented.1 Although, there
are several competing technologies used for local and global planarization (including reactive ion etching and etch back (RIE EB), spin on deposition (SOD), spin etch planarization (SEP), and SOD+EB. CMP is the only technology that can provide excellent local and global planarity on the surface of the wafer at the same time.  

(a) 

Figure 1.1. Schematic demonstrates (a) conventional multilevel interconnect layers, and (b) planer multilevel interconnect layers.  

(b) 

Beyond its development for lithography-driven planarization, CMP has also been an enabling process for IC interconnect development. As feature sizes continued to shrink below the 130 nm node 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. 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, Cu does not form a volatile compound at low enough temperatures to make use of plasma etching/RIE as a feasible means of patterning interconnect lines. Consequently, an inlaid wiring or
‘damascene’ process was developed.\(^{14, 19, 20, 21}\) This entailed the development of Cu CMP as a means to remove excess Cu following interconnect inlay within an ILD.\(^{13}\) Currently, CMP-based damascene processing is now the most practical technique for patterning of Cu interconnect structures for on-chip applications.\(^{22}\) Advances in interconnects technology as well as trends towards 32 nm technology nodes and beyond have been demonstrated in the schematic diagrams in Fig. 1.2.

Moreover, copper is also advantageous because it can be used both as an intra-level interconnect as well as an inter-level via in the so-called dual damascene process.\(^{1,24,25}\) This approach reduces the number of steps in fabrication process as well as the risk of failure between metal and via.\(^1\) A typical process flow for copper dual damascene is shown in Fig. 1.3. Detailed overviews about this process can be found
Examples related to the first demonstration of multilevel copper process technology at various technology nodes have been provided in Fig. 1.4.

Figure 1.3. Schematic diagram (adapted) shows typical ‘Process Flow’ for “Copper Dual Damascene”.
First Declarations of
*Manufacturable Copper Process Technology*

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Figure 1.4. Examples of multilevel copper metallization for different technology nodes. (a) Announcements accelerated industry-wide commitment to switch to copper interconnects.
(b) First incorporate copper with oxide, then introduce low-K dielectrics.

90nm Technology (TSMC, 2002)
1.2: Overview of CMP Process – Experimental Configuration, Process Parameters, Consumables and Slurry

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 protocols. It combines chemical and mechanical interactions to polish (smooth) and planarize surfaces.4 “A successful CMP process is based in fundamental science across the disciplines of mechanical engineering (wear, friction, slip, localized heating), chemical engineering (fluid flow, surface tension, surface reaction kinetics), colloid science (particle interactions, motion, agglomeration), material science (polishing pad hardness, compressibility, abrasive indentation), and chemistry (oxidation/reduction reaction, complexing agents, electro-chemical mechanism)”27

Typically, CMP slurries are composed of aqueous-based chemical solutions and nanoabrasives (in suspension form). 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.4 A typical CMP process is described schematically in Fig. 1.5 and Fig. 1.6. During CMP processing, the wafer (to be polished) is pressed face down against a rotating polishing pad.9 Both wafer and polishing pad rotate independently of each other.11 The rotating pad carries the slurry and delivers it to the wafer surface.28 At the pad-wafer interface, the wafer surface material is chemically modified with the help of slurry chemicals interacting with the material surface.7 For example, in Cu CMP copper oxides (CuO, Cu₂O) and copper hydroxides (Cu (OH)₂) may form on the Cu surface depending upon the pH and electrochemical potential of the Cu in the slurry and the kinetics of the various reactions (thermodynamically favorable at a
given pH and potential).\textsuperscript{22, 29} Simultaneously, the abrasives on the pad surface transmit a downforce to the wafer surface\textsuperscript{1} and (due to repeated sliding, rolling or indentation)\textsuperscript{30} abrade the modified material (layer) on the wafer surface exposing new material for chemical reaction.\textsuperscript{31} In other words, the abrasive causes mechanical damage on the wafer surface, loosening the material or fracturing pieces of the wafer surface in the slurry.\textsuperscript{4} As the pad surface is rough, only the pad asperities will contact the wafer surface and abrasive particles captured on the asperities share the downforce with the pad as shown in Fig. 1.6.\textsuperscript{32} The abraded material dissolves or is swept away.\textsuperscript{4} This is accomplished with the rotating pad that removes polishing residue from the polishing region to promote new polishing reactions during the CMP process.\textsuperscript{28} Primary and main input variables for CMP processing are shown in Table 1.1. It is important to mention that many of the input variables mainly impact primarily a mechanical or chemical component but there is danger in strictly assigning their role as mechanical or chemical as they may show both attributes.\textsuperscript{4} In the case of metal CMP, ideally, the oxidization process on the metal surface should be fast enough to ensure and sustain an acceptable removal rate. Additionally, to avoid high etching rates and to achieve good topography selectivity, balanced etching and passivation reactions are required.\textsuperscript{29}
Figure 1.5. Schematic diagram of chemical mechanical polishing/planarization (CMP) process.

Figure 1.6. Schematic diagram (adapted) showing the interaction among polishing wafer, nanoabrasives and CMP pad surface.32,33
Table 1.1. Main and primary input variables for CMP process.¹,⁴, ³⁰

<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>▪ Oxidizers</td>
</tr>
<tr>
<td>• Back pressures</td>
<td>▪ Complexing agents</td>
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<td></td>
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<td></td>
<td>▪ Dispersants</td>
</tr>
<tr>
<td></td>
<td>• Buffing pads</td>
</tr>
<tr>
<td></td>
<td>• Wafer cleaning brushes and chemicals</td>
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</table>

### 1.3: Defectivity and CMP: CMP-Induced Defects and Particle Adds in IC Processing. Current State of the Technology and ITRS Requirements

It is well known that IC performance degrades as a result of surface defects on a microelectronic device. Therefore, reduction of surface defects receives special attention among the set of key criteria that defines the limits for fabrication of microelectronic device. Strategies to reduce all types of surface defects have appeared as a critical element of the overall roadmap to meet the need to reduce the size of the microelectronic devices.⁴ A variety of defect types has been indentified as the resulting from surface-damage occurring during device fabrication.⁴, ³⁴ A principal source of surface defects is the CMP process itself, and it needs to be tightly controlled to minimize impact on the overall IC.⁷, ³⁴, ³⁵ During a CMP process, polishing surfaces are more susceptible to defects such as micro scratches, particle adhesion, pitting, roughness due to the nature
and complexity of the slurry chemistry, the nanoabrasive characteristics, and the accumulation of nanoabrasives in open pores of the CMP pad.\textsuperscript{1, 34, 35, 36, 37, 38, 39, 40, 41, 42}

1.3.1: Scratches

During copper CMP processing, the formation of scratches is not uncommon\textsuperscript{37} and micro scratching has become a major concern as the IMD (inter metal dielectric) layer becomes thinner.\textsuperscript{43} Scratches can inevitably lead to yield reduction, device deterioration, or in the worst case even circuit failure.\textsuperscript{36, 44} In other words, due to micro scratching, a short circuit and current leakage can occur as well as corrosion resistance (in the metal film) and reduction in breakdown strength (in the polymer dielectric film).\textsuperscript{4, 35} The impact of CMP-induced micro-scratches is expected to be more severe as interconnect dimensions reduce in succeeding technology nodes.\textsuperscript{37} Thus, it is important to minimize these micro-scratches.\textsuperscript{35}

Nanoabrasive type, size distribution, and concentration play an important role in producing micro-scratches.\textsuperscript{35, 38, 47} The density and the size (length and depth) of micro-scratches typically increase with increasing polishing pressure and abrasive particle size, respectively.\textsuperscript{38, 44} The major source of micro-scratching is the larger and harder particles (or particle agglomerates) in the slurry distribution.\textsuperscript{36, 37, 45, 46, 47} Therefore, large particle count (LPC) for slurry is a key analytical metric that is widely used for the prediction of defect creation potential of CMP slurries.\textsuperscript{11, 34} Particles having diameters greater than 0.5 µm are generally considered to generate the vast majority of micro-scratches as compares to relatively smaller particles.\textsuperscript{1, 11, 34, 42}
Slurry nanoparticle agglomeration is one of the major sources of larger particles in the slurry and consequently micro-scratches on the wafer surface.\textsuperscript{36, 37, 40, 43, 47, 48} Agglomeration in the slurry can occur during storage, transport, additive mixing, blending, and handling.\textsuperscript{1} Many types of slurries are unstable colloidal systems and have relatively short shelf life.\textsuperscript{47} Abrasive particle settling or agglomeration is particularly an issue in high ionic strength slurries used in metal CMP, where ions decrease the mutual repulsion among abrasive particles through charge shielding and compression of the electrical double layer around the particles.\textsuperscript{38, 40} Moreover, it has been noticed that the degradation of slurry and generation large particles can result during transport of slurry from container to the CMP tool due to shearing, agglomeration, settling, and solidification or in the slurry supply line where, shearing can also facilitate agglomeration.\textsuperscript{1, 36, 37, 43, 47, 48, 49}

![Scratching defects on different materials and structures](image)

**Figure 1.7.** Scratching defects on different materials and structures. Sources for pictures: Paul Lefevre (Fig. a, b, c & f)\textsuperscript{50}, Paul Fisher (Fig. d)\textsuperscript{50, 51}, and M. Tsujimura (Fig. e)\textsuperscript{23}. 

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1.3.2: Particle Adhesion

In CMP processing, problems resulting from particle contamination on the wafer surface are not too surprising considering that wafers are immersed in slurry containing $\sim 10^{14} - 10^{17}$ particles/l.\(^1\) CMP process contaminates the wafer surface with thousands of particles such as slurry particles as well as generated particles from pad material and polishing films.\(^{52, 53, 54}\) These particles can adhere to wafer surfaces (due to a variety of adhesive forces, and chemical or hydrogen bonding). They can be held by surface topography, or in worst case even be partially embedded in wafer surfaces due to locally high pad pressure.\(^{41, 55, 56, 57, 58}\) Adhesion force increases with increasing particle size and contact area which maximize interfacial contact between wafer and contaminant abrasive particles.\(^{55, 59}\) Typically, more particles are found on the polished wafer when larger (agglomerated) particles are detected in the spent slurry.\(^{60}\) Higher adhesion forces (and larger particle densities) have been observed between alumina abrasives and Cu, Ta or dielectric surfaces as compared to pad particles.\(^{61}\) With respect to abrasive-wafer interaction, Cu, Ta, TaN, and W surfaces have all shown stronger interaction forces with abrasives (alumina and silica) as compared to dielectric surfaces.\(^{41, 61, 62, 63}\) As a result, higher contamination of abrasives on the Cu, Ta and TaN surfaces has been observed as compared to dielectrics.\(^{62}\) For Cu surfaces, it has been observed that higher abrasive particle adhesion force generates not only higher particle contamination but also higher frictional force and consequently deeper scratches on the copper surface.\(^{41, 64}\) Additionally abrasive particle adhesion can cause a local roughness increase, block photolithography, create pinholes in subsequently grown films and lead to electrical shorts.\(^{58}\)
Thus, particle contamination or residual particle adhesion on the polishing surface can lead to functional defects as well as lower the yields in finished integrated circuits. There is not only a need to remove these particles before any further processing but it is also required to perform the removal as quickly as possible because the adhesive force between a particle and a polished surface can increase over time. The removal of particle contamination from dielectric and metal wafers has become a challenge in post CMP cleaning process as the circuit line width continues to shrink.

![Figure 1.8. Particle adhesion (contamination) on the features of the wafers.](image)

![Figure 1.9. The adhesion forces between alumina and wafer surfaces in the acidic, neutral and alkaline pHs.](image)
1.3.3: International Technology Roadmap for Semiconductors (ITRS 2007 & 2008 Update) for CMP: Technology Requirements for Particle Related Defect Reduction for Yield Enhancement

Over the next 12 years the International Technology Roadmap for Semiconductors (ITRS) calls for a reduction in the number of particle defects on the wafer by over an order of magnitude. This requirement will dramatically reduce the acceptable number of nanoabrasive particles (and other defects) following CMP processing.\textsuperscript{65, 66}

<table>
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<tr>
<th>Year of Production</th>
<th>MPU</th>
<th>CMP Metal</th>
<th>CMP Insulator</th>
<th>CMP Clean</th>
<th>DRAM</th>
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Figure 1.10. Technology requirements for defects control of random particles during CMP for (a) MPU, and (b) DRAM. Where, generic tool type scaled to 34 nm and 40 nm critical defect size or greater are considered for MPU and DRAM, respectively. Graphs are drawn from data available in ITRS-2007, Yield Enhancement document.\textsuperscript{65}
1.3.4: Current Strategies in CMP for the Reduction of Particle Related Defects

Primarily, micro-scratching is minimized by the appropriate choice of nanoabrasive type (silica, alumina, ceria, nanoporous silica, coated particles etc.) and optimized nanoabrasive concentration in the slurry formulation. But as described above in section 1.3.1 large (oversized) and agglomerated particles are a main source of micro-scratches. Therefore, well suspended nanoabrasive particles with tight size distributions are required in the slurry for fewer defects on the polishing wafers. This is usually achieved through; (a) maintaining high repulsive electrostatic charge and/or steric barrier between abrasive particles with the help of optimum concentrations of common slurry chemistries (pH stabilizer, oxidizer, complexing agent, corrosion inhibitor, electrolyte or salt etc.) as well as with other chemical additives (ionic and/or non-ionic surfactants, polymers etc.); (b) continuous agitating and appropriate blending to maintain good suspension of the nanoabrasives; (c) removing the agglomerated nanoabrasive particles through flushing off the stagnant slurry in the delivery line before starting actual polishing; (d) lowering shear stresses during slurry circulation in supply line by using appropriate pump system; (e) continuous monitoring and control of slurry health during slurry distribution; (f) using point of use (POU) slurry filters, and (g) mixing the particles with chemicals at POU in case of high ionic strength slurry.

To control contamination of nanoabrasives on the wafer surface, slurry can be designed with chemical additives to enhance the wafer-abrasive repulsive forces, wafer surface smoothness, selectivity etc. Moreover, soft, small, spherical, suspended
and low content abrasive in the slurry can also help to reduce abrasive particle contamination on the polishing wafer. In addition to these Pre-CMP control strategies, Post CMP cleaning processes have also been optimized for the removal of particle contamination introduced by CMP processing. Post CMP cleaning is performed by utilizing any one or the combination of the following: buffing, noncontact megasonics, brush scrubbing, immersion bath, chemical cleaning solutions, integrated CMP toolset (Dry wafer in, dry wafer out). 

During CMP processing, strategies such as lower downforce and speed, prevention of slurry drying, utilization of high-pressure de-ionized water spray, rapid formation of a thick enough passivated layer (to prevent direct interaction of abrasives with bare wafer surface) and multistep polishing on multiple platens can also help to reduce particle adhesion and scratches on the surface of polishing wafers.

1.3.5: Limitations of These Strategies in Real Polishing Environment

Most of the strategies available in literature (as discussed above) to control particle related defectivity are either executed via Pre CMP or Post CMP. Although, particle induced scratches have been reduced to some extend by utilizing pre polishing and multistep (multi platen) polishing strategies, complete removal of scratches remains difficult to achieve. Even after the slurries are filtered to remove large particles, the defect counts on the polished surfaces are often observed to be higher than desired. Large particles (mean size less than 0.5 μm) that can cause scratching, can form during CMP process as a result of agglomeration. This is consistent with (and, in fact, implied by) the discovery of such large particles in the spent slurry. Particles can
agglomerate during CMP processing due to a variety of reasons such as slurry temperature change, shearing, mechanically-induced aggregation of abraded metal ions (Cu $^{2+}$), and chemical reactions occurring at pad/wafer interface. Additionally, larger particles may serve to nucleate larger aggregation that serves to accelerate settling of the slurry. Polishing debris and by-products will also interact with large particles (agglomerated) and can exacerbate these issues. Moreover, open structures of the polyurethane pad may retain the abrasive or agglomerated particles like a filter – this is particularly likely at the pad-wafer interface during polish. Not surprisingly, porous pads have lead to the observation of higher particle concentrations on the Cu wafer surface as compared to non-porous pads. All this indicates that Pre-CMP strategies do not fully provide the control on nanoabrasive induced defectivity in a real polishing platform. Similarly, Post-CMP cleaning methods can not remove the scratches formed during a CMP process and in some cases may not be able to remove all process-induced particles on the wafer surface. Moreover, Post-CMP cleaning methods already face many challenges including cost, number of steps and tools involved in the cleaning process. Therefore, it is very critical to investigate nanoabrasive transport on CMP pads as well as to develop strategies for a real polishing platform to control particle creation that can lead to increased defectivity.

1.3.6: Current Role of Conditioning in Real Polishing Environment

CMP pad conditioning creates reservoirs, reopens the clogged pad pores, removes worn pad surface material (asperities), refreshes the pad surface roughness, changes (increases) the polyurethane pad surface wettability and hydrophilicity. All this serves to
increase the slurry transport to the wafer surface with increased slurry film thickness, restores the intrinsic structure of the pad, prevents pad glazing, and removes slurry residues, abrasives, and polishing debris from pad.\textsuperscript{1, 96, 97, 98, 99, 100} Therefore, pad conditioning increases and stabilizes the material removal rates, improves planarity and uniformity across the wafer as well as reduces the defectivity.\textsuperscript{101} Until now, a variety of pad-conditioning methods has been investigated and adopted. Abrasive pad conditioning using diamond-impregnated disks is found as the most effective method.\textsuperscript{1} In a state of the art process, pad conditioning is performed by making contact between CMP pad surface and diamond abrasive disc or wheel. Details about pad conditioning can be found in chapter 2.

1.4: Research Need: Investigation of Nanoabrasive Transport and Retention in CMP Pads

To date, very little attention has been given to the contamination of residual nanoabrasives on the surface of the pad following a CMP process and it is not well documented in the literature. There are no systematic studies regarding nanoabrasive transport - specifically, nanoabrasive retention, agglomeration and removal mechanisms at pad surfaces (including micro-pores and asperities) that have been exposed (or not exposed) to polishing.

1.4.1: Presence of Retention on CMP Pad Asperities and Open Pores

During the investigations presented in this dissertation, considerable retention of alumina and silica residual nanoabrasive particles as well as Post-CMP Cu (some cases)
have been observed on CMP pad surfaces used in CMP processing. Residual nanoabrasive particle retention has been found both in individual and agglomerated forms on the surface of the pad. Examples of post CMP residual nanoabrasive particle retention in the CMP pad from the work carried out for this dissertation are shown in Fig. 1.11.

**Figure 1.11. Demonstration of the presence of residual (post CMP) nanoabrasives on the surface of CMP pad.**

### 1.4.2: Presence of Retention on Polishing Exposed Areas of CMP Pad

Throughout the investigations undertaken as part of this dissertation, residual nanoabrasive retention was found to be relatively high on pad surface areas that were exposed to the wafer surface during polishing as compared to regions of the pad surface not exposed to the wafer. In most cases, the surface at the very center of the CMP pad
exhibited negligible residual nanoabrasive retention in spite of the fact that slurry was introduced at that point. An illustration of this observation is shown in Fig. 1.12.

1.4.3: Potential Impact of Retention on Wafer Defectivity

Residual nanoabrasive retention and agglomeration on a CMP pad surface (pores and asperities) following CMP process cycles may not only increase the number of actual particles on the wafer surface but may also lead to particle agglomeration and interaction with polishing debris/by-products. During polishing, mixing of these particles with slurry may lead to particle related wafer defectivity (scratches, particles adhesion, rougher surface, pitting, delamination etc.) as well as inconsistency in CMP removal rates. In fact, it has been found that larger particles and residual abrasive particle
retention\textsuperscript{102} (determined indirectly through calibration in slurry transition experiments) affect the MRR. This will be discussed in chapter 2 in greater detail.

Therefore, investigations related to nanoabrasive particle retention and its removal mechanisms are very critical. These studies not only will help to understand residual nanoabrasive transport on the pad surface in a real polishing platform but will also help to improve control of particle-related defectivity. This is critical considering that the ITRS 2007 (and 2008 update) roadmap\textsuperscript{65, 66} demands a reduction in the number of particle defects on the wafer by over an order of magnitude as device dimensions shrink in the coming years. This is also critical considering that the difficulty of removing particles during Post CMP wafer cleaning increases with decreasing particle size\textsuperscript{103, 104} and smaller feature sizes of future ICs will likely drive the utilization of smaller nanoabrasives.\textsuperscript{104, 105}

1.4.4: Evaluation with Conditioner Disk

As mentioned above, a diamond conditioner disk is the most effective method to condition the polishing pad in CMP processing but it is not well documented in the literature that how it can affect the residual nanoabrasive retention on the CMP pad surface (including micro scale open pores and asperities) following a CMP process. Specifically, related quantitative evaluation and modeling is needed. In these investigations, a diamond disk conditioner was used to investigate its effectiveness for the removal of residual nanoabrasive retention on the surface of CMP pads. Conditioning was found to be very effective in reducing the residual nanoabrasive particle retention at the surface of the CMP pad. An example of this capability is shown in Fig. 1.13. Investigations carried out as part of this dissertation determined the role of conditioning
parameters such as conditioner down force, CMP pad/conditioner relative velocity and conditioning time on the nanoabrasive retention at the pad surface. Quantitative evaluation of residual nanoabrasive retention on the surface of the CMP pad (including open pores and asperities) was carried out following CMP processing in all retention experiments. Additionally, models related to removal mechanisms of residual nanoabrasive retention as a function of conditioner parameters were developed.

![Retention without conditioning vs Retention with conditioning](image)

**Figure 1.13.** SEM images show residual (post CMP) nanoabrasive retention on CMP pad surface without & with pad conditioning by using diamond conditioner disk.

### 1.5: Summary of Dissertation Research and Brief Summary of Results

The core objective of this research was to investigate the residual nanoabrasive particle retention and removal mechanisms at the polyurethane polishing IC1000/Suba IV pad surface following Cu CMP. Additionally, retention of removed copper material (from Cu wafer) on the pad surface following Cu CMP was also investigated. After every Cu CMP step, diamond disk CMP conditioning was used ex-situ to reduce the nanoabrasive retention. Experiments were designed in terms of conditioner parameters, slurry chemistry, nanoabrasive composition, and pad life to investigate the residual nanoabrasive retention and removal mechanisms on the pad surface (including inside
open pores and at asperities). After each experiment quantitative analysis (XPS, EDS and Profilometry) as well as qualitative analysis (SEM & ESEM) was carried out on CMP pad samples to investigate and characterize residual nanoabrasive retention, agglomeration, and removal mechanisms. Pad samples taken from pad areas that were exposed to the wafer during CMP processing were compared to pad samples taken from areas that were not exposed to the wafer. Cu material removal rates (MRR) were also determined for each type of slurry. Additionally, in one of the experiments (CMP pad life experiment), the effects of nanoabrasive retention and agglomeration on the MRR and wafer defectivity (scratches and particles adhesion) was also investigated. Moreover, modeling was also carried out to explore residual nanoabrasive retention transport and removal mechanisms in CMP pad surface asperities and open pores.

In these investigations, considerable amounts of residual nanoabrasive retention were found on CMP pad areas that had been exposed to Cu polishing as compared to pad areas not exposed to polishing (e.g. the center of the CMP). Lower residual nanoabrasive retention has been observed on CMP pad asperities as compared to open pores in the pad. Overall, the removal of nanoabrasive retention was found to be a weak function of conditioning disk downforce and pad/conditioner relative velocity but a strong function of overall conditioning time. The decrease in nanoabrasive retention inside open pores with increasing conditioning time was more effective on pad sections having lower pad/conditioner relative velocity. Silica based slurries exhibited less retention as compared to alumina based slurries. Substantial retention of agglomerated nanoabrasive particles was observed.
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CHAPTER 2

SELECTED OVERVIEW OF SLURRY TRANSPORT, CMP

PAD CONDITIONING AND NANOAbrasives in CMP

Glass polishing has been practiced for centuries. According to Sir Isaac Newton in 1721, “nothing is wanting to perfect these telescopes but good workmen who can grind and polish glasses truly spherical”.\(^1\) But there are considerable differences between CMP used historically for glass polishing and the present use of CMP in the manufacturing of silicon integrated circuits.\(^2\) CMP was initially developed in the 1980’s at IBM.\(^3\) Since then CMP has evolved as an enabling technology for the global planarization of multilevel metallization of logic devices and interconnection of memory devices.\(^4\) In addition to its use in the integrated circuits fabrication, CMP is also used in the fabrication of MEMS devices, 3D chips, and in the integration of optoelectronic devices.\(^5\)

With the integration of copper and low-k materials as interconnect and dielectric, the CMP community is facing an ever-increasing demand to reduce defectivity without scarifying production throughput.\(^6\) The total contact area between pad and wafer is directly related to both removal rate and defectivity and has emerged as a key parameter.\(^7\) It has been postulated that slurry fluid motion at the pad-wafer interface has a significant effect on wafer surface wear distribution.\(^8\) For a more complete working model of CMP, a quantitative understanding of the interface of the pad and wafer is fundamental since both the fluid flow and the contact mechanics at this interface have an enormous impact on the polishing process.\(^9\) Consequently, slurry transport on CMP pads and the role of the pad-surface features (grooves, open pores and asperities) is reviewed in detail in
section 2.1. As CMP pad conditioning is also very important in maintaining pad surface morphology and fluid transport, the role of conditioning and its parameters is reviewed in section 2.2. Section 2.3 includes a brief overview of CMP nanoabrasives, their properties, and aspects of agglomeration including a discussion of agglomeration at the pad-wafer interface. On the pad surface the retention and transport of slurry (specifically the residual nanoabrasives) and abraded polished material may potentially impact CMP performance (including issues such as scratches and particle adhesion) and is a central topic of this dissertation research. Therefore, related technical literature is reviewed in section 2.4.

2.1: Slurry Transport in the CMP Pad and the Role of CMP Pad’s Asperities, Open pores and Grooves

2.1.1: CMP Pad Introduction

The polishing pad plays a crucial role in CMP processing. 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).\textsuperscript{5} 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.\textsuperscript{10} It also transmits normal and shear forces from the polisher to the wafer.\textsuperscript{5,11} 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.\textsuperscript{12} 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, modulus) and excellent chemical stability.\textsuperscript{5} Additionally, polyurethane pads are able to transport and deliver aqueous slurry on its surface more uniformly and effectively\textsuperscript{5} as they have the highest critical surface tension values compared with the aforementioned polymeric materials.\textsuperscript{13} 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.\textsuperscript{10} For better polishing, multilayer or stacked pads are normally used which are comprised of a stiff/hard top layer and a soft/flexible substrate.\textsuperscript{5} 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.\textsuperscript{14}

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.\textsuperscript{15}
2.1.2: Role of CMP Pad Grooves in Slurry Transport

Macroscopic grooves in the CMP pad increase the slurry flow rate under the wafer and help to prevent wafer hydroplaning on the pad, facilitate release of wafers from the pad surface after polishing, ensure uniform slurry distribution across the pad surface, and deliver slurry to the wafer center in order to maintain uniform polishing from wafer center to edge. This is particularly important for larger size wafers (300 mm) as well as for polishing reactive metals such as copper. In addition, grooves provide channels for the removal of polishing debris and heat from the pad surface. This helps reduce generation of polishing defects due to debris accumulation on the pad surface and
avoids rapid chemical reaction at localized high temperature regions due to local heating.\textsuperscript{13,15}

![Diagram](image)

**Figure 2.2.** Schematic diagrams show top views of grooves on pad surface, (a) circular grooves and (b) XY grooves.\textsuperscript{17} (c) Schematic diagram show cross-section of stack pad under applied load by conditioner or wafer, grooves as well as top surface (pores and asperities) are also obvious in the diagram.\textsuperscript{18} (Dow Advanced Materials, images reprinted by permission).

### 2.1.3: Role of CMP Pad Surface Pores in Slurry Transport

Polyurethane pads such as IC 1000\textsuperscript{TM} are void-filled polyurethane polymer sheets.\textsuperscript{5} The voids in IC1000\textsuperscript{TM} polyurethane CMP pads are usually not interconnected and have an average diameter of approximately 30 \(\mu\text{m}\). They occupy about 35% of the volume of the pad material. Approximately 50% surface of the pad surface is comprised of exposed pores (Fig. 2.3). Consequently, the surface is relatively rough. Conditioning further adds to this natural roughness in the interpore areas.\textsuperscript{19} Open pores on the pad
surface promote chemical reaction at the wafer surface by aiding slurry transport to all parts of the wafer and facilitating transport of the reaction products away from the wafer surface.\textsuperscript{20} Two dimensional wafer-scale flow modeling (considering pad roughness, elasticity and porosity factors) for CMP shows that the slurry pressure decreases with the increase of porosity, thus allowing the fluid to more easily flow through the porous layer and facilitate debris transport.\textsuperscript{21}

By promoting enhanced slurry transport porous pads lead to higher MRR in Cu and SiO\textsubscript{2} CMP.\textsuperscript{22} Lower porosity (higher density) pads produce lower removal rates since they are less effective in transporting sufficient slurry to the wafer surface.\textsuperscript{23} Figure 2.4 shows that the MRR measured using a nonporous CMP pad (IC2000) is lower compared to the MRR measured using porous CMP pads (IC1000 and IC1400). The IC 1400 pad is a stacked pad comprised of a conventional IC1000 pad and a closed cell foam bottom pad instead of a Suba IV.\textsuperscript{24} Additionally, lower porosity favors CMP operation in the lubrication regime, where a thicker slurry film separates the wafer and pad. This also reduces material removal rate.\textsuperscript{25}

![Figure 2.3. SEM images of a CMP pad before polishing. (a) Surface images. (b) Cross-sectional image. Images show the microscale asperities and pores.\textsuperscript{26}](image-url)

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The open pores on a CMP pad surface may trap the slurry abrasive nanoparticles as well as polishing debris. For example, it has been observed in the case of oxide polishing with silica slurry that pores became filled with aggregated particles. Similarly, during tungsten polishing accumulation of alumina particles and debris in pores has also been observed. The debris effectively reduces the size of the pore and reduces available volume for slurry transport. Additionally, it has been observed that after oxide polishing slurry residue remained in most open pores of the pad surface even after conditioning at 20 °C. Accumulation of abrasives and debris could lead either to scratching of the wafer surface (especially for ductile materials like Cu, Al films) or increased residual particle density on the wafer surface.

It has been shown by Li that the defectivity on the polished wafer surface depends on the number of pores in the CMP pad. This is illustrated in Fig. 2.5 which shows that the number of (residual) particles on polished copper blanket wafers is lower.
for various nonporous NCP CMP pads as compared to porous IC1000 CMP pads.\textsuperscript{5} But in spite of this advantage in defectivity, there are challenges associated with nonporous pads such as edge effects, the need for extensive (harsher and longer) pad conditioning, and lower MRR.\textsuperscript{22} Extensive conditioning is required to create microstructures such as roughness and asperities on the nonporous pad surface for better slurry transport.\textsuperscript{5}

Since porous polishing pads are more commonly used in commercial CMP applications it is critical to more fully understand the particle retention characteristics and mechanisms by which residual particles may be removed from the pad surface. Therefore, in this work, retention and removal mechanisms of post CMP residual nanoabrasive particles from inside pores and at asperities (interpore surfaces) of CMP pads were investigated. These investigations will be discussed in detail in the following chapters.

![Defectivity (residual) particles on polished Cu wafer surface](image)

Figure 2.5. Comparison of normalized defect counts (residual particles) on post CMP processed Cu blanket wafers due to porous (IC 1000) and non-porous (NCP) CMP pads. All polished with 1\textsuperscript{st} step Cu slurries.\textsuperscript{5}
2.1.4: Role of CMP Pad Asperities in Polishing

The interpore surfaces of commonly used porous CMP pads are typically referred to as pad asperities. Slurry not only flows in the pad’s open pores but also in broad thin gaps over the asperities. These surface acts as local hydrodynamic pressure sites enhancing the CMP erosion process. Pad surface asperities are those pad features that actually make contact with the wafer during polishing. Abrasive particles at asperities make abrasive contact with the wafer surface. This abrasive action combined with chemical attack by the chemical components of the slurry on the exposed wafer surface, help in polishing. The average pad asperity height is ~ 20-25 μm. If the slurry film thickness is less than the average pad asperity height the process is said to be in a ‘contact regime’ and higher material removal rate can be expected. Otherwise the CMP operation is considered to be in a ‘lubrication regime’. For the remainder of this dissertation it is assumed that all polishing takes place in the ‘contact regime’.

“Asperities” are the portion of the pad that can be visualized as the red “islands” projected above the contact plane (dotted line in the Fig. 2.6). When load is applied during polishing, the red portion of the data would be compressed. In that figure the dotted line represents the pad-wafer contact surface. The calculated effective asperity modulus for an IC1000 pad surface is ~ 1 MPa.

2.1.5: Role of CMP Pad Surface Roughness

The average depth of pad surface roughness during use results both from pad conditioning and from native porosity within the pad. The average CMP pad asperity can be characterized by its average roughness Ra. The surfaces of new and used pads have average Ra values of 8.596 μm and 6.494 μm, respectively. Therefore, used pads
have lower micro surface roughness. Rougher pads may possibly lead to higher material removal rate.\textsuperscript{33} In Cu CMP processing, pad surface roughness becomes an important parameter for process performance and it also affects step-height reduction in copper CMP.\textsuperscript{34}

![Figure 2.6](image1.png)

**Figure 2.6.** a) a line scan on pad surface and b) a pad height probability distribution. It also illustrates pad wafer contact area estimation based on a predicted volumetric displacement. The height that corresponding to pad wafer contact was estimated as the point at which the predicted volume is equivalent to cumulative displaced volume of the pdf.\textsuperscript{9}

![Figure 2.7](image2.png)

**Figure 2.7.** Slurry flow among asperities when compressed against a wafer to form an obstruct flow volume, a porous media description of asperity layer (Dow Advanced Materials, reprinted by permission).\textsuperscript{15}
When asperities contact a wafer under an applied downforce, the tallest asperities deform until their elastic resistances sum equal the downforce. As a result, a highly obstructed, thin space forms between wafer and compressed pad and comprises the domain through which slurry flows during polishing (Fig. 2.7). This type of flow exhibits features of porous-media flow. Pressure loss is experienced by slurry passing through this porous media.\textsuperscript{35} It has been shown that the pressure drop decreases with increasing characteristic length (as 1\textsuperscript{st} to 2\textsuperscript{nd} power of $D_E$) and void fraction (as 4\textsuperscript{th} to 5\textsuperscript{th} power of $\varepsilon$). Both porous media descriptors ($D_E$ and $\varepsilon$) are shown in Fig. 2.7. In other words, the fluid pressure drop decreases with decreasing surface flow resistance. At higher roughness, lower surface flow resistance for the fluid was observed for both soft\textsuperscript{35} and hard pads.\textsuperscript{15} This is expected for rougher surfaces having larger void fractions.\textsuperscript{15} Moreover, effective slurry thickness increases with increasing pad surface roughness.\textsuperscript{36, 37}

2.2: Conditioning – Role in Maintaining Morphology and Slurry Retention

2.2.1: Un-conditioned Pads and CMP Performance

There is a significant effect of pad surface structure and conditioning (or lack thereof) on CMP process performance. Pad conditioning greatly influences the removal rate, planarization performance and hydrodynamic effects.\textsuperscript{38} No conditioning or insufficient conditioning during polishing leads to ‘glazing’ of the pad surface, wherein particles build up and clog the pad surface pores.\textsuperscript{1, 5, 27, 29} The exposed open pores decrease in volume on the surface of a used pad\textsuperscript{29} leading to a reduction of slurry transport as mentioned in section 2.1.3. Figure 2.10(a) illustrates this effect for oxide
silica slurry.\textsuperscript{28} This alteration of the pad surface morphology also depends on the type of slurry solution used.\textsuperscript{39} Alternately, the glazing phenomenon can result in a decrease of the roughness of the pad surface.\textsuperscript{40, 41} Specifically, pad surface asperities wear off and become glazed or flattened. The higher asperities wear off faster than the lower asperities\textsuperscript{19} resulting in an increase of the area of direct contact between the pad and wafer surface. This leads to a decrease of the average contact pressure and the material removal rate drops rapidly with polishing time\textsuperscript{19, 42} (illustrated in Fig. 2.8).\textsuperscript{5, 42} Similarly, the Cu material removal rate also declines for a CMP process without conditioning. This also results mainly from changes in pad surface morphology.\textsuperscript{43} This leads to lower removal rates and higher wafer-level defectivity.\textsuperscript{27, 28, 41, 42, 43}

![Figure 2.8. The oxide thickness removed as a function of cumulative polishing times on IC1000/Suba IV CMP pads (lot A and lot B). The pads were not conditioned, and cumulative polishing times were acquired using 5 min of polishing.\textsuperscript{5, 42}](image-url)
2.2.2: Role of Pad Conditioning

CMP pad conditioning reopens the pores, helps in removing the slurry abrasive particles, refreshes the pad surface roughness as well as changes (increases) the polyurethane pad surface wettability and hydrophilicity.\(^5\) Fig. 2.10(b) shows that much of the slurry residues are removed from the CMP pad pores after conditioning with DIW water.\(^28\) The slurry film thickness under the polished wafer (Fig. 2.11) also increases for a conditioned pad as compared to an unconditioned pad.\(^44, 45\) Conditioning removes worn surface material (asperities) as well as restores the basic porous structure of the pad.\(^38\) As shown in Fig. 2.12(a), a conditioned pad surface exhibits a surface structure more reminiscent of an unused pad. An unconditioned (glazed) pad surface (2.12(b)) surface exhibits a sharp maximum of height in the distribution near the pad surface which results from the mesa-like asperity structure.\(^9\) Therefore, the conditioning process is indispensable in maintaining the structure of pad surface asperities. Surface roughness (Fig. 2.13(a)) and material removal rate (Fig. 2.13(b)) of a conditioned pad are increased substantially compared to a used, unconditioned polished pad.\(^41\) Where, \(R_{pk}\), represents “reduced peak height” and it is the estimate of peaks above the main plateau and is related to wear characteristics of the pad surface. In other words, \(R_{pk}\) is the area of most rapid wear when polishing is performed. Additionally, pad conditioning improves planarity and uniformity across the wafer and reduces defectivity.\(^35\) The removal rate profile can be maintained stable for hundreds of polishing wafers if the pad conditioning process is repeated after each wafer polishing.\(^13\)

In a state of the art CMP process pad conditioning is performed through contact between the CMP pad surface and a diamond abrasive disc or wheel (illustrated in Fig.
2.9). Abrasive pad conditioning using diamond-impregnated disks has been found to be the most effective method.\textsuperscript{5} A high pressure micro jet (HPMJ) approach was investigated that utilized spraying of pressurized ultra pure water (3-30 MPa) on the pad surface. But results showed that ILD MRR and IC1000 pad surface roughness achieved with this method was lower than obtained with a diamond conditioner. Moreover, lower MRRs were attributed to the radical change in pad surface chemistry.\textsuperscript{46} Similarly, COF and Cu removal rates by using HPMJ conditioner on the IC1000 pad decreased significantly including more collapse in asperities/pores when compared to diamond conditioning.\textsuperscript{47}

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.\textsuperscript{48} 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.\textsuperscript{5} Preferential radial conditioning has been proposed in combination with circular grooves.\textsuperscript{49} This may also serve to reduce wafer nanotopography (groove pattern transfer on wafer due to grooved-scale slurry transport) as observed with radial grooves.\textsuperscript{50}

![Figure 2.9](image)

*Figure 2.9. Cartoon illustrate polishing pad and conditioner geometry as well as the interaction between pad and conditioner surfaces.*\textsuperscript{9}
Figure 2.10. SEM images of the IC-1400 pad surface during the oxide wafer polishing with silica slurry. (a) Polished pad without conditioning process and (b) conditioned pad with DIW at 20 °C.  

Figure 2.11. Top view of fluorescence images of IC1000 pad from a wafer subsection: (a) un-conditioned and (b) conditioned pad. Fluorescence intensity is proportional to the brightness of the image. Where, dark circular region is the mounting post of the glass wafer.  

Figure 2.12. Pad height probability distributions (right) and line scans pad surface data. (a) a fully conditioned and (b) a glazed pad (wafer dominated) surface, it also shows truncated asperity structure (red component in the distribution) induced by polishing many wafers without conditioning. Where, blue component show intrinsic contribution to distribution.
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.

![Figure 2.13](image_url)

**Figure 2.13.** Polishing and surface roughness as a function of polishing time with and without conditioning process. (a) $R_{pk}$ vs. polishing time. (b) Material removal rate vs. polishing time.

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.

### 2.2.3: Effect of Conditioning Time and Pressure on the Surface Morphology

As shown in Fig. 2.14(a), an unused polishing pad has a $R_{pk}$ value of 2.377 μm where $R_{pk}$ refers to the ‘reduced peak height’. After 30 min break-in conditioning time the pad roughness increased to 4.097 μm $R_{pk}$. As shown in Fig. 2.14(b), the $R_{pk}$ value
increased from 3 to 3.7 μm by increasing the conditioning pressure from 60 to 140 g/cm². Increase in the conditioner downforce does not considerably change the intrinsic structure of the pad surface. But the mean peak spacing decreases while the mean peak curvature (a measure of peak sharpness) increases with increasing conditioner downforce. Likewise, the pad surface roughness increases with increasing conditioning downforce.

As shown in Fig. 2.15, conditioning creates significant textures surrounding the open pores. Ridges are formed due to polymer plastic flow at the edges of open pores. Additionally, it has been reported that total asperity area decreases with conditioning time.

![Figure 2.14. Reduced Peak height (Rpk) surface roughness of the pad. (a) as function of pad break-in conditioner time and (b) as function of conditioner pressure (g/cm²).](image)

Figure 2.14. Reduced Peak height (Rpk) surface roughness of the pad. (a) as function of pad break-in conditioner time and (b) as function of conditioner pressure (g/cm²).
Figure 2.15. SEM images of conditioned VP 3000 pads (Dow Advanced Materials, reprinted by permission).  

2.2.4: Pad Profile Optimization and the Role of Pad-Conditioner Relative Velocity and Conditioning time

Fig. 2.16 illustrates the dependence of pad/conditioner relative velocities on a number of CMP tool parameters. A relatively uniform post-conditioning pad profile is more easily maintained by setting the angular velocities of the conditioner and the pad (platen) close to each other. In addition minimizing the ratio of conditioner disk radius to pad radius, widening the conditioner sweeping range, and enlarging the number of zones (segments at equal distance in the sweeping range).  

Conditioning will also impact the degree of pad wear. The wear thickness of the pad, $\Delta h$ can be expressed as

$$\Delta h = K \cdot V_{avg,s}^{1+\alpha} \cdot \frac{1}{\Delta t^{1+\alpha}}$$

Where, $V_{avg,s}$ is the averaged sweeping velocity, $\Delta t$ is the actual conditioning time, and $K$, $\alpha$ & $\beta$ are the adjustable parameters. $K$ is a parameter similar to the Preston constant. Values for the model parameters listed above were determined from two
different experiments. It was found that the velocity term (V_{avg,s}) plays a relatively insignificant role in the wear of the polish pad. In contrast, the actual conditioning time (\Delta t) plays a very important role.\textsuperscript{53}

Figure 2.16. Pad/conditioner relative velocity profile under the conditioner for different angular velocities (\omega_d/\omega_p) and various Dcc distances. Where, \omega_d \& \omega_p are the conditioner disk and platen (CMP pad) angular velocities respectively, and Dcc is the distance between the center of the platen (pad) and center of the diamond disk.\textsuperscript{53}

Moreover, the following equation suggests that the effect of conditioning downforce on pad wear (dressing rate) is greater than pad conditioning velocity.\textsuperscript{48} The same has been also confirmed in other investigations.\textsuperscript{54} The effective pad hardness increases with increasing pad speed which results in a reduce penetration depth of conditioning grit into pad surface.\textsuperscript{55} In relative terms that should also be true for conditioning speed.
In the above equation, $K_D$ is a dressing rate constant, $A$ is the dressing area, $\lambda$ is density of the abrasive distribute, $V_D$ is the higher conditioning velocity, $R$ is the knife-edge of the diamond grit, $d_0$ is the larger size of abrasive, $H_P$ is the hardness of the polishing pad, and $P$ is the conditioning pressure.

2.2.5: Ex-situ and In-situ Conditioning

Pad conditioning in CMP processing is typically carried out in one of two modes: ex-situ and in-situ. For the in situ mode conditioning is performed during wafer polishing. In the ex-situ mode, conditioning is performed before or after the polishing process. In-situ conditioning promotes increased material removal rates as compared to ex-situ conditioning. For a silicon oxide CMP process developed on a Strasbaugh 6DS-SP CMP tool (IC000/Suba IV pad, conditioner (80 grit) with 14 lbs downforce and 20 rpm speed) higher (15 to 20%) oxide material removal rates and lower WIWNU (23 to 45%) were obtained by using in-situ pad conditioning as compared to ex-situ pad conditioning. Ex-situ pad conditioning is not optimal for silicon oxide polishing for since pad glazing can typically occur during a single polish cycle. Additionally, an ex-situ conditioning process increases the CMP process time which is often undesirable. On the other hand, ex-situ processes eliminate, or considerably reduce, the potential side effects caused by conditioning debris interacting with the wafer on the platen. For Cu CMP, in particular, in situ conditioning can cause the wafer to tilt towards the center of the pad due to different pad asperity rebound rates associated with the portions of the pad passing.
under the wafer. The extent of this wafer tilt strongly depends on the conditioner disk pressure. Moreover, slurry film thickness under the wafer decreases with increasing conditioner rotation or oscillation frequency during in-situ conditioning. Therefore, more slurry flow will be required to increase the slurry film thickness under the wafer and decrease the slurry thickness variations between the inside and outside edges of the wafer.\textsuperscript{58}

In terms of a priori predicting or calculating an optimal ex-situ conditioning time, there is currently no well-established strategy. The general rule is to use the shortest time suitable to bring back the removal rate and WIWNU to acceptable levels. It is important to mention here that conditioning with a fixed in-situ or ex-situ recipe may cause severe over/under conditioning as they are applied later in the life cycle of a CMP pad as the properties of the pad drift.\textsuperscript{5}

\subsection*{2.3: Nanoabrasives, Their Properties and Agglomeration at Pad-Wafer Interface}

\subsubsection*{2.3.1: Introduction of Nanoabrasives}

During a given CMP process, slurries consisting of special chemicals and nano-scale abrasive particles are distributed across wafer-pad interface.\textsuperscript{5} These nanoabrasives play an essential role in the CMP process as they are responsible for mechanical abrasion of the surface being polished. Additionally, abrasives can also have chemical effects on the polished surface.\textsuperscript{59}
According to Sir Isaac Newton, “the smaller the particles of the substance, the smaller will be the scratches by which they continually fret and wear away the glass until it polished”.\textsuperscript{60, 61} Due to the small size of the nanoabrasives as well as relatively small fraction of solids in the CMP slurry, the fluid is usually assumed to behave in a Newtonian manner.\textsuperscript{21, 62}

A wide variety of materials such as alumina, silica, ceria, zirconia, titania, and diamond have been used as abrasive particles in CMP processes. For particular CMP applications, the effectiveness and suitability of these particles depend on their bulk properties (hardness, density, particle size, crystallinity etc.) and the surface properties (surface area, OH content, IEP-isoelectric point etc.).\textsuperscript{5}

Abrasive particles’ primary function is to transmit the wafer downforce to the polishing surface and increase the local mechanical interaction with the pad that results in an increased removal rate.\textsuperscript{5} Abrasion typically increases with increasing hardness of the particle as does the potential for substantial surface damage.\textsuperscript{59} The amount of material removal is determined in large part by the contact area of the particles with the polishing surface. This contact area increases with increased particle concentration and reduced particle size. This is true, for the most part for both metal and oxide CMP. Beyond their mechanical role, abrasives serve as adsorption sites. They assist in the transportation or elimination of the reaction by-products and polishing debris from the vicinity of the wafer that may otherwise lead to unwanted defectivity including scratching or corrosion of the wafer. For example, silica abrasive particle surfaces possess a higher number of hydroxyl groups per unit area compared to other abrasives such as alumina, ceria, titania,
and diamond. Clearly, the role of abrasive particles in CMP processing is very dynamic and multifaceted.\textsuperscript{5}

Monodispersion in the abrasive size leads to super polishing (extremely smooth surfaces). It also promotes uniform particle distribution which is desirable to minimize surface defectivity.\textsuperscript{59} In general, to resist agglomeration, a high repulsive electrostatic surface charge (~40 mV and above\textsuperscript{63}) on the abrasive particles is maintained by the chemical composition of slurries.\textsuperscript{5}

Table 2.1. Isoelectric point (IEP) as well as Bulk hardness values of various CMP abrasives, substrates and IC1000 pad particles.

<table>
<thead>
<tr>
<th>Abrasive/pad/substrates</th>
<th>IEP (pH)\textsuperscript{59}</th>
<th>Bulk Hardness (Mho’s Scale)\textsuperscript{5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (Al\textsubscript{2}O\textsubscript{3})</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Silica (SiO\textsubscript{2})</td>
<td>2.2</td>
<td>6-7</td>
</tr>
<tr>
<td>Ceria (CeO\textsubscript{2})</td>
<td>6.8</td>
<td>6 \textsuperscript{64}</td>
</tr>
<tr>
<td>IC1000 pad particles</td>
<td>3 \textsuperscript{65}</td>
<td>---</td>
</tr>
<tr>
<td>Copper</td>
<td>2.5-3.0</td>
<td></td>
</tr>
<tr>
<td>Copper Oxide</td>
<td>3.5-4.0</td>
<td></td>
</tr>
</tbody>
</table>

2.3.2: Nanoabrasives for Copper CMP

Copper CMP slurries are complex mixtures typically comprised of nanoabrasives and chemical components including oxidizers, corrosion inhibitors, buffers, and surfactants.\textsuperscript{5} The most commonly used abrasives in Cu CMP slurries are silica and alumina particles.\textsuperscript{59} Coated or composite particles such as alumina on silica\textsuperscript{66} or polymer\textsuperscript{67} as well as organic particles\textsuperscript{6} have been also tested for Cu CMP.

In the case of Cu damascene CMP processing, alumina is typically used in step 1 (platen 1) to remove the bulk Cu above the patterned features. Silica is often used in step
2 (platen 2) as well as in step 3 (buffing step on platen 3) polishing to remove barrier metals and residual Cu. This multistep copper CMP process provides advantages in terms of copper removal rate, dishing and erosion.

The relative importance of abrasive hardness and particle functional groups was investigated for copper and Ta CMP using alumina, silica and diamond particles. It was found that hydroxyl groups on the abrasive particles have a considerable impact on the polishing rate as well as removal rate selectivity, especially for silica. The amount of copper in the form of oxide adsorbed onto the silica was higher as compared to alumina. However, the removal rate of copper was found to be higher with the alumina abrasives, thus showing the larger impact of the abrasive hardness. Higher CMP removal rates with alumina, as compared to silica, have also been confirmed by other groups. The alumina nanoabrasives are mostly used to obtain higher Cu removal rates in the first step. Colloidal silica is adopted in the second-step CMP, in view of its spherical shape (less damage on polished substrates) and due to its high suspension stability with a wide pH range in slurries. Even in the first step of copper polishing, colloidal silica may be used in place of alumina because of defect concerns. For example, during Cu polishing, alumina introduces more scratches and surface roughness as compared to silica due to its greater hardness. Moreover, scratches are deeper in the case of alumina. For metal CMP, the final surface quality of a polished substrate is also as important as material removal rate. Therefore, one should not trade surface quality just simply for material removal rate, when considering the benefit brought by abrasive particles hardness.
2.3.3: Study on Agglomeration of Nanoabrasives at Pad-Wafer Interface

In general, high repulsive electrostatic surface charge on abrasive particles is maintained by the chemical composition of polishing slurries to stay in suspension and resist agglomeration. A typical DLVO (named after Derjaguin, Landau, Verwey, and Overbeek) potential diagram shown in Fig. 2.17 describes the energy barrier as well as the primary and secondary energy traps for two particles to overcome in order to aggregate. For optimal CMP performance, substantial stability of the slurries under extreme environments is required. Aggregation between particles may significantly increase the mean particle size of the slurry. Even a small amount of relatively harder dry aggregates or large slurry particles in the slurry population can quite dramatically deteriorate the performance of a CMP slurry by producing fatal surface defects such as delamination, embedded slurry particles and microscratches on the wafer. Agglomeration can be inhibited via slurry formulation through proper electrolyte balance as well as through filtration before delivery to the CMP platen.

In practice, optimization of slurry characteristics with respect to wafer defects has proved challenging although considerable progress has been made towards minimizing oversized particles, controlling dispersion stability, and modifying or refining abrasive particles characteristics. It has been speculated that some wafer defects occurring during CMP are caused by the transient soft agglomerate formation in the CMP slurries since high defect counts on the polished surfaces are often observed despite point-of-use filtration. The possibility that large, scratch-inducing particles can be formed during the CMP process as the result of agglomeration is very important issue for
overall defectivity. And since metal CMP slurries are prone to formation of aggregates this issue is even more critical for Cu CMP processing.

Mass balance analysis with spent slurry after Cu polishing with silica and alumina based slurry show that abraded Cu existed both in silica and alumina particle based slurry solutions, ~48% and ~8% respectively. To simulate the slurry during copper CMP, Cu nanoparticles were added in the slurry. It was found that even a small amount of copper in the slurry can increase the alumina agglomeration for higher pH values (especially pH >7). Similarly Cu$^{2+}$ ions also stimulate silica agglomeration. In other investigations, large particle count (LPC) analysis of spent slurry showed a direct correlation between wafer defectivity and LPC counts. Where, nanoabrasive type and concentration as well as polishing material have significant effect on agglomeration behavior.

Heating and shear rates experienced by CMP slurries on the pad during CMP may also affect agglomeration. High shear rates of $10^5$–$10^7$ 1/s are very common during CMP processing based on measurements of slurry film thickness at the pad/wafer interface and nominal velocities during polishing. Shear conditions may lead to the breakdown of repulsive force balance between abrasive particles. If fluid shear can deliver enough energy to particles to lessen their separation, van der Walls intermolecular attractive forces can dominate repulsive electrostatic forces. This can result in particle agglomeration explained by the DLVO theory. In addition to shearing, the possibility of fluid cavitation also can increase. (It was found that cavitation plays a more significant role than shear in agglomeration of slurry particles.) The frictional heat (temperature) generated in CMP also affects the characteristics of the slurry. The agglomeration of abrasive particles may occur above a certain temperature through changes the local pH.
value of the slurry. The friction coefficient and polishing temperature are changed significantly during the first (initial) stage of polishing. Reaction temperature rise to 12 °C, just only on the surface of the copper wafer as observed through temperature simulations. In other investigations, changes in the characteristics of silica slurry including particle size, pH, zeta potential, and conductivity have been confirmed as function of local polishing temperature. 

![Figure 2.17. Schematic of DLVO potential. Where, $V_R$ and $V_A$ represent the repulsive electrostatic potential and attractive van der Waals potential respectively.](image)

Of course, open structures of the polyurethane pad may retain the abrasive particles like a filter and may play a key role in particle agglomeration. This is particularly true at the pad-wafer interface during CMP. Larger particles retained in open pores of the pad may act as a ‘seed’ for further agglomeration. Clearly, pore-based
retention may occur more readily if the slurry exhibits particle ‘settling’. Alumina-based slurry typically has more severe particle settling issues than silica-based slurries because of the particle density difference.\(^5\) Particle settling is particularly a problem in high ionic strength slurries, where large amounts of ions cause to increase the shielding of surface charges and compression of the electrical double layer around the particles.\(^2\) Moreover, ionic strength and the pH of the solution changes during dilution with water. Both have been shown to influence aggregation as well as electric double layer characteristics of particles.\(^5, 87\) Consequently, any instability associated with slurry particle suspension at the pad surface could have dramatic impact on the particles and/or agglomerates retained in or on the pad after CMP.

2.4: Retention and Transport on CMP Pad

2.4.1: Slurry Retention and Transport in Copper CMP Process\(^88, 89\)

Efficient transport of slurry on pad surface is important to minimize particle defectivity on the wafer. The relevant literature related to slurry transport for Cu CMP is reviewed in this section.

2.4.1.1: Silica Nanoabrasive Retention and Transport\(^88\)

In Cu CMP, silica nanoabrasive retention on the pad surface has been confirmed on two types of CMP pads through affected polish rates (Fig. 2.18). As reported in Ref. 88 the CMP process used in the investigation consisted of two steps. In the first step, slurry containing silica particles (slurry “II” in Ref. 88) was supplied for 30 seconds.
Then immediately followed a second step in which the same slurry but without silica particles (Ref. I slurry) was supplied through separate slurry line for additional polishing time (30, 60, 90, 120 and 150 seconds). In the second step, for all polishing times, chemicals only slurry (slurry “I” in Ref. 88) demonstrated higher copper polish rates compared to actual polish rate offered by this slurry. Hence, it confirmed the significant nanoabrasive retention originating in slurry “II” on the pad surface that mixed with slurry “I” during second step polish. The calculated “effective” average particle concentrations on the pads after time “t” are summarized in Table 2.2. These are the concentrations in the slurry “which yields the same steady state polish rates as that of the combination of a 30 second supply of slurry “II” followed by a supply of slurry “I” for “t” seconds”.

Additionally, the authors also described silica nanoabrasive retention in other slurry-step-flow experiments by using D.I. water only or no slurry in the second step for 150s.

The findings of Ref. 88 provided evidence of nanoabrasive retention on CMP pad surfaces. But the presence of residual nanoabrasive was only represented in terms of effective copper removal rates and provided little quantitative information. Therefore, quantitative analyses are required directly on the surface of the pad (including both asperities and open pores) not only for quantifying nanoabrasive retention but also to investigate removal mechanisms for residual nanoabrasives.
Figure 2.18. Slurry-step-flow experimental results to investigate silica nanoabrasive retention on the pad surface. Plots show copper polish rates verses polish time with Ref. I slurry (chemicals only) following an initial 30s of polishing with Ref. II slurry (chemicals and 3 wt % of silica). Cu polish rates of Ref. I and Ref. II slurries are shown on left side. Chemicals means here 5 wt.% H₂O₂ + 1 wt.% glycine at pH 4.

Table 2.2. Effective average silica nanoabrasive concentration (retention) on pad surface after different polishing time intervals of second step in slurry-step-flow experiments when no abrasive particle (chemical only) Ref. I slurry was used (adapted).

<table>
<thead>
<tr>
<th>Time, t (seconds)</th>
<th>Effective average particle concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC 1400</td>
</tr>
<tr>
<td>30</td>
<td>3.0</td>
</tr>
<tr>
<td>60</td>
<td>2.5</td>
</tr>
<tr>
<td>90</td>
<td>1.7</td>
</tr>
<tr>
<td>120</td>
<td>1.3</td>
</tr>
<tr>
<td>150</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.4.1.2: Slurry Chemicals Retention and Transport

Similar to the aforementioned slurry-step-flow experiments, retention and transport of glycine and H₂O₂ has also been investigated. It was observed that effective concentration of glycine was retained at the pad for 15 seconds while H₂O₂ was retained.
for an even longer time in the 2nd step polish. Similar to the descriptions provided in previous section, no corresponding chemical component was used in the slurry for the 2nd step polish. The effective concentration of hydrogen peroxide was still 0.2 wt% out of 5 wt% on pad surface even after 150 seconds. Moreover, it has been found in investigations by other researchers that a smaller amount of H$_2$O$_2$ (0.1 wt %) in a Cu-H$_2$O-glycine system actually increased the agglomeration (alumina).\textsuperscript{80} Though both findings are independent, they indicate the possibility of agglomeration of alumina at pad/wafer interface due to retention of H$_2$O$_2$ on pad surface.

2.4.2: Cu Transfer (Retention) on CMP Pad during Copper CMP

Ying Li and co-workers\textsuperscript{70} investigated the amount of Cu on the pad surface after Cu polishing with silica and alumina based slurries by using a mass balance analysis. In this study, the amount of Cu was determined quantitatively by atomic absorption (AA) spectrophotometry. In their results, abraded Cu from the wafer was found on the CMP pad surface for both silica and alumina based slurries; ~8.7% and ~3.7% respectively.

Moreover XPS analysis\textsuperscript{90, 91} on the urethane polishing pad was carried out during Cu/urethane pad friction tests experiments in dry and wet conditions. The friction-induced transfer of atoms from the copper surface to the urethane pad surface was determined. The transferred Cu was in the form of copper oxide under wet conditions and elemental copper under dry condition. XPS analysis (related to oxide layer on Cu wafer and pad surface) further showed that adhesion of copper oxide was stronger for the urethane pad surface than for the copper wafer surface.
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CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1: CMP Tool: Configuration and Specifications

3.1.1: Strasbaugh 6DSSP (200mm CMP Tool)

A Strasbaugh 6DSSP 200 mm CMP tool (Fig. 3.1) was utilized for nanoabrasive retention investigations following Cu polishing. An ex-situ conditioning protocol was used. It is a fully automated system to polish 200mm wafers and has two platens; one can be used for polishing and the other for buffing or second step polishing.

![Strasbaugh 6DSSP CMP Tool](image)

Figure 3.1. Strasbaugh 6DS-SP CMP Tool photographs (courtesy of Strasbaugh).
3.1.2: Tool Configuration and Working Procedure

The wafer to be polished is placed at load/unload station on the shuttle (Fig. 3.2) which 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 (table 1 or table 2). The table 1 platen is a circular polished granite slab ~ 30 inch in diameter. The CMP pad (28 inch in diameter) is attached to the platen via a backside adhesive. To polish a wafer, bridge transports the loaded carrier from the shuttle position to table 1. Both the carrier (holding the wafer) and table 1 (holding CMP pad) are rotated independently with particular angular velocities (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, generally having nanoabrasives, is continuously supplied with a specific slurry flow rate (S.F.R) at the center of the pad until the end of CMP process. The rotation of table 1 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) denoted as D.F and back pressure donated 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 tool also possesses force ramp (F.R) and back pressure ramp (B.P.R) parameters which can be varied to optimize a given process. The wafer is polished for certain amount of time (known as polish time,
During or after each wafer polish on table 1, CMP pad is in-situ or ex-situ conditioned, respectively, using a diamond studded CMP conditioning wheel. In-situ and ex-situ conditioning depend on the nature of the CMP process. For example, Cu polishing usually utilizes ex-situ conditioning. The CMP conditioner is lowered, rotated, and swept onto the rotating pad with desired conditioning parameters by a robotically controlled conditioning arm. After completion of polishing, the spindle/carrier lifts up the polished wafer from the pad surface. The bridge moves back towards load/unload station and brings the polished wafer over table 2.

Figure 3.2. Interior of the 6DS-SP from the top-down (courtesy of Strasbaugh).

Table 2 is a buffing table that is used to clean the surface of the wafer by removing polishing debris, slurry residue and film particulates. Buffing steps on table 2 and related processing parameters are similar to polishing steps. However in buffing steps D.I water is typically used in place of slurry. After completion of the buffing and rinsing steps, the carrier leaves the wafer on the shuttle (unload station).
3.2: CMP Consumables

In terms of consumables, the nanoabrasive retention experiments described in this dissertation utilized IC1000/Suba IV stacked CMP pads, two commercial slurries, and an in-house formulated slurry. The commercial slurries were selected on the basis of their industry-wide use, their Cu polishing performance and nanoabrasive particle composition. The first, Cabot 5001 commercial Cu slurry, employed alumina nanoabrasives. The second, JSR commercial Cu slurry, employed silica nanoabrasives. The in-house formulated slurry utilized alumina nanoabrasives synthesized by Applied NanoWorks (ANW). The performance of the optimized ANW slurry formulation was comparable to latest Cabot C7092 Cu slurry (for 130nm - 45nm technology nodes). A Strasbaugh 6DSSP tool-conditioning disk (Sample Marshal Disk) was used for ex-situ pad conditioning in all experiments. Relevant features and/or properties of these consumables including relevant SEM and optical images are given in following sections.

3.2.1: CMP Pad

Concentric circular grooved IC1000/Suba IV stacked CMP pads (28” diameter) were used in these investigations. For each experiment a new pad was used. A pad mounted on the CMP tool platen (table 1) is shown in the left panel of Fig. 3.3. The slurry supply line is also visible in the image. Circular grooves on the pad surface are shown in right panels of Fig. 3.3.

To explore the features of the polyurethane IC1000/Suba IV CMP pads in more detail, SEM micrographs of the pad are shown in Fig 3.4. Top and cross-sectional views in the left panels of Fig. 3.4 show the pad grooves in more detail and also show the micro
scale open pore distribution in the CMP pad. The pores within the pad are mainly spherical. However, the pore size and shape are modified at the surface of the pad due to polishing. The IC1000/Suba IV stacked pad’s top layer consists of the polyurethane IC1000. The bottom layer consists of a foam Suba IV pad (cross-sectional SEM image in lower left panel of Fig. 3.4). The IC1000 is relatively hard compared to the Suba IV pad.$^{1,2}$

![Figure 3.3. Images of Polyurethane IC1000/Suba IV pad surface. Left and bottom right are digital images and top right is the optical images.](image)

IC1000 asperities and open pores are shown in Fig. 3.5 with higher magnification SEM images taken at different scan angles (normal and 45° angle). The asperities are the areas between the open pores at the top of CMP pad surface. During polishing, the wafer interacts with nanoabrasives and the pad surface mainly through these asperities. The top surface of the pad is a relatively rough surface as shown in the 45° angle SEM image (right panel of Fig. 3.5). Additional information about IC1000 and Suba IV pads features and properties are given below in Table 3.1.
Figure 3.4. SEM images of cross-section and surface of Polyurethane IC1000/Suba IV stacked CMP pad.

Figure 3.5. SEM images of surface morphology of IC1000/Suba IV CMP pad at different scan angles.
Table 3.1. Key features and properties of Polyurethane IC1000/Suba IV (circular grooved) CMP pad. Where, groove information was found from SEM images.

<table>
<thead>
<tr>
<th>Top pad (IC1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Porosity (# of pores/mm²)</td>
</tr>
<tr>
<td>Void or pore content per unit volume</td>
</tr>
<tr>
<td>Pore diameter</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Compressibility</td>
</tr>
<tr>
<td>Hardness Shore D</td>
</tr>
<tr>
<td>Groove width</td>
</tr>
<tr>
<td>Distance between grooves(center to center)</td>
</tr>
<tr>
<td>Groove depth</td>
</tr>
<tr>
<td>Grooves type</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bottom pad (SubaIV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Compressibility</td>
</tr>
<tr>
<td>Weight density</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
</tr>
</tbody>
</table>

3.2.2: Nanoabrasives

SEM images of slurry nanoabrasives investigated for this dissertation are shown below. For SEM imaging of each slurry nanoabrasives, the slurry was diluted in D.I water and a small amount of the solution was dried on carbon tapes for 24 hours in clean environment to avoid air contaminants.

3.2.2(a) Cabot (5001) Alumina Nanoabrasives

The Cabot 5001 commercial Cu slurry contains alumina nanoabrasives as shown in Fig. 3.6. The average size of the nanoabrasive was approximately 70 nm.
3.2.2(b) JSR Silica Nanoabrasives

The JSR commercial Cu slurry used in these investigations contains silica nanoabrasives (Fig. 3.7). The average size of the nanoabrasive was approximately 50 nm.
3.2.2(c) Applied NanoWorks (ANW) Alumina Nanoabrasives

Applied NanoWorks Inc. (ANW) alumina nanoabrasives (Fig. 3.8) were used to develop an in-house slurry for Cu polishing. One of the optimized slurry formulations using these nanoabrasives was also used in nanoabrasive retention investigation experiments. The average particle size was approximately 50 nm.

Figure 3.8. ESEM (top) and SEM (bottom) images of ANW alumina nanoabrasive particles.
3.2.3: Slurries

During use, both commercial and in-house formulated slurries were agitated to homogenize the slurry during use (per vendor specifications for the Cabot and JSR slurries). In addition to this, re-circulation pumps, attached to the Strasbaugh 6DSSP CMP tool, provided slurry agitation to maintain nanoabrasive suspension.

3.2.3(a) Cabot iCue 5001 Cu Slurry

Cabot iCue 5001 was a first-step Cu CMP commercial slurry. For the nanoabrasive retention experiments, either 2% or 6% hydrogen peroxide (by volume) was added to the slurry (per vendor recommendations). After adding hydrogen peroxide in the slurry, slurry mixing was continued with mechanical stirrer at operating speed of ~350 rpm for 10-15 minutes before polishing. The slurry composition and physical/chemical properties of the slurry are given below in Table 3.2 and Table 3.3, respectively. The Cu material mean removal rates (MRRs) achieved with this slurry (on 6DSSP CMP tool in our lab) by mixing different amounts (by volume) of hydrogen per oxide are shown in Fig. 3.9. The highest and lowest MRRs were achieved after mixing this slurry with 2% and 0% H₂O₂ (by volume), respectively.

Table 3.2. Composition/information on Cabot iCue 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 3.3. Physical and chemical properties of Cabot 5001 alumina slurry.\textsuperscript{8, 9}

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
</tr>
<tr>
<td>Solubility in water</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Boiling point</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
</tbody>
</table>

Figure 3.9. Average Cu MRR on circular rings at certain radii of the 200mm Cu wafer as a function of H\(_2\)O\(_2\) concentration (by volume) mixed with Cabot 5001 slurry.\textsuperscript{10} Polishing downforce was 2 psi and wafer was polished on 6DSSP tool.

3.2.3(b) Applied NanoWorks (ANW) Baseline Cu Slurry

Using alumina nanoabrasive supplied by Applied NanoWorks (ANW) Inc. a baseline Cu slurry was formulated, characterized and optimized. Properties of the ANW alumina nanoabrasive solution are shown in Table 3.4. The slurry mixing procedure to formulate a Cu baseline slurry with these nanoabrasives is provided below (Table 3.5). The concentrations of chemicals and abrasive used to formulate baseline slurry for nanoabrasive retention experiments are given in Table 3.6.
Table 3.4. ANW Al₂O₃ nanoabrasive solution (D.I water + alumina) information.¹¹

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH range</td>
<td>7-8</td>
</tr>
<tr>
<td>Melting point</td>
<td>2000 C/3632 F</td>
</tr>
<tr>
<td>Specific gravity (water=1)</td>
<td>4</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

Table 3.5. Slurry mixing procedure of ANW baseline slurry.

<table>
<thead>
<tr>
<th>Step #</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Measure out appropriate amount of D.I water necessary to reduce alumina</td>
</tr>
<tr>
<td></td>
<td>concentration from 5 wt% (as-received) to 0.44 wt%</td>
</tr>
<tr>
<td>#2</td>
<td>Add required amount of BTA to DI water and stir for 3-5 minutes</td>
</tr>
<tr>
<td>#3</td>
<td>Add required amount of glycine to DI water/BTA mixture and mix/stir for 5</td>
</tr>
<tr>
<td></td>
<td>minutes (or until fully dissolved)</td>
</tr>
<tr>
<td>#4</td>
<td>Add required amount of 5 wt% (as-received) ANW alumina nanoabrasive</td>
</tr>
<tr>
<td></td>
<td>suspension to DI water/BTA/glycine mixture</td>
</tr>
<tr>
<td>#5</td>
<td>Add required amount of hydrogen peroxide to mixture (stirring)</td>
</tr>
<tr>
<td>#6</td>
<td>Adjust pH of slurry with KOH (to pH 8.5)</td>
</tr>
</tbody>
</table>

Table 3.6. ANW alumina based baseline slurry formulation parameters (chemicals and abrasive concentrations).

<table>
<thead>
<tr>
<th>H₂O₂ (1 wt %)</th>
<th>ANW Abrasives (0.44 wt %)</th>
<th>BTA (0.0005M)</th>
<th>Glycine (2 wt %)</th>
<th>D.I water</th>
<th>Total</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>451.61gms</td>
<td>1,232gms</td>
<td>0.834gms</td>
<td>280gms</td>
<td>12035.5 ml</td>
<td>14 lit</td>
<td>8.5</td>
</tr>
</tbody>
</table>

This baseline slurry formulation provided higher Cu MRR (Fig. 3.10) and comparable Cu wafer surface roughness (RMS ~ 2 nm) as compared to the latest commercial version of the Cabot Cu slurry (Cabot C7092, for 130nm - 45nm technology nodes) on the 200 mm wafer Strasbaugh 6DSSP CMP tool. These Cu removal rates were somewhat higher than the Cu removal rates obtained with the commercial JSR silica-based Cu slurry (Fig. 3.12) on the 200mm Strasbaugh 6DSSP CMP tool.
3.2.3(c) JSR Cu Slurry

The JSR Cu polishing commercial slurry (containing silica nanoabrasives) was also used in the nanoabrasive retention experiments. This slurry consisted of 3 components (chemical/nanoabrasive solutions). 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. 3.11. Slurry additives concentrations as well as physical and chemical properties are shown in Table 3.7 and Table 3.8. The final JSR slurry pH was measured in the lab and was found to be ~ 8.3. This slurry provided an average Cu MRR of roughly 400nm/min on 200mm wafer 6DSSP Strasbaugh CMP tool (Fig. 3.12).
Figure 3.11. Slurry mixing procedure of JSR silica slurry. Wt % concentrations are not shown due to proprietary information.

Table 3.7. Slurry additives concentrations in JSR Cu slurry/chemical solutions (CMS7401 & CMS7452).\(^\text{12, 13}\)

<table>
<thead>
<tr>
<th></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 3.8. Physical and chemical properties of JSR Cu slurry/chemical solutions (CMS7401 & CMS7452).\(^\text{12, 13}\)

<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>Ca. 100° C</td>
<td>Ca. 100° C</td>
</tr>
</tbody>
</table>
Figure 3.12. Average Cu MRR on circular rings at certain radii of the 200mm Cu wafer polished with JSR Cu slurry on 6DSSP 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.

3.3: Conditioning Features of the Tool

To perform ex-situ conditioning during nanoabrasive retention experiments, a diamond conditioning disk (Sample Marshal Disk) was used on the Strasbaugh 6DSSP CMP tool. A photograph and specifications of the disk are shown in Fig. 3.13 and Table 3.9, respectively. During conditioning steps, the slurry is continuously supplied at the center of the CMP pad as shown in Fig. 3.14. With both the platen and conditioner disk rotating at user-selected velocities, the conditioner arm is programmed to sweep a particular distance along the radial direction of the CMP pad. The sweep range – the radial distance that the conditioner travels on the surface of the pad – consists of 20 equal segments (in inches). The length of each segment depends on the given inner and outer position (measured from the polishing table center) of the sweep range. Conditioning
time and conditioning downforce for each segment is set in seconds and lbs/psi, respectively. Although the Strasbaugh 6DSSP CMP tool supports both ex-situ ((after polishing) and in-situ (during polishing) conditioning, only ex-situ conditioning was used for the Cu CMP investigated here. Specifically, one-way (outer to inner position) ex-situ conditioning was performed on CMP pad surfaces exposed to Cu polish.

![Figure 3.13. Photograph of Strasbaugh 6DSSP conditioning disk _ Sample Marshall Disk.](image)

### Table 3.9. Specifications of Strasbaugh 6DSSP conditioner (Sample Marshall Disk)

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product name</td>
<td>6DSSP, diamond conditioning disk, PLTD</td>
</tr>
<tr>
<td>Disk diameter</td>
<td>4”</td>
</tr>
<tr>
<td>Diamond grit</td>
<td>100 grit</td>
</tr>
<tr>
<td>Seasoned</td>
<td>yes</td>
</tr>
<tr>
<td>Applications</td>
<td>Oxide CMP applications (both in-situ and ex-situ)</td>
</tr>
<tr>
<td>Applications</td>
<td>Metal CMP applications (ex-situ only)</td>
</tr>
</tbody>
</table>
3.4: Experimental Setup of Conditioning and Polishing for Nanoabrasive Retention Investigations

In each nanoabrasive retention experiment, a new polyurethane CMP pad was installed and a pad ‘break-in’ procedure was completed (4 successive 1-minute Cu CMP cycles with ex-situ conditioning after each polish). After pad break-in the nanoabrasive retention experiments were carried out. The polishing and conditioning strategies as well as parameters for each experiment are given in the following sections.

3.4.1: Copper Polishing Parameters

The polishing process parameters used for 200mm blanket Cu wafer polishing on the Strasbaugh 6DSSP CMP tool during nanoabrasive retention experiments are shown in Table 3.10. For each nanoabrasive retention experiment, the Cu wafer underwent 30 individual 1-minute polishing steps. The schematic diagram (Fig. 3.15) shows the landing
position of a 200mm Cu wafer on the surface of the 28 inch diameter polyurethane CMP pad (platen 1). The Cu wafer landing position on pad surface placed its inner edge 3 inches from the pad center and its outer edge 11 inches away from pad center. The wafer center was 7 inches away from the pad center. The oscillatory motion of the Cu wafer on pad was set to zero. After the completion of each polishing step, the wafer was also polished on second table (buffing table) for 30 seconds with 2 psi downforce to clean wafer (or to reduce polishing debris, byproducts, particle contamination or small scratches from wafer etc.). During the buffing step D.I water was used rather than slurry.

Table 3.10. Polishing process parameters for Cu polishing during nanoabrasive retention experiments with different slurries.

<table>
<thead>
<tr>
<th>Main polishing parameters</th>
<th>Experiments with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cabot 5001 slurry</td>
</tr>
<tr>
<td>Polishing time</td>
<td>60 seconds</td>
</tr>
<tr>
<td>Spindle speed</td>
<td>60 rpm (ccw)</td>
</tr>
<tr>
<td>Table speed</td>
<td>45 rpm (ccw)</td>
</tr>
<tr>
<td>Polishing force</td>
<td>5 Psi</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>150 ml/min</td>
</tr>
<tr>
<td>Total # of Cu polishing steps</td>
<td>30</td>
</tr>
</tbody>
</table>

![Figure 3.15. Schematic shows the wafer landing location on CMP pad surface. Where, slurry was supplied over the center of the pad surface.](image)
3.4.2: Ex-situ CMP Pad Conditioning Parameters and Strategies

In each nanoabrasive retention experiment, one way, ‘outer to inner’, ex-situ conditioning was performed on the CMP pad surface along the radial direction of pad. The CMP pad and conditioner were rotated at equal angular velocities (45 rpm ccw) to obtain the most uniform pad conditioning profile as discussed in chapter 2. During conditioning a constant amount of slurry (100 ml/min) was continuously supplied on the pad surface. The ex-situ conditioning was performed following the Cu polishing step during each Cu polish cycle. As each nanoabrasive retention experiment consisted of 30 Cu polishing steps, there were 30 ex-situ conditioning steps for the 30 Cu polishing cycles. A summary of the conditioning parameters is given in Table 3.11.

Table 3.11. Conditioning parameters common for all experiments.

<table>
<thead>
<tr>
<th>Common conditioning parameters</th>
<th>All experiment (with Cabot 5001, ANW baseline and JSR slurries)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditioning &amp; sweep style</td>
<td>Ex-situ, outer to in, one way</td>
</tr>
<tr>
<td>Conditioner speed</td>
<td>45 rpm</td>
</tr>
<tr>
<td>Pad speed</td>
<td>45 rpm</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>100 ml/min</td>
</tr>
<tr>
<td>Total ex-situ conditioning steps</td>
<td>30</td>
</tr>
</tbody>
</table>

For all nanoabrasive retention experiments, the pad conditioning was performed only on the pad surface locations that were exposed to Cu polishing. This is illustrated in the schematic diagrams of Fig. 3.16 & 3.17. As mentioned above, the diameters of the Cu wafers and pad conditioner were 8 inch and 4 inch respectively; and the landing position of the wafer on the 28 inch pad surface comprised an annular ring with an inner radius of 3 inches and an outer radius of 11 inches – both measured from the center of the polish pad. Therefore, during each ex-situ conditioning step, the conditioner motion was set in
such a way that the conditioner spent half its time on pad surface exposed to the outer half of the 200mm wafer and the other half of its time on the pad surface exposed to the inner half of the 200mm wafer. Specifically, an annular region of the pad with an inner radius of 7 inches and an outer radius of 11 inches was exposed to 50% of the conditioning per cycle. A second annular region of the pad with an inner radius of 3 inches and an outer radius of 7 inches was exposed to the remaining 50% of the conditioning cycle. Moreover, during conditioning at both these sections, the conditioner sweeping motion was set almost to zero. Therefore, the center of the conditioner during conditioning time at both sections was at 9” inch and 5” inch away from the center of the pad. As both outer and inner conditioning sections widths were exactly equal to conditioner diameter, therefore, there was no overlapping of conditioning at any of the pad section (outer or inner) from the conditioning done at other pad section. In most of the nanoabrasive retention experiments described herein, conditioner downforces of 18 lbs and 10 lbs were selected for the outer and inner half sections of the wafer-exposed pad surface, respectively. This is schematically described in Fig. 3.16 with additional information provided in Table 3.12.

During the conditioner downforce experiments, all Cu slurries (mentioned above) were investigated for nanoabrasive retention. But as both pad and conditioner were rotated at 45 rpm (counter clockwise) during conditioning, distinct pad/conditioner relative velocities of 1.07 m/s and 0.59 m/s existed on the outer and inner half sections of the pad surface exposed to wafer polishing. This relative velocity differential is in addition to the distinct conditioning forces of 18 lbs and 10 lbs applied to these two pad sections are noted above. Therefore, to decouple the effects of conditioner downforce and
pad/conditioner relative velocity on the nanoabrasive retention, an experiment was designed – referred to as a pad/conditioner relative velocity experiment – in which the conditioner downforce was set constant (10lbs) at both pad sections exposed to Cu polishing. This provided an opportunity to take advantage of the intrinsic pad/conditioner relative velocity difference of 0.48 m/s to investigate the nanoabrasive retention in terms of pad/conditioner relative velocity. For this set of experiments, the conditioning strategy is illustrated in a schematic diagram (Fig. 3.17) with specific conditioning parameters provided in Table 3.13. In addition, a third nanoabrasive retention experiment was designed (using Cabot 5001 slurry) in which the pad surface exposed to Cu polishing was conditioned with three different conditioning downforces of 18 lbs, 14 lbs and 10 lbs. These conditioning downforces were applied to three annular regions of the CMP pad with radial extents of 13 inches to 9 inches, 9 inches to 5 inches, and 5 inches to 1 inch, respectively, from the center of the pad surface. In this last experiment, Cabot 5001 slurry was mixed with 6% H₂O₂ (by volume). But for other experiments completed with Cabot 5001 slurry as described above, 2% H₂O₂ (by volume) was mixed in Cabot 5001 slurry. It is important to mention here that different conditioning times were chosen for each nanoabrasive retention experiment completed with Cabot 5001 slurry to investigate the nanoabrasive retention as a function of conditioner time. For nanoabrasive retention experiments using ANW and JSR slurries, the conditioner time was set to 20 seconds, based on the conditioning time information obtained from experiments done with Cabot 5001 slurry. Details will be discussed in the following chapters.
Figure 3.16. Schematic of conditioning downforce experiments.

Figure 3.17. Schematic of conditioning relative velocity experiment.
Table 3.12. Conditioning parameters for conditioning downforce nanoabrasive retention experiments. Where, 18 lbs and 10 lbs conditioning downforce was applied respectively at outer and inner section of the pad surface exposed to Cu polishing. Where, for experiment completed with Cabot 5001 slurry mixed with 6% H₂O₂, third pad section between outer and inner pad sections was also selected. On this section, 14 lbs conditioning downforce was applied for 11 seconds.

<table>
<thead>
<tr>
<th>Slurry type</th>
<th>Ex-situ conditioning time per conditioning step, i.e. after each Cu polish step</th>
<th>Ex-situ conditioning downforce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outer pad conditioning section</td>
<td>Inner pad conditioning section</td>
</tr>
<tr>
<td>Cabot 5001 alumina slurry mixed with 2% (by vol) H₂O₂</td>
<td>17 seconds</td>
<td>17 seconds</td>
</tr>
<tr>
<td>Cabot 5001 alumina slurry mixed with 2% (by vol) H₂O₂</td>
<td>23 seconds</td>
<td>23 seconds</td>
</tr>
<tr>
<td>Cabot 5001 alumina slurry mixed with 6% (by vol) H₂O₂</td>
<td>11 seconds</td>
<td>11 seconds</td>
</tr>
<tr>
<td>ANW baseline alumina slurry</td>
<td>20 seconds</td>
<td>20 seconds</td>
</tr>
<tr>
<td>JSR silica slurry</td>
<td>20 seconds</td>
<td>20 seconds</td>
</tr>
</tbody>
</table>

Table 3.13. Conditioning parameters for pad/conditioner relative velocity nanoabrasive retention experiment completed with Cabot 5001 slurry. Conditioning downforce (10 lbs) was constant for both pad sections exposed to Cu polish.

<table>
<thead>
<tr>
<th>Slurry type</th>
<th>Ex-situ conditioning time per conditioning step, i.e. after each Cu polishing step</th>
<th>Pad/conditioner relative velocity (at constant, 10 lbs, conditioning downforce)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outer pad conditioning section</td>
<td>Inner pad conditioning section</td>
</tr>
<tr>
<td>Cabot 5001 alumina slurry mixed with 2% (by vol) H₂O₂</td>
<td>21 seconds</td>
<td>21 seconds</td>
</tr>
</tbody>
</table>
It is important to note here that no conditioning and polishing was performed at the center of the pad as obvious from the above schematic diagrams (Fig.3.16 & 3.17) and discussion. Only slurry was supplied over the pad center. Consequently, pad samples were also taken from this center area to use as a reference in order to compare the nanoabrasive retention from sections of the pad not exposed to polishing and/or conditioning to those exposed to polishing and/or conditioning. Therefore, for convenience, in the following discussion and chapters, samples taken from the pad center for nanoabrasive retention investigation are referred to as having experienced 0 lbs conditioner downforce or 0 m/s pad/conditioner relative velocity samples.

3.5: Characterization

After the completion of each nanoabrasive retention experiment, CMP pad samples were characterized for nanoabrasive retention by using a variety of characterization techniques. This characterization was done for samples as functions of conditioning parameters, slurry chemistry, nanoabrasive composition, and pad life. For quantitative analysis of nanoabrasive retention on the CMP pad surface, x-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) were utilized. XPS probed elemental concentration over a wide area scan (data collection from numerous asperities and open pores) and EDS enabled local probing (data collection from individual asperities and open pores). Additionally, SEM and ESEM techniques were used for qualitative analysis of nanoabrasive retention on pad surface, particle sizing of nanoabrasives of all slurries used in these experiments, and for morphology investigations of pad surface and cross-section. Profilometry was also used to
characterize the roughness of the pad surface (macro and micro analysis) in terms of conditioning parameters. Four-point probe was used to determine the material removal rate (MRR) and within wafer nonuniformity (WIWNU) of 200 mm Cu wafers after polishing with each type of slurry used in these experiments. Moreover, during pad life experiments, atomic force microscopy (AFM) was used to characterize scratches and particle adhesion at the Cu wafer surface in terms of nanoabrasive retention and/or agglomeration.

3.5.1: Sample Preparation

After the completion of Cu polishing and conditioning in each experiment, the CMP pad was dried for at least 24 hours on the CMP pad platen of the Strasbaugh 6DSSP tool. Drying the pad on the CMP tool not only provided the opportunity to avoid foreign particle contamination on the pad surface but also to maintain the environment of the tool during idling time. Later, CMP pad samples were cut for characterization. The size of each pad sample was ~13 mm in radial direction of the pad and 25 mm in circumference direction of the pad. CMP pad samples were cut from pad areas exposed to Cu polishing and conditioning and from pad areas not so exposed. The center of the pad was selected as the ‘unexposed’ area. For pad areas exposed to polishing and conditioning, pad samples were cut in the radial direction from a radial distances from 4 inches and 10 inches (both positions served as central point of samples). The 4 inch region was exposed to a lower amount of conditioning (downforce and pad/conditioner relative velocity) and the 10 inch region was exposed to a higher amount of conditioning (pad/conditioner relative velocity and/or conditioning downforce). Further details can be found in section
3.4.2 as well as in schematics shown in Fig. 3.16 & Fig. 3.17. For good cross sectional SEM analysis, CMP pad samples were broken after immersion in liquid nitrogen. For SEM and EDS analysis, CMP pad samples were coated with gold palladium (12 nm in thickness) to avoid charging effects on its insulating (polyurethane). For particle sizing of slurry nanoabrasives, all utilized slurries were diluted in D.I water with various ratios including 1:10, 1:50, 1:100 and 1:200 (slurry: D.I water), depending on the concentration (wt %) of nanoabrasives in slurry, to get acceptable SEM imaging of the nanoabrasive. A small amount of the solution was dried on carbon tapes for 24 hours in a clean environment to avoid air particle contaminants. With reference to characterization of Cu wafers by using 4-point probe and AFM analysis, polished wafers were first cleaned and dried in a spin rinse dry system (SRD).

3.5.2: X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface sensitive quantitative analytical technique that provides compositional as well as chemical bonding information of elements in the outer atomic layers of a sample. It can be used for all elements except hydrogen and helium, sensitivity in the range 0.1-1% in the outer atomic layers.\textsuperscript{14} The fundamental principal behind this spectroscopy technique is the photoelectric effect, an explanation of which was given by Albert Einstein in 1905.\textsuperscript{15}

In XPS spectroscopy, the specimen is first placed in an ultra high vacuum environment and then irradiated with monoenergetic soft x-rays of known energy (h\nu). Generally Al and Mg K\alpha X-rays with characteristic energies at 1486.6 eV and 1253.6 eV respectively are used to irradiate the sample.\textsuperscript{16} The energetic x-ray photon ionizes an
atom, producing free electrons from the atomic core shells of the elements present near the sample surface. A fraction of these photoelectrons find their way out of the material and escape into vacuum.\textsuperscript{17} The kinetic energy of the ejected photoelectron is dependent on the energy of the impinging photon and can be expressed as

\[ KE = h\nu - E_b - \Phi_{sp} \]

Here, KE is the kinetic energy of the electron ejected, \( h\nu \) is the energy of incoming photon, and \( E_b \) is the binding energy of the ejected electron to the core shell. \( \Phi_{sp} \) is the spectrometer’s work function (typically around 4.5 eV)\textsuperscript{18}, a combination of the work function of the sample, \( \Phi_s \), and work function induced by the analyzer.\textsuperscript{19} As the incoming x-ray photon energy \( h\nu \) is known and KE is measured with the help of an electron spectrometer, BE of the ejected electron is determined. As binding energies of core atomic orbitals of each element are unique, the peaks in an XPS spectrum help to indentify elements present on the surface of the specimen being analyzed. Additionally, BE of the electron also provides information of the atomic energy level of the parent element.\textsuperscript{17} Ejected electrons that leave the surface without energy loss produce well defined peaks in the spectra. Ejected electrons that suffer inelastic collisions give rise to background signals at relatively higher binding energies.
Figure 3.18. (a) Schematic diagram (adapted)\textsuperscript{17} representing the photoionization of an atom by the ejection of a 1s electron during the XPS process. (b) Schematic representation (adapted)\textsuperscript{19} of the photoemission process.

A typical XPS spectrum consists of the number of electrons detected (counts/s) versus electron binding energy as shown in plots in Fig 3.19 (b) & (c) The area under each peak is a measure of the relative amount of that element. To quantify electron spectra, many factors related to either spectrometer or sample must be considered. Sample related factors include the cross-section for emission and the escape depth of the electron.\textsuperscript{17} Spectrometer related factors include the transmission function of the spectrometer, the efficiency of the detector and stray magnetic fields.\textsuperscript{17} Atomic percentage of the elements concerned can be determined by dividing the peak area by the sensitivity factor and then expressing it as a fraction of the summation of all normalized intensities.\textsuperscript{17}
Figure 3.19. (a) Illustration of XPS spot size with SEM image on CMP pad surface. Plots in panels (b)-(c) demonstrate the XPS data collected on pad samples to determine residual alumina and silica retention on pad surface exposed to Cu wafer during CMP process.

In our investigations, elemental surface atomic concentrations were obtained using XPS technique to determine relative nanoparticle density (e.g. Al for alumina, Si for silica abrasives) on post-CMP pad samples. XPS surface characterization was carried out using a ThermoVG Thetaprobe equipped with a hemispherical analyzer and a monochromated Al Kα x-ray source (1486.6 eV) operated at 100W. The instrument has a 24 element multichannel detection system. The beam diameter used for analysis was 400μm in spot mode for area-averaged analyses. Pass energies 300 eV was used for surveys.
Surface charging of CMP pad samples during XPS spectra acquisition was neutralized by flooding the analytical area with -5eV electrons from a separate electron flood gun. Samples were mounted on a stainless steel stage using metal clips to minimize surface charging. The analytical chamber was maintained at a pressure of $2 \times 10^{-9}$ Torr during analyses. Clean tweezers and talc-free gloves were used for all samples handling to minimize contamination. XPS data was collected at three different locations on each CMP pad sample. An average value and standard deviation for the atomic concentration of each element of interest were determined for each sample in order to characterize the nanoabrasive retention.

3.5.3: Monte Carlo Simulations

Before EDS analysis, Monte Carlo simulations were performed to characterize the generation of secondary electrons and x-rays from the pad samples. For this purpose, the Casino v2.42 modeling tool was used. Details about these simulations can be found elsewhere. The goal of this modeling was to investigate the interaction volume of the electron beam, backscattered electrons (B.E), electron energies, as well as x-ray intensities generated by the interaction of the primary electron beam of the SEM with the CMP polyurethane pad surface and alumina or silica particles resident on its porous surface. These attributes were explored to investigate the possibility of local probing of EDS separately at asperities and open pores on the pad surface to determine the nanoabrasive retention present. For example, modeling was undertaken to determine if the interaction volume of electrons was confined to particular asperity regions on the pad or if the interaction volume spanned neighboring closed pores below an asperity. Similar
issues were addressed for open pores. This helps to ensure that data collected from particular pad features (asperity or pore) can be uniquely associated with that same feature. During simulations, thin films of alumina (50 nm and 100 nm) or silica (50 nm) were considered present on the surface polyurethane pad (substrate) to simulate the presence of nanoabrasive. These selected values of thicknesses were based on the alumina and silica nanoabrasive sizes that were used in the retention experiments. Additionally, simulations were also used to estimate the detected x-rays intensities of Al and Si emitted from alumina and silica thin films over polyurethane substrates, respectively. This helped to determine whether the detected x-ray intensities in EDS varied with increasing alumina thickness (from 50 nm to 100 nm) or varied by changing the type of film from alumina to silica (both having the same 50 nm thicknesses), over the polyurethane substrate under the same operating conditions. This information is useful when comparing nanoabrasive retention on the pad surface, for example, between Cabot 5001 alumina (~70 nm), ANW alumina (~50 nm), and JSR silica (~50 nm) retention. The modeling was also used as a first order approximation for quantitative comparison of EDS nanoabrasive retention data related to all the aforementioned slurries used in these experiments. Details are discussed in chapter 5. To get more precise simulations results, large number of electrons, 185,000, were simulated (electron beam radius was 100 nm). Although the actual electron beam radius of SEM is much less than this value at 15 KeV EHT and at 13 mm WD, the advantage in using this beam radius is to see the maximum spread of interaction volume. The pad density (0.78 gm/cm³) and urethane composition (C₁₀H₁₆N₂O₄) were used in simulations for IC1000 pad, based on literature and certificate of analysis.²², ²³, ²⁴
Figure 3.20. Monte Carlo simulations results show the backscattering coefficients as well as interaction volumes of electron beam for (a) 100nm (left image) and 50 nm (right image) alumina thin films, and for (b) 50 nm silica thin film. Where, thin films are considered over urethane substrate (representing polyurethane CMP pad) as shown in the schematic diagram (bottom right).
Through these simulations it has been observed (Fig.3.20) that the backscattering coefficient and interaction volume (depth and width) of the electron beam does not considerably change as the alumina thickness is increased from 50 nm to 100 nm or as the film composition changes from alumina to silica (50 nm thickness). The width (9.8-9.4 μm) and depth (6.1-6.0 μm) of the interaction volumes are quite small relative to the average pore and asperity volumes. So it is reasonable to assume that a given EDS measurement (scan) is localized to a single asperity or pore as also shown in Fig.3.23. Additionally, simulation results for electron energies in a given interaction volume within a pore suggest that the effective width associated with this volume is further reduced by approximately 50% (to ~ 5 μm). This is illustrated in Fig. 3.21. This is the case since electrons extending beyond this volume (outside the red lines in Fig. 3.21) do not have sufficient energy to generate Kα x-rays for Al (1.487 KeV) or Si (1.740 KeV).
Figure 3.21. Monte Carlo simulation ‘Energy by position’ results, showing the % energy of electrons at different locations in the interaction volume. Ka lines average energy values (in KeV) are also shown at bottom right. Where, symbols in parenthesis indicate an overlapping elemental line. Measurements are also shown along the depth and width of red line curve that represents the boundary where electron will have 10% of the initial beam energy (15 KeV) that is almost close to the Ka lines average energy values of Si and Al.

Monte Carlo simulation results shown in Fig. 3.22 (a), for all alumina and silica film thicknesses imply that the backscattered electron (B.E.) intensity at any surface radial distance (from center of the electron beam on specimen surface) is more than 900 times smaller than from the electron intensity delivered through the primary beam at the specimen surface (~184,000 electrons used in the simulation). Consequently, it is reasonable to ignore the contribution of x-rays generated by backscattered electrons from the alumina or silica. Additionally, the simulation data in Fig. 3.22 (b), show that the backscattered electrons (B.E.) at any specimen surface radius (from the incident beam
position) have insufficient energy to produce additional Kα x-rays from Al or Si. Consequently, it is reasonable to ignore any contribution from B.E. generated x-rays from neighboring pores or asperities. Additionally, the x-ray intensity vs. radial distance results (not shown here) show that the most of the characteristic x-rays from Al and Si elements (of alumina and silica respectively) are generated within the landing area of the primary electron beam.

Therefore, if the beam radius is equal or less than the silica or alumina abrasive particle radius we can assume that the EDS information from each single particle present on the polyurethane pad surface can be collected without interference of the EDS signal from the neighboring abrasives present on the pad surface.

![Figure 3.22](image_url)

**Figure 3.22.** Monte Carlo simulation results vs. specimen surface radius (from the primary beam landing position on the specimen surface) for alumina (100nm and 50nm) and silica (50 nm) thick films on urethane substrate. (a) # of backscattered electrons (B.E.) coming out of surface vs. specimen surface radius (b) Energy of backscattered electrons coming out of surface vs. radial escape position.
3.5.4: Energy Dispersive Spectrometry (EDS)

EDS is typically used in conjunction with a SEM as an attached module. During EDS data acquisition the surface of the specimen is exposed to the primary electron beam of the SEM. The incident electrons excite the inner shell electrons of atoms on the surface of the specimen to a higher energy state. De-excitation of the electron results either in the emission of characteristic x-ray or the emission of an Auger electron. Both of these can be used for elemental analysis. In EDS the emission of an x-ray with energy characteristic of an element present on the surface or inside of the specimen and this information is used for compositional analysis. In EDS, the emission of x-rays is more pronounced for heavier elements. EDS can be used to analyze surfaces with relatively high spatial resolution due to the small spot size of an electron beam. The electron-
beam generated x-ray spectrum in an EDS measurement is recorded using a multichannel analyzer with a spectral resolution around \( \Delta E_x \approx 150-180 \text{ eV} \). A practical elemental detection limit for EDS is approximately 1 weight percent. Typically, EDS analyses employ an accelerating voltage from 15 to 25 KV and typical values of the beam current range from 0.1-1 nA. Increasing the beam current increases the number of electrons that interact with the sample and produce x-rays; therefore, within limits, it has the same effect as increasing the counting time.

After the completion of each nanoabrasive retention experiment, EDS analysis was performed on the pad surface to determine the nanoabrasive retention on the CMP pad. For this purpose, samples were taken from the pad areas exposed and unexposed to Cu polishing and conditioning during the Cu polishing process. Two types of EDS scans, 200 x 200 μm\(^2\) and 25 x 25 μm\(^2\), were performed on the surface of each CMP pad sample. The 200 x 200 μm\(^2\) EDS scans were performed to compare the nanoabrasive retention results with wide area XPS results. The 25 x 25 μm\(^2\) scans were performed for local probing to investigate retention separately at asperities and inside open pores of the pad surface. Such a small scan was not possible with XPS due to the x-ray beam size. EDS data was collected for a live time of 300 seconds for experiments with Cabot slurry and 600 seconds for experiments with ANW alumina and JSR silica slurries. In the LEO 1550 SEM, a Noran EDS detector with Si (Li) 10 mm\(^2\) crystal was used for EDS analysis. The, working distance, electron beam energy, electron probe current and take-off angles used were 13 mm, 15 KeV, 1 nA, and 35\(^\circ\), respectively. In each experiment, the same operating conditions were used. Additionally, during each retention experiment, all CMP pad samples taken from pad surface (both exposed and un-exposed to polishing and
conditioning) were loaded in the SEM for EDS analysis. On each sample, three measurements of each kind of scan (200 x 200 μm² wide area scans as well as 25 x 25 μm² scans on asperities and open pores) were taken, and then the average values and standard deviation were determined for characterization of nanoabrasive retention. Since the Kα average energy of Cu is 8.041 KeV, an electron beam energy of 15 KeV was used to also enable the investigation of Cu retention on the surface of pad.

Figure 3.24. EDS scan results at asperity and open pore are shown in (b) & (d) respectively for demonstration purposes. Both results show the presence of ANW slurry alumina (Al peak) retention at asperity and open pore of the CMP pad surface exposed to Cu polishing and 10 lbs conditioner downforce. Where, corresponding EDS scan areas (squares) at asperity and open pore are shown in SEM images in (a) & (c) respectively. For these scans, EHT was 15 KeV and scan time was 600 seconds.
3.5.5: Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is one of the most versatile tools available for characterization of microstructures. It is used for the inspection and analysis of the microstructure morphology as well as characterization of chemical composition.\textsuperscript{29} It can be used not only to image and analyze the surface or near surface, but also the structure of bulk specimens. It has the capability of imaging large, rough specimens from low to high magnification (~ 10x to greater than 100,000x).\textsuperscript{30} Electrons generated through thermionic, Schottky or field-emission cathode are accelerated by using voltage difference (0.1-50 KeV) between cathode and anode\textsuperscript{27} and focused to a spot size in the range of 2-10 nm.\textsuperscript{31} When an electron beam, with certain energy penetrates into specimen, interactions between the electron beam and atoms composing the specimen provide a large variety of information through the emission of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE), photons, characteristic x-rays, continuum x-rays, and heat.\textsuperscript{32}

![Figure 3.25. Demonstration (adapted)\textsuperscript{29} of several signals generated by the electron beam-specimen interaction in the scanning electron microscope and the regions from which different signal can be detected.](image)
Secondary electrons (SE) are emitted from within a few nanometers of the sample surface and have low energy, usually less than 50 eV.\textsuperscript{33} Hence, secondary-electron yield is sensitive to the surface topography. Secondary-electron (SE) images are most commonly used for surface microscopy. The Secondary electron (SE) yield improves on decreasing the angle between beam and specimen surface.\textsuperscript{34} The backscattered-electron (BSE) signal is also very useful. A fraction of the electrons that undergo elastic scattering at the sample are ultimately directed back out of the specimen as BSE.\textsuperscript{32} BSEs carry information about features that are deep below the specimen surface. The images obtained with BSE are principally used to reveal compositional variations.\textsuperscript{34, 35} The BSE signal tends to concentrate around the beam axis.\textsuperscript{36} 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.\textsuperscript{30}

As mentioned, characteristic x-rays are also emitted in the SEM as a result of electron (beam) bombardment. The analysis of this radiation was discussed above and can be utilized to obtain qualitative as well as quantitative elemental information about the specimen.

Qualitative analysis of nanoabrasive retention, agglomeration and transport was carried on CMP pad sample by using Hitachi S-4000 and LEO 1550 field emission scanning electron microscopes. Imaging resolution is 1.5 nm @ 30 KV and 1 nm @ 15 KV for the Hitachi S-4000 and the LEO 1550 SEM, respectively. Slurry nanoabrasive sizes were also determined by using these microscopes. Inspection of CMP pad pore sizes, grooves, and cross-section also utilized SEM imaging for both coated and uncoated samples. For detailed analysis of pad surface roughness and nanoabrasive retention
(particularly inside open pores) tilted (45°) sample holders were used in addition to un-tilted (0°) sample holders. Primary electron gun voltages of 10 KV and 7 KV were employed for high resolution imaging (at 60-100 Kx magnification) of coated and un-coated samples, respectively. Pad sample imaging was also carried out at lower electron gun voltages of 3 KV and 1 KV for coated and un-coated pad samples, respectively, for low magnification imaging (40x, 300x, 600x, 1Kx and 6Kx). 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.

3.5.6: Low Vacuum (Environmental) Scanning Electron Microscopy (ESEM)

Low vacuum (environmental) scanning electron microscopy SEM or ESEM is also a high-resolution imaging technique. It has the ability to obtain secondary electron images of uncoated, nonconductive specimens through the presence of a low pressure gas in the specimen chamber. The gas pressure is ten thousand times higher than that of conventional SEM. Air, nitrogen, argon, water vapor or other gases may be used. The gas ions, the specimen, and the secondary electrons interactions give rise to contrast mechanisms that are unique in these types of instruments. In addition to dielectric materials, conductive substances (electrically isolated from ground) can also be analyzed by using this technique.

When an electron beam in a conventional SEM impinges on insulating samples, negative charge accumulates and produces charging on the sample. Classic effects associated with charging, such as bright emission ‘flares’ and image distortions due to
beam deflection are because of the fields created by trapped electrons.\textsuperscript{40, 41} In an insulator, excited electrons acquire less energy to escape, can be captured by a charge trap (available states in the forbidden energy gap created by chemical, structural, or electronic defects in the system).\textsuperscript{39} In conventional high vacuum SEM, the beam energy is intentionally lowered to implant electrons close to the surface of uncoated insulator samples to achieve stable imaging. Alternately, imaging artifacts associated with charging can be minimized by coating the specimen with a layer of grounded metal or carbon. But, in case of such a coating, all the SE emission then originates from the metal coating because the escape depth of secondary electrons from metal is only a few nanometers.\textsuperscript{39} Hence, for coated insulators, SE images represent imaging of surface topography only, and therefore, do not contain any information on the electronic structure of the material. Under high vacuum conditions, no microstructural contrast can be seen either in backscattered or SE modes when flat polished specimens of certain dielectric materials are observed, regardless of the beam energy used.\textsuperscript{39} These issues can be resolved by introducing gas in the specimen chamber of a low vacuum SEM (ESEM). The gaseous positive ions (ionized by primary and ejected electrons) tone down the surface potential, degree of specimen charging, and charge related imaging artifacts.\textsuperscript{39} Through recombination, the flux of ions landing on the specimen surface provides a path for the removal of excess electrons.\textsuperscript{37} In general as shown in Fig.3.26 (a), only those electrons having a sufficiently large normal component of the velocity (w.r.t. surface) can overcome the surface barrier. But this surface barrier is reduced as ions are absorbed on the surface, Fig.3.26 (b). As a result the electrons in the conduction band that normally would not be able to escape, can now can move to an ion via resonant states represented
as dashed lines, and be transported away. Additionally, as shown in Fig.3.26 (c), the escape barrier for secondary electrons is lowered in the presence of an external field such as that created by negative charging within the sample.39

Figure 3.26. Simplified schematic energy diagrams (adapted).39 (a) When ion approaches to surface. $E_{\text{vac}}$, $E_c$ and $E_v$ represent the energy of vacuum level, bottom of conduction band, and top of valence band. (b) When ion absorbed onto surface, dashed lines represent the resonant states. (c) When external field is present. Where, escape barrier is represented by dotted lines and bending of surface band has not been included in the diagram for simplicity purposes.

As mentioned low vacuum/environmental SEMs incorporate a high gas pressure in the specimen chamber that can range from 10 Pa to 2700 Pa.42 However, the electron-optical column is operated at a high vacuum, as any scattering can deteriorate the focusing optics of the electron beam. To meet these requirements, the specimen chamber is separated from the high vacuum of the electron optics. Pressure limiting apertures (PLAs) are inserted in the column to maintain the pressure gradient as shown in
Fig. 3.27(a). PLAs are inserted at locations where there is minimal conflict with the optical ray paths. To get progressively higher vacuum (moving up in the column), the volume between each set of apertures is pumped. As primary electrons are certainly scattered by gas molecules but it does not deteriorate resolution over the pressure range typically used (roughly less than 1000 Pa).

Both backscattered and secondary electrons can be used for imaging in the ESEM. ESEM imaging mechanisms, particularly SE imaging, rely on the amplification of the signal by the ionization of gas molecules in the chamber. In general, an anode biased to a few hundred volts is placed in the specimen chamber, somewhere in the neighborhood of the specimen. An electric field is set up between the anode and the sample as the sample is usually on a grounded stub. The gas cascade amplified SE signal can then be detected. It is well-known that the maximum SE emission coefficients from dielectrics are noticeably larger than for metals. In the case of an uncoated insulator such as a polyurethane CMP pad, an internal dipole field is created between the centers of positive and negative charge. A negative charge is implanted by the primary electrons at a distance below the specimen surface inside the interaction volume and a positive charge develops due to residual holes (depleted electrons due to SE emission) on the surface layer. As a result, the landing energy of the electron beam is reduced and will decrease the penetration depth of the beam and foreshorten the interaction volume. As a result, SE emission will increase because more SEs will be generated within the escape depth.
Figure 3.27. (a) Schematic of vacuum system of an environmental scanning electron microscope. PLA separate regions of the column those are differentially pumped. RP, DP, IP are the roughing, diffusion and ion pumps respectively.\cite{37} (b) Idealized cross section of the surrounding region of the specimen for one possible configuration. Where, $d$, $V_a$, $wd$ represent the gap distance, anode voltage ($+300$ - $+600$ V) and working distance respectively.\cite{37} (c) Photograph of Nova 600 NanoSEM, used in the analysis of CMP pad samples during nanoabrasives retention experiments.
An FEI Nova 600 NanoSEM (ESEM) was utilized for low vacuum imaging of CMP pad samples for qualitative analysis of nanoabrasive retention on CMP pad surface following Cu CMP. This instrument provided excellent imaging results on the very challenging insulating materials considered in this work including oxide nanoparticles and polymeric porous materials. At optimum working distance (WD), this instrument provided spatial resolutions of 1.5 nm and 1.8 nm at 10 KV and 3 KV HV (high voltage), respectively in low vacuum environment by using the Helix™ detector. Further details about this tool can be found in its product datasheet. During imaging, CO₂ was used as the auxiliary gas. Both low vacuum secondary electron detectors (LVD and Helix) were operated for ESEM imaging of nanoabrasives on CMP pad surface (uncoated samples). LVD was used for better field of view to locate the features where imaging was required. The Helix detector was used for high-resolution work. In the case of the Helix detector, ESEM imaging was carried out at various pressures and voltages, ranging from 0.295-0.673 Torr and 5-15 KV respectively at a working distance (WD) of 5mm. Optimal imaging was achieved around 0.301-0.310 Torr pressure and at 10 & 15 KV high voltage. For the LVD (low vacuum detector), the same pressure ranges were tested. But 5 KV, 7 KV and 10 KV (mainly 10 KV) high voltages and 5mm, 7mm and 13 mm (mainly 5mm) working distances were selected. Additionally, a wide range of magnification was utilized during ESEM imaging: 4Kx to 300Kx with Helix detector and 0.25 Kx to 2.5 Kx with the LVD detector.
3.5.7: Profilometry

A Tencor AlphaStep 200 Profilometer was used to measure the surface roughness (Ra) of the CMP pad samples. During profilometry measurements the stylus directly contacts the measuring surface (in a non-destructive way) and scans over the sample surface. Sample leveling is automatically computed after the scan. This profilometer takes 1 and 25 samples per micrometer for horizontal range (scan length) of 80 microns and 2,000 microns, respectively. It has vertical resolution of 0.5 nm and 5 nm for the 100 nm mode and micrometer mode, respectively. Horizontal resolution is about 40 nm. Further details can be found elsewhere.48

After the completion of each nanoabrasive retention experiment, pad samples were cut from the CMP pad for profilometry analysis. Profilometry scan lengths of 2,000 µm and ~30 µm were selected for macro scan analysis (passing over numerous asperities and pores), and for micro scans analysis (on individual asperities of CMP pads). During macro scanning, scans were performed on the pad surface area in between the grooves in a direction parallel to the groove lengths so that stylus could avoid groove crossover during its scanning motion. For each pad sample, surface roughness (Ra) data for 15 macro scans and 45 micro scan was collected. Later, these data values were averaged and the standard deviation was determined for each sample. These profilometry results are shown in chapter 5. The time per scan was 40 seconds and stylus tracking force was 12 mg.
Figure 3.28. Demonstration of Profilometry scan (for 2,000 micron scan length) by using Alpha Step 200 Profilometer.

3.5.8: Four-Point probe

The 4-point probe technique is generally used for the measurement of the average sheet resistance ($R_s$) of thin conducting films. The units of sheet resistance are ohms per square. One square of the material in the horizontal plane would have a resistance equal to the sheet resistance. Sheet resistance is a function of the material only as it is independent of any geometrical dimensions. In this method, the conducting film is probed with four equally spaced metal in-line tips (probes) as shown in Fig. 3.29 (a). The two outer tips are connected to a current supply, and the inner two tips to a voltage meter. During testing, the voltage drop across the inner probes is measured as current flows between the outer probes. The sheet resistance of the material that is under test can be expressed as shown below.

$$R_s = k \left( \frac{V}{I} \right)$$
If the units of sheet resistance ($R_s$) are in $\Omega$/square, voltage drop (V) in mV, and the current (I) in mA, the $k$ represents a geometric factor equal to 4.53 for sample areas much larger (> 40x) than the probe spacing and sample thickness less than half of the probe spacing.\textsuperscript{51, 52} To avoid measurements errors, it is important that the probe spacing should be much less than the diameter of the wafer as well as much larger than the thickness of the film.\textsuperscript{53} Typical probe radii and probe spacing are in the ranges of 30-500 $\mu$m and 0.5-1.5mm respectively. From a sheet resistance measurement either the resistivity or the thickness of the conducting layer can be determined if the other is known:

$$ \text{Resistivity} = R_s \times t $$

‘t’ is the thickness of the conducting layer and has the units in centimeters, and the resistivity ($\rho$) has the units of ohm-cm. It is commonly required that an insulating layer, e.g. silicon dioxide, exist between the silicon substrate and the film to be measured; otherwise, the sheet resistance measured will be erroneous.\textsuperscript{54}

During four point probe testing all the above requirements were met. The probe spacing was in the order of millimeters (25 mils = 635 $\mu$m), the probe tip radius was 1.6 mils = 40.6 $\mu$m, while the Cu films (1 $\mu$m or less in thickness) were always on an insulator ($SiO_2$) layer deposited on the Si wafer (200mm or 300mm in diameter) substrates. For 4-point probe measurements, a Signatone QuadPro automatic test system was used on test wafers as shown in Fig.3.29. With 4-point probe, the sheet resistances ($R_s$) data for Cu thin films were collected on the 200 mm Cu blanket wafers. Wafer mapping was accomplished by stepping the 4-point probe at regular intervals (49 points) across the wafer as shown in Fig. 3.30 (a). The sheet resistance values were determined
for both pre-CMP and post-CMP process Cu blanket wafers. Then this sheet resistance values were used to find out the pre and post CMP process thicknesses, at 49 points on the 200mm Cu wafers, by using above equation and the resistivity value of Cu thin films \((2.08 \times 10^{-6} \text{ ohm-cm})\). Later, these pre and post thicknesses values were used to find out the Cu film material removal rates (MRR), at 49 points, due to CMP process as shown in Fig. 3.30 (b) & (C). Additionally, by using this information average MRR as well as within wafer nonuniformity (WIWNU) values were also obtained.

Figure 3.29. Demonstration of 4-point probe. (a) Schematic shows the mechanism of 4-point probe measurements on Cu thin film wafer. (b) & (c) represents the digital photographs of 4-point probe over 200mm wafer and the Signatone QuadPro resistivity system respectively (reprinted with permission from Lucas Signatone Corp.).
Figure 3.30. Demonstration of measurements with 4-point probe. (a) Representation of 49 points used to measure sheet resistance (reprinted with permission from Lucas Signatone Corp.). (b) & (c) demonstrates the material removal rates (MRR) and thickness measurements by using sheet resistance values determined at 49 points.

3.5.9: Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) measures the force between a probe and the sample surface utilizing a cantilever that contains a sharp tip attached to its working end. The cantilever is normally made of silicon, silicon oxide or silicon nitride. Typically, a cantilever is 100 µm long, 20 µm wide, and 0.1 µm thick, but other dimensions can also
be used. The vertical sensitivity of the cantilever depends on its length. To obtain topographic imaging, the tip is brought into contact with the sample and scanned across the surface of the sample. The force between the sample surface and tip causes a cantilever deflection (deflection proportionally to the exerted force) which is detected with a laser beam.\textsuperscript{57} The reflected laser beam from the cantilever is commonly sensed either into a two-segment or four-segment, position sensitive photodiode, as shown in Fig. 3.31.\textsuperscript{56,58} During scanning, the cantilever motion and deflection cause the reflected laser beam to fall on different segments of the photodiode. Where, the cantilever’s horizontal motion is detected by $x = (A + B) - (C + D)$ and the vertical motion by $z = (A + C) - (B + D)$. The sample height variation is obtained by maintaining a constant photodiode signal (equivalent to constant cantilever deflection) through a feedback-driven variation of the sample height.

![Diagram of atomic force microscope (AFM)](image)

Figure 3.31. (a) Schematic diagram (adapted)\textsuperscript{56} of atomic force microscope (AFM). (b) Photograph of Dimension 3100 Scanning Probe Microscope (courtesy of Veeco Instruments Inc.).\textsuperscript{59}
Atomic force microscope can be operated in various modes. The two commonly used operation modes are the contact mode and the tapping mode. In the contact mode, the cantilever tip is dragged across over the sample surface. The topographic images of the scanned surface are recorded at a constant cantilever deflection. The major advantage of the contact mode is that it permits relatively fast scans.\textsuperscript{60} Though this approach also has some shortcomings. For example, sample and tip could be damaged as well as artifacts in the data could be created due to the dragging motion of the probe tip combined with adhesive forces between tip and sample surface.

Tapping mode allows high resolution topographic imaging of samples surfaces and it also works well with fragile, soft, or adhesive samples. Tapping mode scanning is implemented with alternately bringing the probe tip into contact with the surface to provide high resolution and then lifting off the tip from the surface to prevent dragging motion of the tip over the surface.\textsuperscript{56, 61} In addition, as the applied force is always vertical, shear forces that can dull the tips or distort data are minimized.\textsuperscript{60, 62, 63} During scanning, the cantilever is vertically oscillated in ambient air at or near its resonance frequency with the help of piezoelectric crystal. The amplitude of the oscillating cantilever is typically in the range of 20nm to 100 nm.\textsuperscript{60} The cantilever oscillating frequencies are typically in the range of 50-500 kHz.

Tapping mode imaging works well for soft, adhesive, or fragile samples, allowing high resolution topographic imaging of sample surfaces that are easily damaged or otherwise difficult to image by other AFM techniques. It overcomes problems associated with friction, adhesion, electrostatic forces, and other difficulties that can plague conventional AFM scanning methods.
A Dimension 3100 Scanning Probe Microscope with Nanoscope IV controller was used to investigate the scratches and residual nanoparticles adhered on the polished 200mm Cu wafers during nanoabrasive retention experiments when polished with ANW slurry by using expired and un-expired new CMP polyurethane pads. Additionally, surface morphology was also investigated in these experiments. Tapping mode was used for the analysis and the cantilever was oscillated at or close to its resonance frequency. Tapping mode etched silicon probe (uncoated) cantilevers having 125 µm length, 4 µm thickness, 40 N/m spring constant, and 300 kHz resonance frequency were used in these studies. The tip and cantilever were an integrated assembly of single crystal silicon. The tip was symmetric and consisted of ~10 nm radius and 15-20 µm height. AFM scans of various sizes such as ‘1 µm x 1 µm’, ‘5 µm x 5 µm’, and ‘20 µm x 20 µm’ were performed at center, 1 inch, 2 inch as well as 3 inch away from the center of the 200mm polished Cu 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 in terms of nanoabrasive retention introduced by expired and un-expired pads. For the above mentioned scan sizes, the selected scan rates were 1.0-5.0 Hz, 0.75-2.0 Hz, and 0.25-1.0 Hz, respectively, depending on the wafer samples. Images were collected with a resolution of 512 x 512 data points (number of samples).
Figure 3.32. Demonstration of tapping mode AFM scan (1 µm x 1 µm) results of the surface of Cu wafers polished with ANW slurry (a) un-expired pad, (b) expired pad.

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CHAPTER 4

EXPERIMENTAL RESULTS

4.1: Brief Overview of Data Presentation

CMP slurries consist of nanoabrasive particles and a variety of chemical additives for planarization processing of Si wafers. These nanoabrasives help in removing material from the wafer surface via direct mechanical contact between the wafer and the CMP pad asperities. These nanoabrasive particles may remain on the surface of pad after a CMP process and can be a potential source of defects on the wafer surface (scratches, particles, etc.). This dissertation describes a quantitative investigation of the retention of nanoabrasives on CMP pads resulting from Cu CMP processing. This investigation was carried out using XPS, EDS, SEM and ESEM analyses. The quantitative component of the nanoabrasive retention study utilized XPS and EDS. EDS, in particular was instrumental for local probing of nanoabrasive retention and transport at individual asperities and inside open pores of the CMP pad (Chapter 3 sections 3.5.3 & 3.5.4).

This chapter presents the primary experimental data corresponding to the nanoabrasive retention experiments outlined in Chapter 3. As noted previously, Cabot 5001 alumina nanoabrasive commercial slurry was selected for the first phase of these investigations. Nanoabrasive transport (retention and removal) mechanisms were investigated as a function of pad conditioner (diamond disk) parameters. Specifically, the role of pad conditioner downforce, pad/conditioner relative velocity and conditioning time was investigated with regards to the transport of Cabot 5001 alumina nanoabrasives.
The second phase of the slurry retention and transport investigations focused on the impact of slurry chemistries, nanoabrasive compositions and concentrations of H$_2$O$_2$. For this purpose, an in-house developed ANW alumina slurry and a commercial JSR silica slurry were used to compare with the data acquired using the Cabot 5001 alumina slurry. Moreover, the impact of polyurethane CMP pad life on the retention and transport of nanoabrasives was also evaluated.

For all CMP slurries noted above it was observed that nanoabrasive retention was found primarily on the CMP pad sections that were exposed to Cu polishing. Virtually no nanoabrasive retention was observed at the CMP pad center or pad sections not exposed to Cu polishing. This is in spite of the fact that the slurry was supplied over the center of CMP pad surface (Strasbaugh 6DSSP tool configuration). To illustrate the observation of nanoabrasive retention on CMP pads, ESEM images related to alumina retention from ANW slurry are presented in Fig. 4.1 and Fig. 4.2.

![ESEM images](image_url)

**Figure 4.1.** High-resolution ESEM micrograph of residual alumina nanoabrasive: (a) From the center of the CMP pad not exposed to the Cu wafer during CMP. (b) From section of the CMP pad exposed to the Cu wafer during CMP. A substantial amount of aggregated nanoabrasive is evident for the CMP pad exposed to the Cu wafer during CMP. On close inspection, individual nanoabrasive particles (~ 70 nm diameter) are evident.
High-resolution ESEM micrographs in Fig. 4.1 clearly show that the alumina nanoabrasive retention is mainly present on the CMP pad section that was exposed to the Cu wafer during CMP processing. The same behavior was observed both on asperities and inside open pores of the CMP pad as shown in Fig. 4.2.(a-d).

Figure 4.2. (a) ESEM micrograph of CMP pad asperity from section not exposed to Cu wafer during CMP (b) ESEM micrograph of CMP pad asperity from section exposed to Cu wafer during CMP. (c) ESEM micrograph of CMP pad pore from section not exposed to Cu wafer during CMP. (d) ESEM micrograph of CMP pad pore from section exposed to Cu wafer during CMP. Where, ANW alumina nanoabrasive-based baseline slurry was used both for polishing and conditioning.
4.2: Alumina Nanoabrasive Retention

4.2.1: This section describes experimental results regarding alumina retention resulting from Cu CMP using Cabot 5001 slurry. Alumina retention in the CMP pad was investigated as a function of the pad conditioner downforce (D.F.), CMP pad/conditioner relative velocity (Vrel), and oxidizer concentration.

4.2.1.1: Alumina retention for Cu CMP using Cabot 5001 slurry mixed with 2% H₂O₂.

Results for Conditioner Downforce Experiments:

For these experiments, 2% (by volume) of H₂O₂ was mixed with Cabot 5001 slurry, as it gives maximum copper material removal rate (MRR) as mentioned in chapter 3 (section 3.2.3a). Two different sets of experiments were investigated in terms of ex situ conditioning time. In the first and second experiment conditioning times per pad section exposed to Cu polishing of 17 seconds and 23 seconds were selected, respectively. These times reflect a 15% increase and a 15% decrease, respectively, with respect to the 20 second conditioning time baseline established upon initial qualification of the 6DSSP CMP tool. For each conditioning time conditioning downforces of 18 lbs and 10 lbs were applied on two neighboring sections of a new polyurethane (IC1000/SubaIV) CMP pad surface under the landing area of 200mm Cu wafer (see Fig. 3.16). These two values represent high and low limits of the conditioner downforce with respect to a 14 lbs...
conditioning baseline established upon initial qualification of the 6DSSP CMP tool. It is important to mention here is that ex-situ conditioning (18 lbs and 10 lbs on two different pad sections under landing area of Cu wafer) was performed following each of the 30 Cu CMP sequence. Hence, each pad sample was exposed to 30 ex-situ conditioning steps. Therefore, an overall conditioning time difference of 180 seconds existed between the ’23 second’ and ’17 second’ experiments. After the completion of each experiment, CMP pad samples were cut from pad sections exposed to 18 lbs and 10 lbs conditioning as well as from the CMP pad center (referred to as 0 lbs conditioning downforce with no wafer exposure and used as a reference) for XPS, EDS, SEM and profilometry analyses. Details about sample preparation and experimental techniques can be found in section 3.5.

Similar to Fig. 4.1, SEM images of the pad sections for the conditioner downforce experiments revealed that substantially lower alumina nanoabrasive retention was found at the center (area not exposed to Cu wafer during polishing) of the pad surface (both at asperities and inside open pores) as compared to the area of the pad surface exposed to the wafer during Cu polishing. Substantial nanoabrasive retention is evident in the SEM images from the pad section with 18 lbs conditioning (exposed to Cu wafer during polishing) as shown in Figs. 4.3 & 4.4. The SEM images of areas from the 10 lbs conditioning pad section (also exposed to wafer during polishing) are not shown here for brevity but they also show very higher alumina nanoabrasive retention as compared to the pad center. Additionally, the SEM images in Fig. 4.3 & 4.4 suggest that nanoabrasive retention decreased with increasing conditioning time both at pad asperities and open pores. To further investigate this observation quantitative elemental analysis was undertaken.
Figure 4.3. (a) SEM image of alumina nanoabrasive retention at a CMP pad asperity (exposed to the Cu CMP sequence) following 17 seconds of conditioning with a conditioner downforce of 18 lbs. (b) SEM image of alumina nanoabrasive retention at a CMP pad asperity (exposed to the Cu CMP sequence) following 23 seconds of conditioning with a conditioner downforce of 18 lbs. (Cabot 5001 commercial alumina nanoabrasive-based slurry.)

Figure 4.4. (a) SEM image of alumina nanoabrasive retention within a CMP pad pore (exposed to the Cu CMP sequence) following 17 seconds of conditioning with a conditioner downforce of 18 lbs. (b) SEM image of alumina nanoabrasive retention within a CMP pad pore (exposed to the Cu CMP sequence) following 23 seconds of conditioning with a conditioner downforce of 18 lbs. (Cabot 5001 commercial alumina nanoabrasive-based slurry.)

Elemental information was collected for all CMP pad samples involved in all slurry retention experiments via XPS and/or EDS analysis. This information was converted into atomic concentration (at %). An elemental compositional XPS profile of one of the samples has been shown as an example in Fig. (4.5). The Al peak in that spectrum is attributed solely to retained alumina nanoabrasive.
Figure 4.5. X-ray photoelectron spectroscopy (XPS) survey scan from a location on the CMP pad sample exposed to the Cu CMP sequence – 10 lbs conditioning downforce, 23 seconds conditioning time, XPS spot size of 400 µm in diameter and 208 seconds scan time. (Cabot 5001 commercial alumina nanoabrasive-based slurry.) The aluminum peak is attributed solely to retained slurry nanoabrasive.

XPS analyses on the surface of the pad for both sets of experiments show that the retention of alumina nanoabrasives decreases somewhat with increasing conditioner downforce, as shown in Fig. 4.6 (a & b). As noted above, lower slurry retention was observed at the center of the CMP pad as compared to CMP pad sections exposed to Cu CMP sequence. XPS results in Fig. 4.6 (a & b), also show that the retention of alumina nanoabrasive depends more substantially on conditioning time than conditioning downforce. Lower retention of alumina nanoabrasive was found for higher conditioning time (23 seconds). As the scan (spot) size of the x-ray beam was 400 µm in diameter the data collected with XPS samples numerous CMP pad asperities and open pores. Similarly, wide area EDS analyses (200x 200 µm² scan size) was also carried out to collect similar information from numerous asperities and open pores and to confirm the XPS results for both sets of experiments (23 & 17 seconds conditioning time and 2% H₂O₂).
Figure 4.6. XPS analyses of alumina nanoabrasive retention from CMP pad samples exposed to the Cu CMP sequence. Nanoabrasive retention is proportional to surface aluminum compositional fraction. (a) Alumina retention as a function of conditioner downforce for a conditioning time of 17 seconds. (b) Alumina retention as a function of conditioner downforce for a conditioner time of 23 seconds. Each data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter.

As shown in Fig 4.7 (a-b) the wide area EDS analyses agree well with the XPS data from Fig. 4.6. That is, the residual nanoabrasive retention decreased with increasing conditioning downforce (from 10 lbs to 18 lbs) and conditioning time (from 17 to 23 seconds).

Figure 4.7. Wide-area EDS analyses of alumina nanoabrasive retention on CMP pad sections exposed to Cu CMP. Nanoabrasive retention is proportional to EDS aluminum counts. (a) Alumina retention as a function of conditioner downforce for a conditioning time of 17 seconds. (b) Alumina retention as a function of conditioner downforce for a conditioning time of 23 seconds. Scan area was 200 x 200 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.
EDS analyses carried out on the asperities of CMP pads exposed to Cu polishing showed that the retention of alumina nanoabrasives statistically decreased with increased conditioning downforce (Fig.4.8 (a)). However, as the conditioning time was increased from 17 seconds to 23 seconds, the retention of alumina nanoabrasives on pad asperities exposed to Cu polishing decreased by a factor 8 for low conditioning downforce (10 lbs) and by a factor of 5 for high conditioning downforce (18 lbs) (4.8 (b)). Clearly, the EDS analysis at pad asperities show that conditioning time has a substantially greater impact compared to conditioner downforce in terms of reducing local nanoabrasive retention.

![Figure 4.8. EDS analyses of alumina nanoabrasive retention on CMP pad asperities exposed to Cu CMP. Nanoabrasive retention is proportional to EDS aluminum counts. (a) Alumina retention as a function of conditioner downforce for a conditioning time of 17 seconds. (b) Alumina retention as a function of conditioner downforce for a conditioning time of 23 seconds. Scan area was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.](image)

Inside open pores on the CMP pad, the trends for alumina nanoabrasive retention contrasted strongly with the corresponding results from CMP pad asperities. This is shown in Fig. 4.9 (a & b). Alumina nanoabrasive retention statistically increased with increased conditioner downforce. Conditioning was demonstrably less effective at
reducing nanoabrasive retention inside open pores as compared to pad asperities. The large error bars on the EDS data in Fig. 4.9 reflect substantial pore-to-pore variations in local particle density. EDS analyses inside open pores also revealed that the retention of alumina nanoabrasive decreased as the conditioning time was increased from 17 seconds to 23 seconds for pad sections where 10 lbs conditioner downforce was applied. EDS analyses inside open pores for both sets of experiments also revealed that the nanoabrasive retention was substantially lower at the center of the CMP pad which was not exposed to wafer polishing. This agrees with both XPS data and wider area EDS data. It is clear from the data in Fig. 4.8 and Fig. 4.9 that the overall alumina nanoabrasive retention was higher inside open pores of CMP pad sections exposed to Cu polishing as compared to asperities.

Figure 4.9. EDS analyses of alumina nanoabrasive retention inside open pores on CMP pad surface exposed to Cu CMP. Nanoabrasive retention is proportional to EDS aluminum counts. (a) Alumina retention as a function of conditioner downforce for a conditioning time of 17 seconds. (b) Alumina retention as a function of conditioner downforce for a conditioning time of 23 seconds. Scan area was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.
Results for CMP Pad/Conditioner Relative Velocity ($V_{rel}$) Experiments

As mentioned in Chapter 3 the two 4”-wide annular regions of the CMP pad corresponding to the inner and outer regions of the 200mm wafer possessed different pad/conditioner disc relative velocities (see Fig. 3.16). The 4” annular region of the CMP pad corresponding to the outer half of the 200mm wafer (i.e. the pad section exposed to 18 lbs conditioning force described above) possessed a pad/conditioner relative velocity of 1.07 m/sec. The inner section (i.e. the pad section exposed to 10 lbs conditioning force described above) possessed a pad/conditioner relative velocity of 0.59 m/sec. Further details about this can be found in section 3.4.2. Therefore, to decouple the effects of CMP pad conditioner downforce and pad/conditioner relative velocity on the retention and transport of nanoabrasives, an additional set of experiments was undertaken where, the conditioning downforce was kept constant (10 lbs) on both pad sections to see the impact of pad/conditioner relative velocities on the retention of alumina nanoabrasives on the pad exposed to the Cu polish.

As with the previous experiment, Cabot 5001 slurry was mixed with 2% H$_2$O$_2$. The conditioner downforce was kept constant at a value of 10 lbs on both conditioning pad sections of the CMP pad under the 200mm Cu wafer. As mentioned above, the pad/conditioner relative velocities were 1.07 m/sec and 0.59 m/sec at the outer and inner sections of the CMP pad respectively (Fig. 3.17). The conditioning time per pad section during each Cu CMP sequence (total 30 sequences), was set to 21 seconds. As for the previously described experiments, a new polyurethane CMP pad (IC1000/SubaIV) was used in this set of experiments.
First, XPS analyses on the surface of the CMP pad were carried out. Results are shown in Fig 4.10. XPS analyses showed that at constant conditioning downforce (10 lbs), the retention of nanoabrasives decreased with increased pad/conditioner relative velocity. Lower retention was found at the CMP pad center (unexposed to wafer during polishing) as compared to pad sections exposed to Cu wafer during polishing.

![Graph showing XPS analyses of alumina nanoabrasive retention from CMP pad samples exposed to the Cu CMP sequence as a function of CMP pad/conditioner relative velocities at constant conditioning downforce 10 lbs. Nanoabrasive retention is proportional to surface aluminum compositional fraction. Each data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter.](image)

Figure 4.10. XPS analyses of alumina nanoabrasive retention from CMP pad samples exposed to the Cu CMP sequence as a function of CMP pad/conditioner relative velocities at constant conditioning downforce 10 lbs. Nanoabrasive retention is proportional to surface aluminum compositional fraction. Each data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter.

As the XPS beam diameter was 400 µm in spot mode, the data includes contributions from numerous open pores and asperities. Therefore, to see the individual role played by asperities and open pores in terms of nanoabrasive retention and transport, EDS data was also collected from individual open pores and asperities with a scan size of 25x25 µm².
EDS analyses on asperities showed little change in the alumina retention both at high and low relative velocity sections as compared to CMP pad center (Fig. 4.11). The EDS aluminum signal at the center of the pad (the data point in Fig. 4.11 acquired at the center of the CMP pad) was substantially larger than that seen in Figs. 4.8 and 4.9. This is possibly an experimental aberration as one measurement showed a very large Al signal (hence the large error bar in Fig. 4.11), although a causal relationship to the conditioner downforce or pad/conditioner relative velocity cannot be ruled out.

![Figure 4.11](image)

**Figure 4.11.** EDS analyses of alumina nanoabrasive retention on CMP pad asperities exposed to Cu CMP as a function of CMP pad/conditioner relative velocity at constant conditioning downforce. Nanoabrasive retention is proportional to EDS aluminum counts. Scan area was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.

Similarly EDS analysis was carried out inside open pores to examine the relationship between alumina nanoabrasive retention and pad/conditioner relative velocity. This data is shown in Fig. 4.12. Based on EDS count rates the conditioner appeared substantially less effective at lowering nanoabrasive retention inside the open pores as compared to the asperities of the CMP pad. As with the data shown in Fig. 4.11,
the data shown in Fig. 4.12 indicates a large amount of retained nanoabrasive at the pad center. The large error bars for the data in Fig. 4.12 result from large sample-to-sample variations in alumina particle density. It seems unlikely that this results solely from the particular set of conditioning parameters used. It may reflect a peculiar nanoabrasive agglomeration or an unusual property of the particular pad used. But statistically, the minimum alumina retention was found at 0.59 m/sec relative velocity section of the CMP pad.

Figure 4.12. EDS analyses of alumina nanoabrasive retention inside open pores on CMP pad exposed to Cu CMP as a function of CMP pad/conditioner relative velocity at constant conditioning downforce (10 lbs). Nanoabrasive retention is proportional to EDS aluminum counts. Scan area was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.
4.2.1.2: Alumina retention for Cu CMP using Cabot 5001 slurry mixed with 6% H₂O₂

To evaluate the impact of higher % of H₂O₂ (by volume) on the retention, agglomeration, removal of alumina nanoabrasive from CMP pad surface, 6% of H₂O₂ was mixed with Cabot 5001 slurry.

For this set of experiments, 6% (by volume) of H₂O₂ was mixed with Cabot 5001 slurry. The Cu MRR for this slurry was lower in comparison with the Cu MRR obtained with Cabot 5001 slurry mixed with 2% H₂O₂ (see Fig. 3.9). Each Cu CMP sequence (polishing and ex-situ conditioning) was carried out by applying 18 lbs, 14 lbs and 10 lbs ex-situ conditioning on different (but separate) sections of a new polyurethane CMP pad (IC1000/SubaIV). Each of these sections was directly under the exposed/landing area of Cu wafer. A conditioning time of 11 seconds was set on each section during each ex-situ conditioning step. This relatively low conditioning time ensured that substantial nanoabrasive was present on the pad asperities and in the pad pores to facilitate evaluation of the conditioner downforce variation for the 6% H₂O₂/Cabot 5001 slurry. Conditioner downforces of 18 lbs, 14 lbs and 10 lbs were applied respectively to three annular regions of the pad (13 inches to 9 inches radii, 9 inches to 5 inches radii, and 5 inches to 1 inches radii). The Cu wafer landing position on the CMP pad surface during polishing was between 11 inches to 3 inches inch radial distance from the center of the pad. In this way the CMP pad area exposed to the Cu wafer during polishing had three values of conditioning force (18 lbs, 14 lbs and 10 lbs) on three separate CMP pad sections. Although this approach convolved conditioner/pad relative velocity with conditioner downforce variation, it was judged useful to include an additional data point.
at 14 lbs since higher H₂O₂ concentrations can lead to nanoabrasive agglomeration and conditioner downforce many play a role in transporting agglomerates off the pad.

As in previous experiments, 30 Cu wafer polish steps were executed per experiment resulting in 30 ex-situ conditioning steps. Pad samples were cut from pad sections exposed to Cu wafer during polishing (from 18 lbs, 14 lbs and 10 lbs conditioning sections) as well as from the center of CMP pad (not exposed to Cu wafer during polishing). As described previously, the latter samples were identified as having “0 lbs conditioning downforce” and served as a reference for XPS, EDS and SEM analyses.

A relatively small amount of retained alumina nanoabrasive was observed at the pad center (area unexposed to wafer) as compared to the pad areas exposed to Cu wafer polishing (both at asperities and inside open pores) as shown anecdotally through SEM images of Fig. 4.13 (a-b) and Fig. 4.13 (c-d), respectively. In these SEM images alumina nanoabrasive retention is evident both in individual and agglomerated form. Only SEM images from the pad section conditioned with 18 lbs conditioner downforce are shown here for purposes of brevity. SEM images of pad sections conditioned with 14 lbs and 10 lbs downforce (not shown) also exhibited substantial retention compared to the pad center. As with the previous experiment SEM images did not provide quantitative information on nanoabrasive retention. Therefore, XPS and EDS techniques were utilized to quantify nanoabrasive retention.

XPS analyses of the pad sections for this experiment (Fig. 4.14) show that the minimum alumina nanoabrasive retention existed at the center of the CMP pad (not exposed to Cu wafer polish). Alumina nanoabrasive retention was higher for pad
sections conditioned with 18 lbs, 14 lbs and 10 lbs conditioning downforce (exposed to Cu wafer polish). The nanoabrasive retention was observed to peak at a conditioner downforce of 14 lbs. Conditioning at 18 lbs downforce reduced the nanoabrasive retention.

Figure 4.13. SEM images of retained alumina nanoabrasive for a Cu CMP slurry with 6% H₂O₂ slurry oxidizer concentration (Cabot 5001 commercial slurry). (a) SEM micrograph of CMP pad asperity from section not exposed to Cu wafer during CMP. (b) SEM micrograph of CMP pad asperity from section exposed to Cu wafer during CMP (18 lbs conditioning). (c) SEM micrograph of CMP pad pore from section not exposed to Cu wafer during CMP. (d) SEM micrograph of CMP pad pore from section exposed to Cu wafer during CMP (18 lbs conditioning).
Figure 4.14. XPS analyses of alumina nanoabrasive retention from CMP pad samples exposed to the Cu CMP sequence (6% H₂O₂ slurry oxidizer concentration) as a function of conditioner downforce. Nanoabrasive retention is proportional to surface aluminum compositional fraction. Each data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter.

Wide area EDS analyses (scan area 200 x 200 µm²) was also carried out to confirm the results in Fig. 4.14. This data is shown in Fig. 4.15 and agrees well with the XPS data of Fig. 4.14.

Figure 4.15. Wide-area EDS analyses of alumina nanoabrasive retention from CMP pad sections exposed to the Cu CMP sequence (6% H₂O₂ slurry oxidizer concentration) as a function of conditioner downforce. Nanoabrasive retention is proportional to EDS aluminum counts. Scan area was 200 x 200 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.
The maximum in the aluminum retention at 14 lbs conditioner downforce in the data presented in Figs. 4.15 and 4.14 prompted a spatially resolved EDS compositional analysis similar to that presented in earlier sections of this chapter. EDS data acquired from inside open pores (with scan area 25 x 25 µm²) is shown in Fig. 4.16. This data shows very large retention of alumina abrasive within the pore at a conditioning downforce of 10 lbs. Substantial amounts of this nanoabrasive are displaced upon increasing the conditioner downforce to 14 lbs. However, it apparently remains on the CMP pad as implied by the data in Figs. 4.14 and 4.15. On increasing the conditioner downforce to 18 lbs the alumina is not only liberated from the pores, but also more effectively transported from the pad.

![Figure 4.16. EDS analyses of alumina nanoabrasive retention inside open pores on CMP pad exposed to the Cu CMP sequence (6% H₂O₂ slurry oxidizer concentration) as a function of conditioner downforce. Nanoabrasive retention is proportional to EDS aluminum counts. Scan area was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.](image)

Such large Al counts from the EDS data in Fig. 4.16 imply the presence of substantial alumina agglomerates. Such agglomerates lead to nanoscratching of the Cu
surface or trapping of abraded Cu material that would normally be transported away from
the wafer surface. To investigate this, XPS and wide area EDS analyses (shown in Fig.
4.17) were carried out to measure the presence of post CMP Cu on the surface of the
CMP pad (exposed to the Cu wafer) when polished with Cabot 5001 slurry mixed with
6% H₂O₂. The data in Fig. 4.17 (a), show post CMP Cu retention on all CMP pad
sections exposed to the Cu wafer during CMP. The maximum post CMP Cu retention
was found on the pad section that was conditioned with 14 lbs conditioner downforce
directly under the central area of the Cu wafer). The post CMP Cu retention decreased as
conditioner downforce was increased to 18 lbs. Wide area EDS analyses, Fig. 4.17 (b),
revealed post CMP Cu retention only on the pad section that was conditioned with 14 lbs
conditioner downforce. No amount of post CMP Cu was found at the center of the CMP
pad (area not exposed to Cu CMP sequence) during both XPS and wide area EDS
analyses. (Likewise, no Cu retention was seen for any measurements carried out on pad
samples exposed to Cabot 5001 + 2% H₂O₂ slurry formulations.)

![Figure 4.17](image)

**Figure 4.17.** (a) XPS and (b) wide-area EDS analyses of Cu retention from CMP pad
samples exposed to the Cu CMP sequence (6% H₂O₂ slurry oxidizer concentration)
as a function of conditioner downforce. Each XPS data point was acquired with an
XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter. EDS scan
area was 200 x 200 µm² and EHT was 15 KeV. EDS scan time was 300 seconds.
EDS analyses inside open pores (Fig. 4.18) revealed post CMP Cu retention on CMP pad sections conditioned with 10 lbs and 14 lbs conditioner downforce (exposed to the Cu wafer). The maximum post CMP Cu retention inside open pores was also observed for the section of the pad conditioned with 14 lbs downforce. No amount of post-CMP Cu retention was found at the center of CMP pad (not exposed to Cu CMP sequence). Nor was post-CMP Cu retention observed at pad sections conditioned with 18 lbs downforce. EDS analyses in open pores showed higher amount of post CMP Cu retention than that was observed in wide area EDS analyses. Implications of this data are discussed in Chapter 5.

![Graph showing copper retention as a function of conditioner downforce](image)

**Figure 4.18.** EDS analyses of Cu retention inside pores of CMP pad samples exposed to the Cu CMP sequence (6% H$_2$O$_2$ slurry oxidizer concentration) as a function of conditioner downforce. EDS scan area was 25 x 25 µm$^2$ and EHT was 15 KeV. EDS scan time was 300 seconds.
4.2.2: Alumina Retention for Custom Slurry (ANW-Applied Nanoworks):

Alumina Retention as a Function of Conditioner Downforce for 20 Seconds Conditioning Time

To evaluate the impact of slurry chemistry on the alumina nanoabrasive retention and transport; a custom formulated slurry was utilized for comparison with the alumina-particle based Cu commercial slurry (Cabot 5001 slurry). The former used nanoabrasives synthesized by Applied Nanoworks Inc. (ANW).

The slurry composition of the ANW slurry and the conditioning and polishing parameters for this set of experiments were described in chapter 3 (sections 3.2.3 (b) and 3.4). For the ANW alumina slurry two sections of the CMP pad directly under the landing area of the Cu wafer were conditioned with 18 lbs and 10 lbs conditioning downforce as outlined in Fig. 3.16. This approach parallels that of Section 4.2.1.1. During each conditioning step of the Cu CMP sequence, the conditioning time was set to 20 seconds for each CMP pad section. The conditioning time of 20 seconds was selected on the basis of previous results obtained with Cabot 5001 slurry where it was determined that the nanoabrasive retention was a weak function of conditioner downforce and/or relative velocity when the conditioning time substantially exceeded 20 seconds per cycle. As in all previous experiments, 30 Cu CMP cycles were carried out for the experiment (including ex situ conditioning). Likewise, a new polyurethane CMP pad (IC1000/SubaIV) was used for this experiment. Pad samples were cut from the CMP pad sections exposed to Cu CMP and conditioning as well as from the center of CMP pad which was not exposed to the Cu wafer (referred to as 0 lbs conditioning downforce with and used as a reference)
Selected ESEM micrographs acquired at asperities and inside open pores of pads following the Cu CMP with ANW alumina slurry are shown in Fig 4.19 and Fig. 4.20 to illustrate relative nanoabrasive retention at CMP pad center and at the pad areas in contact with the Cu wafer.

Figure 4.19. (a) ESEM micrograph of CMP pad asperity from section not exposed to Cu wafer during CMP (ANW alumina slurry). (b) ESEM micrograph of CMP pad asperity from section exposed to Cu wafer during CMP (ANW alumina slurry) with a conditioner force of 10 lbs. (c) ESEM micrograph of CMP pad asperity from section exposed to Cu wafer during CMP (ANW alumina slurry) with a conditioner force of 18 lbs.

Figure 4.20. (a) ESEM micrograph inside a CMP pad pore from section not exposed to Cu wafer during CMP (ANW alumina slurry). (b) ESEM micrograph inside a CMP pad pore from section exposed to Cu wafer during CMP (ANW alumina slurry) with a conditioner force of 10 lbs. (c) ESEM micrograph inside a CMP pad pore from section exposed to Cu wafer during CMP (ANW alumina slurry) with a conditioner force of 18 lbs.
XPS analyses of these sections are shown in Fig. 4.21 (a). These data show that very small amounts of ANW alumina nanoabrasive were retained at the CMP pad center (pad area not exposed to polishing and conditioning). More substantial ANW alumina nanoabrasive retention was observed on CMP pad sections exposed to polishing and conditioning downforce of 10 lbs. This retention decreased significantly as the downforce was increased to 18 lbs. In fact, the nanoabrasive retention measured at the pad area conditioned with a 18 lbs downforce was comparable to the retention at the CMP pad center. Therefore, the decrease in ANW alumina nanoabrasive retention was a stronger function of conditioning downforce as compared to that of the Cabot slurry.

The XPS data agrees well with wide-area EDS data (shown in Fig. 4.21 (b) which also showed that a conditioning downforce of 18 lbs was sufficient to reduce nanoabrasive retention to level near that observed at the CMP pad center.

![Graph](image.png)

**Figure 4.21.** (a) XPS and (b) wide-area EDS analyses of alumina retention from a CMP pad sample exposed to the Cu CMP sequence (ANW alumina baseline slurry) as a function of conditioner downforce. Each XPS data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter. EDS scan area was 200 x 200 µm² and EHT was 15 KeV. EDS scan time was 600 seconds.
Small-area EDS analyses on CMP pad asperities (Fig. 4.22 (a)) revealed that ANW alumina retention was not appreciably larger than retention measured at the CMP pad center for both 10lbs and 18 lbs conditioning downforce (20 seconds of conditioning time). Either a relatively modest conditioner downforce was sufficient to remove residual nanoabrasive or very little nanoabrasive was retained at asperities during the polish steps.

Small-area EDS analyses inside open pores (Fig. 4.22 (b)), on the other hand, revealed nanoabrasive retention within the pad pores that remained after conditioning with a 10 lbs downforce. However, conditioning with an increased downforce of 18 lbs was sufficient to reduce the nanoabrasive retention to the level seen at the CMP pad center. It is concluded that most of the nanoabrasive retention observed for the XPS and wide-area EDS scans was resident in the CMP pad pores and that the conditioner was effective in removing the ANW alumina nanoabrasive from inside open pores.

Figure 4.22. (a) EDS analyses of alumina nanoabrasive retention on CMP pad asperities exposed to the Cu CMP sequence as a function of CMP conditioner downforce (ANW alumina baseline slurry). (b) EDS analyses of alumina nanoabrasive retention inside CMP pad pores exposed to the Cu CMP sequence as a function of CMP conditioner downforce (ANW alumina baseline slurry). Nanoabrasive retention is proportional to EDS aluminum counts. Scan area for each data point was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 600 seconds.
4.3: Silica Nanoabrasive Retention:

Silica (JSR Slurry) Nanoabrasive Retention as a Function of Conditioner Downforce for 20 Seconds Conditioning Time

To evaluate the impact of slurry nanoabrasive composition on nanoabrasive transport, retention and removal from the CMP pad surface, a commercial JSR Cu slurry incorporating amorphous silica nanoabrasives was used.

Experimental details regarding the composition of amorphous silica based commercial JSR Cu slurry as well as conditioning and polishing parameters for this set of experiments have been given in sections 3.2.3 (c) and 3.4 of Chapter 3. As in previous experiments 18 lbs and 10 lbs ex situ conditioning was performed separately on two different sections (outer and inner sections) of the CMP pad directly under the landing area of the 200mm Cu wafer during the 30-cycle Cu CMP sequence. Similarly, conditioning time on each pad section was set to 20 second/step. The outer (18 lbs conditioning) and inner (10 lbs conditioning) pad sections were exposed to 1.07 m/sec and 0.59 m/sec pad/conditioner relative velocities, respectively. A new polyurethane CMP pad (IC1000/SubalV) was used in this set of experiments with a JSR amorphous silica Cu slurry. As in previous experiments CMP pad samples were cut from pad sections exposed (pad sections with 18 lbs and 10 lbs conditioner downforce) and not exposed (center of the pad) to Cu CMP sequence. The latter sample was used as a reference point (denoted as 0 lbs conditioner downforce) for XPS, EDS and ESEM analyses.

ESEM micrographs on asperities (Fig 4.23) and inside open pores (Fig 4.24), of the CMP following the Cu CMP cycles with JSR silica slurry showed that silica
nanoabrasive retention at the CMP pad center (pad area unexposed to Cu CMP sequence) was relatively low compared to the pad section with 18 lbs conditioner downforce.

![Figure 4.23](a) ESEM micrograph of CMP pad asperity from section not exposed to Cu wafer during CMP (JSR commercial silica-based slurry). (b) ESEM micrograph of CMP pad asperity from section exposed to Cu wafer during CMP (JSR commercial silica-based slurry) with a conditioner force of 18 lbs.

![Figure 4.24](a) ESEM micrograph within CMP pad pore from section not exposed to Cu wafer during CMP (JSR commercial silica-based slurry). (b) ESEM micrograph within CMP pad pore from section exposed to Cu wafer during CMP (JSR commercial silica-based slurry) with a conditioner force of 18 lbs.

XPS results shown in Fig. 4.25 (a) revealed that silica nanoabrasive retention was relatively low at 10 lbs pad conditioning but increased upon conditioning with 18 lbs downforce. This trend was confirmed with wide-area EDS analysis. Results are shown in
Fig 4.25 (b). This behavior contrasts strongly for both alumina-based slurries used for the previous retention experiments.

![Graph](image)

**Figure 4.25.** (a) XPS and (b) wide-area EDS analyses of silica retention from a CMP pad sample exposed to the Cu CMP sequence (JSR commercial silica-based slurry) as a function of conditioner downforce. Nanoabrasive retention is proportional to XPS or EDS Si counts. Each XPS data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter. EDS scan area was 200 x 200 µm² and EHT was 15 KeV. EDS scan time was 600 seconds.

Small-area EDS analyses on asperities shown in Fig. 4.26 (a) mirrored the behavior of the data in Fig. 4.25. Small-area EDS analyses inside open pores shown in Fig. 4.26 (b) showed somewhat similar features. Firstly, this particular sample exhibited high silica retention at the pad center. This is likely due to an anomalous amount of retained silica as the wide-area analysis of Fig. 4.25 show relatively low silica at the pad center. Putting this data point aside for the moment, the trend on conditioning with 10 lbs and 18 lbs downforce agreed with the data in Fig. 4.25 and Fig. 4.26 (a). Large variation in data (error bars) were observed inside open pores as well as asperities attributed to local changes in particle density.
Figure 4.26. (a) EDS analyses of silica nanoabrasive retention on CMP pad asperities exposed to the Cu CMP sequence as a function of CMP conditioner downforce (JSR commercial silica-based slurry). (b) EDS analyses of silica nanoabrasive retention inside CMP pad open pores exposed to the Cu CMP sequence as a function of CMP conditioner downforce (JSR commercial silica-based slurry). Nanoabrasive retention is proportional to EDS Si counts. Scan area for each data point was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 600 seconds.

Although the overall EDS counts (and XPS atomic concentrations) were relatively low the behavior of the silica retention compared to alumina retention is quite distinct. Even considering the different slurry chemistries used, it appears that the composition of the particle may have a strong effect on relative retention in the CMP pad. This point is discussed further in Chapter 5.

4.4: Impact of Polyurethane CMP Pad Life on Cu Polishing as well as on Nanoabrasive Retention and Agglomeration on CMP Pad Surface

In this section, investigations related to the impact of CMP pad life on the transport, retention, agglomeration and removal mechanisms of nanoabrasives from CMP pads are presented. In addition, the impact of pad life on the Cu polishing results, for example, Cu MRR and Cu surface finish (scratches, nanoabrasive and wafer surface roughness) are also discussed.
Typically CMP pads are usually purchased in quantities of 5-10 CMP pads where each pad can be used to polish hundreds of wafers. Pads are typically provided with an ‘expiration date’ owing to the fact that exposure to light and humidity may alter their mechanical properties and, hence, CMP performance. This expiration date is typically one year from the manufacturing date. It is presumed that pads close to their expiration date provide the same CMP performance as ‘unexpired’ new pads if left unexposed to ultraviolet light and stored in a humidity-controlled environment. Since particle generation is a problem sometimes observed with aged CMP pads, experiments were designed to investigate the relationship between pad age and nanoabrasive retention. For this, two new (in original packaging) polyurethane CMP pads (IC1000/Suba IV) – one close to its expiration date (just ‘expired’) and other newly purchased (manufactured) – were chosen. They are referred to herein as new ‘expired’ and new ‘unexpired’ CMP pads. ANW alumina baseline slurry was used and Cu wafers were polished 30 times (with ex-situ conditioning after every Cu polishing step) as described for each of the aforementioned experiments.

Cu polishing results showed reduced MRR, increased scratching, increased contamination (particle adhesion) and higher surface roughness on the surface of the Cu wafer that was polished with the ‘expired’ CMP pad as compared to the ‘unexpired’ CMP pad. Similarly, higher alumina nanoabrasive retention, as well as a nanoscale web-like structures (pores), were observed on the surface of the ‘expired’ CMP pad as compared to ‘unexpired’ CMP pad. These results will be discussed in detail in the following section.

The experimental procedure is the same as mentioned in section 4.2.2 for both the ‘expired’ new polyurethane CMP pad (IC1000/SubaIV) and the ‘unexpired’ new
polyurethane CMP pad (IC1000/Suba IV). The ANW Cu slurry was used. Atomic force microscope (AFM), optical microscope, and sheet resistance measurements were used to characterize post CMP Cu wafer surfaces. While, XPS, EDS and ESEM techniques were used for the investigation of alumina nanoabrasive retention on the surface of both ‘expired’ and ‘unexpired’ CMP pads. XPS and wide area EDS scans were able to scan the larger area of the pad surface to collect information from numerous open pores and asperities. Smaller EDS scans of 25x25 µm² sizes were also performed both on individual asperities and open pores of all CMP pad samples to investigate the individual role played by asperities and open pores in terms of alumina nanoabrasive retention on both CMP pads (‘expired’ and ‘unexpired’).

ANW alumina nanoabrasive retention results with the ‘unexpired’ pad have already been presented in section 4.2.2 and will be used here again for comparison with the alumina nanoabrasive retention results obtained with the ‘expired’ CMP pad.

ESEM micrographs in Fig. 4.27 illustrate the overall retention of ANW alumina nanoabrasives inside open pores and on asperities of the CMP pad surfaces. Overall more alumina nanoabrasive retention was observed on the surface of the ‘expired’ CMP pad as compare to the ‘unexpired’ CMP pad. ESEM micrographs shown in Fig. 4.28 and Fig. 4.29 illustrate ANW alumina nanoabrasive retention on pad asperities and inside open pores respectively of both CMP pads (‘expired’ and ‘unexpired’).
Figure 4.27. ESEM micrographs of asperity and open pore structures. (a) ‘unexpired’ polyurethane CMP pad. (b) ‘expired’ polyurethane CMP pad.

Figure 4.28. ESEM micrographs on CMP pad asperities illustrating alumina retention (ANW alumina-based baseline slurry). ‘Unexpired’ pad: Panels (a)-(c) show ESEM images corresponding to an unexposed pad, exposed pad with 10 lbs conditioner downforce, and exposed pad with 18 lbs conditioning downforce, respectively (reprinted from Fig. 4.19). Panels (d)-(f) show corresponding ESEM images from an ‘expired’ CMP pad.
Figure 4.29. ESEM images within CMP pad pores illustrating alumina retention (ANW alumina-based baseline slurry). ‘Unexpired’ pad: Panels (a)-(c) show ESEM images corresponding to an unexposed pad, exposed pad with 10 lbs conditioner downforce, and exposed pad with 18 lbs conditioning downforce, respectively (reprinted from Fig. 4.20). Panels (d)-(f) show corresponding ESEM images from an ‘expired’ CMP pad.

In Fig 4.30 (a & b), XPS and wide-area EDS analyses showed that the ‘expired’ CMP pad retained only slightly higher residual nanoabrasive as compared to the ‘unexpired’ CMP pad at the respective centers of each pad (not exposed to Cu CMP). This difference did not exist upon conditioning with 10 lbs and 18 lbs downforce as shown by the XPS data (Fig. 4.30 (a)). However, wide-area EDS implied that more alumina retention occurred in the ‘expired’ pad on conditioning (Fig. 4.30 (b)). This result must be tempered by the relatively large error bars for the wide-area EDS data. Overall, the alumina nanoabrasive retention trends for both ‘expired’ and ‘unexpired’ CMP pads were similar as a function of conditioner downforce, i.e. alumina nanoabrasive
retention decreased with increased conditioning downforce for both ‘expired’ and ‘unexpired’ CMP pads.

![Figure 4.30. (a) XPS and (b) wide-area EDS analyses of alumina retention from ‘unexpired’ (blue triangle symbols) and ‘expired’ (black circle symbols) polyurethane CMP pad sample exposed to the Cu CMP sequence (ANW alumina baseline slurry) as a function of conditioned downforce. Nanoabrasive retention is proportional to XPS or EDS Al counts. Each XPS data point was acquired with an XPS scan time of 208 seconds and an XPS spot size of 400 µm in diameter. EDS scan area is 200 x 200 µm² and EHT is 15 KeV. EDS scan time was 600 seconds.](image)

Small-area EDS analyses on CMP pad asperities of an ‘unexpired’ CMP pad (Fig. 4.31 (a)) revealed that after 20 seconds of conditioning, the alumina retention at CMP pad sections with 10 lbs and 18 lbs conditioner downforce was no higher than that at the center of the pad. In contrast, small-area EDS analyses on CMP pad’s asperities of ‘expired’ pad showed higher alumina nanoabrasive retention at a CMP pad section conditioned with 10 lbs downforce as compare to a CMP pad section conditioned with 18 lbs downforce. This difference is statistically significant.

Small-area EDS analyses was also carried out inside open pores of both CMP pads (‘expired’ and ‘unexpired’). Results are shown in Fig. 4.31 (b). Based on the error
bars shown with the data there is no statistical difference in the nanoabrasive retention in the pores between the two pads at areas conditioned with 10 lbs or 18 lbs downforce.

The data in Fig. 4.31 implies different interactions between slurry nanoabrasives and the asperities on ‘expired’ versus ‘unexpired’ pads. Such a difference may well effect the Cu mean removal rate (MRR). Cu MRR from both ‘expired’ and ‘unexpired’ CMP pads using ANW alumina slurry are shown in Fig. 4.32. The average Cu MRR for the ‘unexpired’ CMP pad was almost 34% higher than the Cu MRR with the ‘expired’ CMP pad (Fig 4.32 (inset)). Average Cu MRRs at various radial positions of the 200mm Cu wafer are also shown in Fig. 4.32. The variation of the MRR across the Cu wafer did not show a dependence on pad expiration.

Figure 4.31. (a) EDS analyses of alumina nanoabrasive retention on CMP pad asperities exposed to the Cu CMP sequence as a function of CMP conditioner downforce (ANW alumina baseline slurry). (b) EDS analyses of alumina nanoabrasive retention inside CMP pad pores exposed to the Cu CMP sequence as a function of CMP conditioner downforce (ANW alumina baseline slurry). Nanoabrasive retention is proportional to EDS Al counts. Scan area for each data point was 25 x 25 µm² and EHT was 15 KeV. EDS scan time was 600 seconds. Blue triangle symbols and black circle symbols represent new ‘unexpired’ and ‘expired’ polyurethane CMP pads.
Figure 4.32. Average Cu material removal rates (MRR) of all measured points of each ring (at certain surface radial distance from Cu wafer center). Where, inlet represents the mean Cu MRR of all measuring points (49 points, of all rings on Cu wafers surface). Where, ANW alumina slurry was used in these experiments. Blue triangle symbols and black circle symbols represent new ‘unexpired’ and ‘expired’ polyurethane CMP pads.

AFM and optical images of the Cu wafer surface were also collected to gain more insight regarding the surface quality (finishing) of Cu wafers polished with ‘expired’ and ‘unexpired’ CMP pads by using the ANW slurry. The Cu wafer polished with the ‘expired’ pad showed numerous thick scratches as compared to the Cu wafer polished with the ‘unexpired’ pad (Fig.4.33 (c-d) and Fig.4.33 (a-b), respectively). The scratches that were observed on the wafer polished with the ‘unexpired’ pad were most likely due to the tip of the four point probe (instrument used for measurement of Cu sheet resistance/thickness).
AFM scans showed that the wafer polished with the ‘unexpired’ new pad showed no scratches at the center of the wafer as well as at distances of 25mm, 50mm and 75 mm from the center of the wafer (scan sizes of 1 µm$^2$ and 25 µm$^2$). For purposes of brevity two AFM scans from this wafer are shown in Fig. 4.34 (a-b). In contrast, AFM scans on a Cu wafer polished with the ‘expired’ pad showed not only scratches but also particle contamination all over the wafer surface for each scan size (1 µm$^2$, 25 µm$^2$ and 400 µm$^2$). AFM scan images (25 µm$^2$) for the Cu wafer polished with the expired pad are shown in Fig. 4.34 (c-d). It is likely that the particles evident on the sample surface correspond to
alumina nanoabrasive although polyurethane particulates may also be present. Presuming that the particles are primarily alumina, the AFM data in Fig. 4.34 (c-d) implies substantial agglomeration. No alumina nanoabrasive particle adhesion (contamination) was observed for the Cu wafer polished with the ‘unexpired’ CMP pad as shown in Fig. 4.34 (a-b).

![AFM scans](image)

**Figure 4.34.** AFM scans (5 μm x 5 μm) of 200 mm Cu wafer polished with ANW baseline Slurry. (a) Area at center of Cu wafer polished with ‘unexpired’ polyurethane CMP pad; (b) Area 75 mm from center of wafer polished with ‘unexpired’ polyurethane CMP pad; (c) Area at center of Cu wafer polished with ‘expired’ polyurethane CMP pad; (d) Area 50 mm from center of wafer polished with ‘expired’ polyurethane CMP pad.
Cu wafers surface roughness was also investigated via AFM at various wafer locations (0mm, 25mm, 50mm, 75mm distances away from center of the wafer). These results are shown in Fig. 4.35. Overall, the Cu wafer polished with the ‘unexpired’ CMP pad showed lower surface roughness as compared to the Cu wafer polished with the ‘expired’ CMP pad. The average surface roughness (Ra values) of the Cu wafers polished with ‘expired’ and ‘unexpired’ pads was 4.70 nm and 1.17 nm, respectively. This difference is attributed primarily to scratching and particle contamination.

![Graph showing surface roughness as a function of AFM scan size](image)

**Figure 4.35.** Surface roughness (as a function of AFM scan size) from 200 mm Cu wafers polished with ANW alumina baseline slurry using both ‘expired’ and ‘unexpired’ polyurethane CMP pads.

ESEM images taken for both ‘expired’ and ‘unexpired’ CMP pads showed ‘web-like’ nanoscale structures (~100 nm diameter) present on the surface of asperities and open pores of the ‘expired’ pad. No similar structures were found on the ‘unexpired’ CMP pad surface used in this experiment (nor for any of the pads used in the experiments described previously in this chapter). ESEM images taken inside open pores for both ‘unexpired’ and ‘expired’ pad are shown in Fig.4.36 (a-b) and Fig.4.36(c-d) respectively.
Nanoscale web-like structures and possible nanoabrasive agglomeration are visible in the ESEM images of the ‘expired’ pad as shown in Fig 4.36 (c-d).

Taking the ESEM, XPS, EDS and AFM dataset as a whole, there is a strong correlation between pad age and nanoabrasive agglomeration and retention. Although in-depth modeling of this observation is beyond the scope of this dissertation, a detailed study of particle retention as a function of pad use would be of great interest from a perspective of wafer defectivity.

Figure 4.36. (a)-(b) ESEM images from inside open pores near center of ‘unexpired’ polyurethane CMP pads. (c)-(d) ESEM images from inside open pores near center of ‘expired’ polyurethane CMP pads. Note ‘web-like’ nanoscale structure area apparent in the ‘expired’ pad.
CHAPTER 5

COMPARATIVE AND QUANTITATIVE ANALYSES OF NANOABRASIVE RETENTION IN POLYURETHANE CMP PADS

In this chapter, comparative and quantitative analyses of nanoabrasive retention in polyurethane CMP pads will be presented. The primary nanoabrasive retention data presented in Chapter 4 will be summarized and discussed in terms of overall trends and conditioning parameter significance. Next, empirical models to describe the behavior of nanoabrasive retention in CMP pads as a function of dominant conditioning parameters will be developed and discussed. In the following sections, a comparative analysis between alumina nanoabrasive retention with Cabot 5001 slurry will be undertaken with respect to alumina nanoabrasive retention of a custom-formulated (ANW) slurry and with respect to silica nanoabrasive retention of commercial JSR slurry. This comparative analysis will focus on the XPS and EDS data compiled for nanoabrasive retention for individual slurries at polyurethane pad asperities and in pad pores. Monte Carlo simulation results will also be discussed to aid in facilitating a quantitative comparison of the EDS data between silica and alumina nanoabrasives. First, however, the physical impact of conditioner parameters on the pad surface roughness will be discussed to facilitate interpretation and analysis of the retention data for quantitative modeling.
5.1: Effect of Conditioning Downforce and Pad/Conditioner Relative Velocity on Pad Surface Roughness

The effect of conditioning on the local and global surface morphology of polyurethane CMP pads (IC1000/Suba IV) was characterized via profilometry as a function of conditioning downforce and pad/conditioner relative velocity. The profilometry scan length was 2000 µm for large scans (passing over numerous asperities and pores) and was 30 µm for small scans on single pad asperities.

From the large-scan profilometry, analysis showed that the overall surface roughness of the pad does not change with CMP pad conditioning (downforce and pad/conditioner relative velocity) as shown in Fig. 5.1 (a). In contrast, profilometry results on asperities (scan length 30 µm) show that pad conditioning primarily affects the asperity surface roughness as shown in the lower plot of Fig 5.1 (b). That is, asperity surface roughness increases by nearly a factor of 2 as the conditioning downforce is increased from 10 lbs to 18 lbs and/or the pad/conditioner relative velocity is increased from 0.59 m/s to 1.07 m/s. Error bars in Fig. 5.1 can be attributed to intrinsic pad surface roughness variation due to random pore size and location distribution.

As noted in Chapter 3, the points on the pad from which surface roughness measurements were acquired as a function of conditioning downforce experienced different relative pad conditioner velocities. To separate the effects of conditioning downforce and pad/conditioner relative velocity on the pad morphology the conditioning downforce was held constant (10 lbs) while increasing pad/conditioner relative velocity from low (0.59m/sec) to high (1.07 m/sec). The corresponding data is shown in the top plot of Fig. 5.1 (b).
Figure 5.1. Profilometry macro (asperities and pores) and micro (asperities) results shown in (a) & (b), respectively, reveal CMP pad surface roughness as a function of conditioning downforce and pad/conditioner relative velocity. In (a) and (b) the top graphs plot pad roughness as a function of pad/conditioner relative velocity (at constant downforce 10 lbs) and the bottom graphs plot pad roughness as a function of conditioning downforce. Scan lengths for macro and micro scans are 2000 µm and 30 µm respectively.
An increase in pad/conditioner relative velocity also resulted in the increase of the asperity surface roughness by nearly a factor of 2. This is essentially the same as the differential roughness increase determined from the conditioning downforce experiment. Therefore, it can be concluded that the increase in the surface roughness of asperities primarily resulted from an increase in the pad/conditioner relative velocity, and was less dependent on the increase in the conditioning downforce (from 10 lbs to 18 lbs). It suggests that applied conditioning downforce mainly contributes to compression of the stacked polyurethane pad.

This increase in the surface roughness of asperities by increasing pad conditioning strongly implies that the direct mechanical interaction between the pad and the conditioner is likely to be a primary mechanism of nanoabrasive removal at pad asperities. It validates the intuitive assumption that the conditioner can be used and correlated with the removal of post CMP residual nanoabrasive particles present on the asperities of CMP pad’s surface.

5.2: Effect of Conditioning Downforce, Pad/Conditioner Relative Velocity and Conditioning Time on the Alumina Nanoabrasive Retention of Cabot 5001 Slurry (Mixed with 2% H₂O₂) on Polyurethane CMP Pad Surface

5.2.1: Large Area Analysis (XPS):

As presented in Chapter 3, XPS was used to characterize relative alumina nanoabrasive concentration (over pores AND asperities) through measurement of surface
Al atomic %. The XPS probed an area with spot size of 400μm in diameter CMP pad. This area included a large number of pores and asperities.

Firstly, the XPS data shown in Fig. 5.2 confirmed that the Cu CMP process is primarily responsible for nanoabrasive retention in the pad. This is evident from the lack of nanoabrasive retention at the center of the CMP pad where the slurry is dispensed, compared to the relatively high XPS Al signal at points on the pad under the Cu wafer.

![Figure 5.2. XPS results for alumina retention vs. conditioning parameters (Cabot 5001 slurry with 2% H₂O₂). The top graph shows Al atomic concentration vs. pad/conditioner relative velocity (at constant downforce 10 lbs). The bottom graph shows Al atomic concentration vs. conditioning downforce for different conditioning times. As noted in Section 5.1 the pad/conditioner relative velocity is not constant for this data due to the pad sampling approach.](image-url)
Secondly, the data in Fig. 5.2 show that pad conditioning is effective in removing the alumina nanoabrasive retention as a function of conditioning parameters. Aluminum atomic % (taken as proportional to alumina nanoabrasive retention) decreased slightly when conditioning downforce increased from 10 lbs to 18 lbs and pad/conditioner relative velocity increased from 0.59 m/s to 1.07 m/s. But the strongest effect evident is that of conditioning time. That is, the aluminum atomic % (alumina nanoabrasive retention) decreases much more substantially by increasing conditioning time both at higher and lower pad/conditioner relative velocity as shown in Fig. 5.3. Therefore, it is concluded that the decrease in alumina retention is a weak function of conditioning downforce and pad/conditioner relative velocity but a strong function of conditioning time.

Figure 5.3. Summary of XPS analyses for alumina retention as a function of conditioning time per cycle both at low and high (insert) pad/conditioner relative velocity (Cabot 5001 slurry mixed with 2% H₂O₂).
The % decrease in alumina retention due to increased conditioner downforce, pad/conditioner relative velocity, and conditioning time is summarized in Table 5.1. This table reinforces the graphical data presented in Figs. 5.2 and 5.3. The overall conditioning downforce and pad/conditioner relative velocities are less important in terms of removing the alumina nanoabrasive of Cabot 5001 slurry from the surface of CMP pad as compared to conditioning time, especially for higher conditioning times.

Table 5.1. XPS results in terms of % decrease in Al wt % (alumina retention-Cabot 5001 slurry) in response to % increase in conditioning parameters.

<table>
<thead>
<tr>
<th>Conditioning parameter</th>
<th>Percentage increase in conditioning parameter</th>
<th>Percentage reduction in Al atomic % (alumina retention)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditioning downforce</td>
<td>80% (from 10 lbs to 18 lbs)-conditioner downforce experiment with 17 seconds conditioning time</td>
<td>21%</td>
</tr>
<tr>
<td>Conditioning downforce</td>
<td>80% (from 10 lbs to 18 lbs)-conditioner downforce experiment with 23 seconds conditioning time</td>
<td>16%</td>
</tr>
<tr>
<td>Pad/conditioner relative velocity</td>
<td>80% (from 0.59 m/s to 1.07 m/s)-relative velocity experiment with 21 seconds conditioning time</td>
<td>18%</td>
</tr>
<tr>
<td>Conditioning time per conditioning step</td>
<td>35% (from 17 sec to 23 sec)- at pad section with low (0.57 m/s) pad/conditioner relative velocity</td>
<td>65%</td>
</tr>
<tr>
<td>Conditioning time per conditioning step</td>
<td>35% (from 17 sec to 23 sec)- at pad section with high (1.07 m/s) pad/conditioner relative velocity</td>
<td>63%</td>
</tr>
</tbody>
</table>

As was noted in Chapter 3, the X-ray beam simultaneously samples many open pores and asperities of the CMP pad surface (probe area of 400μm in diameter). Therefore, to collect compositional data representative of individual CMP pad asperities or pores, local probing was performed using SEM-based EDS analyses. The EDS data for
alumina nanoabrasive retention from Cabot 5001 Cu slurry on asperities and inside open pores will be discussed in sections 5.2.2 and section 5.2.3 respectively.

5.2.2: EDS Analyses of Alumina Retention on Asperities

To investigate local variations in alumina nanoabrasive concentration of Cabot 5001 slurry, SEM-EDS was used for atomic compositional characterization of individual CMP pad asperities and open pores. The probe area was approximately 25 µm x 25 µm.

During SEM-EDS analyses on asperities (see Chapter 4) a relatively small amount of nanoabrasive retention was observed at the CMP pad center for all experiments in agreement with the XPS analyses. Large error bars as shown in Fig. 5.4 were attributed to local changes in particle density due to intrinsic pad surface roughness and asperity size variation.

The EDS data in Fig. 5.4 show that alumina nanoabrasive retention (Cabot 5001) on CMP pad asperities is a weak function of conditioning downforce and pad/conditioner relative velocity. This agrees with the interpretation of the XPS data. There is only a nominal decrease in alumina retention with increased conditioning downforce and pad/conditioner relative velocity. Decrease in nanoabrasive alumina retention depends to some extent on conditioning downforce and pad/conditioner relative velocity for a conditioning time (per step) less than 20 seconds. But after 20 seconds of conditioning time (per step), the decrease in the residual alumina on asperities is mainly a function of conditioning time (per step).
Figure 5.4. EDS analyses of alumina retention as a function of conditioning downforce and pad/conditioner relative velocity for all conditioning experiments (Cabot 5001 slurry mixed with 2% H₂O₂). Top graph plots EDS Al counts vs. pad/conditioner relative velocity (at constant downforce 10 lbs). The bottom graph plots EDS Al counts vs. conditioning downforce.

This trend is clearly evident on plotting EDS Al counts versus conditioning time for both high and low relative pad/conditioner velocities (Fig. 5.5). There is a 81% (88%) decrease in alumina retention at pad asperities as the conditioning time is increased from 17 seconds to 23 seconds for a pad/conditioner relative velocity of 1.07 m/s (0.59 m/s).
5.2.3: EDS Analyses inside Open Pores

SEM-EDS was also used inside open pores (as for asperities) for atomic compositional characterization to investigate local variations in alumina nanoabrasive retention (Cabot 5001 slurry). The probe area was (25 µm x 25 µm).

SEM-EDS analyses inside open pores exposed to wafer polishing and pad conditioning (Fig 5.6) show that there is a nominal increase in alumina retention with increased conditioning downforce and/or pad/conditioner relative velocity. These trends are opposite to those observed at pad asperities. Large variations (error bars) in the data in Fig. 5.6 are attributed to local changes in particle density due to intrinsic pore size/depth variation.
Figure 5.6. EDS analyses of alumina retention inside open pores as a function of conditioning downforce and pad/conditioner relative velocity (Cabot 5001 slurry mixed with 2% H$_2$O$_2$). Top graph plots EDS Al counts vs. pad/conditioner relative velocity (at constant downforce 10 lbs). The bottom graph plots EDS Al counts vs. conditioning downforce.

Figure 5.7 plots the EDS data acquired from open pores in the CMP pad as a function of conditioning time for sections of the pad with low pad/conditioner relative velocity (0.59 m/s) and high pad/conditioner relative velocity (1.07 m/s). There is a substantial (93%) decrease of residual alumina nanoparticles with increased conditioning time (per step) at areas of the CMP exposed to low pad/conditioner relative velocity. In
contrast, pad sections having experienced high pad/conditioner relative velocity (1.07 m/s) and/or conditioning downforce (18 lbs) exhibit only a nominal (12%) decrease in the amount of residual alumina nanoabrasives with increasing conditioning time (per step) from 17 seconds to 23 seconds. In other words, inside open pores, it seems that for higher relative velocities, the conditioning time has almost no effect in removing the residual alumina nanoabrasives. Overall, the conditioner is less effective in removing nanoabrasive inside open pores as compared to asperities for Cabot 5001 slurry.

![Figure 5.7. EDS analyses of alumina retention in open pores as a function of conditioning time (per cycle) at low and high (insert) pad/conditioner relative velocities (Cabot 5001 slurry mixed with 2% H₂O₂).](image)

It is clear that nanoabrasive retention and removal mechanisms are sensitive to the combined effects of conditioning parameters as well as to the nanoabrasive location on the CMP pad (pores or asperities). Therefore, it is important to develop empirical models
for help in understanding the interactive effects of conditioning parameters, pad locations (asperity and open pores), nanoabrasive composition and slurry chemistry on residual nanoabrasive retention and removal. Hence, three empirical models were developed and applied to the dataset presented in Chapter 4 and in Sections 5.1 and 5.2. These models are distinguished by the nature of the nanoabrasive removal per conditioning step. The first model discussed utilized a linear relationship between nanoabrasive removal and the number of conditioning steps. The second and third models utilized a non-linear relationship between nanoabrasive removal and the number of conditioning steps. These models and their agreement with experimental data is presented in Section 5.3.


Introduction and Rationale – Three Models: Linear (Constant Removal/Turn); Nonlinear-(Increasing Removal/Turn)

During ex-situ conditioning, it has been observed experimentally that there is a characteristic length of conditioning time during which CMP process byproducts remain on the pad surface. Beyond this conditioning time the removal of these byproducts from the pad surface is relatively rapid. Additionally, it is well known from the literature that MRR decreases if no pad conditioning (dressing) is performed.1, 2, 3, 4, 5 Also, according to literature, slurry film thickness is reduced in the absence of pad conditioning, i.e. slurry transport is reduced.6 The length of the ex situ conditioning time which restores (or nearly restores) the pad to its pre-polish state will most definitely depend on the kind of
pad used as well as on the conditioning and polishing parameters. As shown by the data in Chapter 4 and from Section 5.2 there is likewise a minimum time required to remove CMP process by-products (residual nanoabrasives), i.e. shorter conditioning times will promote accumulation of residual nanoabrasives on the pad surface. Sufficient conditioning time will not only return the pad to its original topographical state, but will also remove residual nanoabrasives and prevent accumulation that would impede fresh slurry transport. However, there is no \textit{a priori} reason to expect that the minimum conditioning time required to prevent excessive nanoabrasive retention is the same as the minimum conditioning time needed to restore the topographic state of the pad. Therefore an effective model to understand the time-evolution of nanoabrasive retention is essential.

Figure 5.8 provides a schematic illustration of the trend observed for nanoabrasive retention on the pad versus conditioning time. Three time-regimes are described. The first regime (low conditioning time) corresponds to substantial accumulation of nanoabrasives at pad asperities and in pores. The transition region (second regime) represents the situation for intermediate ranges of conditioning times, where residual nanoabrasive retention starts to decrease rapidly with increasing conditioning time. The removal regime (third regime) is characterized by conditioning times sufficient to maintain stable MMR as well as constant pad morphology with minimal retention of residual nanoabrasive. Further increase in conditioning time beyond this would only be expected to lead to excessive pad wear.
Figure 5.8. Schematic diagram showing the experimentally observed features of nanoabrasive accumulation vs. conditioning time.

To quantitatively describe the experimental results in terms of this behavior three empirical models related to Post-CMP nanoabrasive retention, transport and removal mechanisms on porous CMP pad surfaces have been developed and applied. These models take into consideration the number of polishing cycles as well as both steps of each Cu polishing cycle, that is, retention introduced through the CMP polishing step as well as nanoabrasive removal through subsequent ex-situ conditioning. In these models, the residual nanoabrasive removal efficiency, $\eta$, of the conditioner/slurry system is a parameter that characterizes how effectively the conditioner removes nanoabrasive deposited during the preceding polish. In the first model (linear model) the residual nanoabrasive removal has been considered constant for each CMP pad turn during the conditioning step. In other words, residual nanoabrasive removal is constant for every conditioning step and is independent of the amount of nanoabrasive already present on
the pad surface. In contrast, for non-linear models (second and third models), the residual nanoabrasive removal per pad turn (during conditioning step) is not considered constant, but rather is dependent on the previous amount of residual nanoabrasive present on the pad surface. The second model considers the residual nanoabrasive removal efficiency, $\eta$, independent of the conditioning time. The third model assumes the residual nanoabrasive removal efficiency, $\eta$, increases as conditioning time is increased during the conditioning step. Each of these three models will be discussed in detail in Sections 5.3.1-5.3.3 and will be used for the quantitative analysis of the nanoabrasive retention versus conditioning time data.

The nanoabrasive (i.e. proportional to XPS Al At% or Al EDS ‘counts’) introduced per polish step ($R_o$) may vary due to the type of pad surface feature (asperities and open pores) and amount of conditioning. Therefore during fitting analysis with the models discussed in the preceding paragraph, the variation in $R_o$ as a function of pad/conditioner velocity for each dataset (XPS Al At%, EDS-Al at asperities, or EDS-Al in pores) will be discussed.

5.3.1: Empirical Linear Model

For this model a constant amount of residual nanoabrasive removed per pad turn (during each conditioning step of Cu polishing cycles) is assumed.

The following are the primary parameters and definitions used in this model.

$n = \text{Cu polishing cycle #} \ (each \ cycle \ consists \ of \ polishing \ step \ and \ ex-situ \ conditioning \ step). \ A \ total \ of \ 30 \ cycles \ were \ used \ in \ the \ experiments.$

$R = \text{Nanoabrasive (counts) per unit pad area}$
\( R_o \) = Nanoabrasive (counts) per unit area introduced by the polishing step of a polishing cycle

\( t \) = Total conditioning time of a conditioning step

\( \gamma \) = Pad turns (rotations) per second during conditioning step

\( \eta \) = Total removal efficiency of conditioner/slurry system per pad/conditioner turn

\( \eta \) is defined here as a function of pad/conditioner relative speed, and conditioning downforce. It would also be expected to depend on pad/conditioner contact area cross-section (probability), nanoabrasive particle suspension, as well as nanoabrasive composition. The latter dependencies are discussed later in this chapter.

**Definition for Residual Nanoabrasive Removal**

Residual nanoabrasive removal per pad turn is considered constant in this model and is represented by \( \eta R_o \). The values of both \( \eta \) and \( R_o \) have been considered constant in this model for a particular set of conditioner, polishing, and slurry parameters and for a given location on a pad surface. Related calculations are provided below.
General calculations for residual nanoabrasive removal during the n\textsuperscript{th} polishing cycle:

*Total initial accumulated nanoabrasive retention before the start of conditioning step in any n\textsuperscript{th} polishing cycle*

\[ R_o = \text{Residual nanoabrasive introduced by a Cu CMP polishing step} \]
\[ R_{f(n-1)} = \text{Total residual nanoabrasive present on pad surface at the end of the (n-1)\textsuperscript{th} polishing cycle} \]
\[ R_{i_n} = \text{Total residual nanoabrasive present on the pad surface at the start of conditioning of the n\textsuperscript{th} polishing cycle} \]

Therefore,

\[ R_{i_n} = R_o + R_{f(n-1)} \] \hspace{1cm} (5.2)

*Total residual nanoabrasive removed from pad surface by the conditioner after completion of conditioning step (by utilizing N pad turns) at the n\textsuperscript{th} polishing cycle*

After a given polishing step, the conditioning step during the n\textsuperscript{th} cycle will reduce residual nanoabrasive. So, according to the removal definition provided above (i.e. constant retention removal)

Nanoabrasive removed after 1\textsuperscript{st} pad turn = \eta R_o = 1 \times (\eta R_o)

Nanoabrasive removed after 2\textsuperscript{nd} pad turn = \eta R_o + \eta R_o = 2 \times (\eta R_o)

Nanoabrasive removed after 3\textsuperscript{rd} pad turn = \eta R_o + \eta R_o + \eta R_o = 3 \times (\eta R_o)

Similarly, the residual nanoabrasive removed after the N\textsuperscript{th} pad turn = N \times (\eta R_o)

But according to Equation 5.1, \( N = \gamma \times t \). Therefore, the residual nanoabrasive removed after N\textsuperscript{th} pad turn is

\[ R_C = (\gamma \times t) \times (\eta R_o) \] \hspace{1cm} (5.3)
In our experiments, the value of $\gamma$ was 0.75. Therefore, Equation 5.3 can be rewritten as:

$$R_C = (0.75 \times t) \times (\eta R_o).$$

It is important to mention here that the amount of nanoabrasive removal (from the pad surface) by the conditioner is constant for all conditioning steps of all polishing cycles because $\gamma$, $t$, $\eta$, and $R_o$ are considered constant.

**Calculations for residual nanoabrasive removal during 1st cycle (n=1):**

**Polishing Step:**

The nanoabrasive (counts/area) introduced by polishing step of 1$^{st}$ cycle is $R_n = R_1 = R_o$.

The nanoabrasive present on the pad surface due to previous cycle, i.e. $R_{f(n-1)} = 0$.

Therefore, according to Equation 5.2, the total initial nanoabrasive on a pad surface just after the first Cu polish step is: $R_{in} = R_{i1} = R_o + 0 = R_o$

**Conditioning Step:**

According to Equation 5.3 the nanoabrasive removed by conditioner after the completion of conditioning step (after N pad turns) = $R_C = \gamma t \eta R_o$

Therefore, the final amount of residual nanoabrasive left (retained) on the pad surface after the completion of the 1$^{st}$ polishing cycle, $R_{f1} = R_{i1} - R_C = R_o - \gamma t \eta R_o = (1 - \gamma t \eta)R_o$

**Calculations for residual nanoabrasive removal during 2$^{nd}$ polishing cycle (n=2):**

**Polishing Step:**

The nanoabrasive (counts/area) introduced by polishing during the 2$^{nd}$ cycle is $R_n = R_2 = R_o$

The nanoabrasive present on the pad surface due to previous cycle (1$^{st}$ cycle) is $R_{f(n-1)} = R_{f1} = (1 - \gamma t \eta) R_o$ (from above). Therefore, according to Equation 5.2 the nanoabrasive
resident on a pad surface just after the 2nd polishing step is: \( R_{ia} = R_{i2} = R_o + (1 - \gamma \eta) R_o = (2 - \gamma \eta) R_o \)

**Conditioning Step:**

According to Equation 5.3 the nanoabrasive removed by the conditioner after the conditioning step (after N pad turns) = \( R_C = \gamma \eta R_o \).

Therefore, final nanoabrasive resident on the pad surface after the completion of the 2nd polishing cycle, \( R_{f2} = R_{i2} - R_C = (2 - \gamma \eta) R_o - \gamma \eta R_o = 2 \times (1 - \gamma t \eta) R_o \).

**Calculations for residual nanoabrasive removal during n\textsuperscript{th} polishing cycle:**

Based on the nanoabrasive retention results as shown above, the final nanoabrasive resident on the pad surface after the \( n \textsuperscript{th} \) polishing cycle can be expressed as

\[
R_{fn} = n \times (1 - \gamma \eta) R_o, \text{ or } R_{fn} = n R_o - n \gamma \eta R_o
\]

Equation 5.4 is the equation for a straight line with a slope \((-\eta \gamma R_o)\). During the nanoabrasive retention experiments, there were a total of 30 polishing cycles \((n)\) and the pad speed was 0.75 rotations per second. Therefore, Equation 5.4 can be written as

\[
R_{f30} = 30 R_o - 22.5 \times \eta R_o
\]

Representative plots based on Equation 5.5 are shown in Fig. 5.9 for prediction of nanoabrasive retention. These data are plotted for different values of nanoabrasive removal efficiency \((\eta)\) and Cu polishing cycles \((n)\). As shown in Fig. 5.9(a) the nanoabrasive retention for the linear model decreases linearly with increasing conditioning time and removal efficiency, \(\eta\). This is not unexpected. Figure 5.9(b) shows clearly the rapid accumulation of nanoabrasive for conditioning times less than that required to remove the nanoabrasive deposited in the pad during a single cycle \((\sim R_o)\).
expected the nanoabrasive retention is linearly proportional to the cycle number, n, and decreases linearly as the clearing time/step is approached.

Figure 5.9. Representative nanoabrasive retention trends based on the linear model (Equation 5.5). (a) Plot shows a decrease in nanoabrasive retention with increase in the removal efficiency and conditioner time (n=30). (b) Plot shows nanoabrasive retention over 30 cycles as a function of conditioner time per step. For this plot $\eta = 0.05$. For both plots $\gamma = 0.75$ and $R_a = 800$.

Figure 5.10(a) shows results of fitting the experimental XPS data for alumina retention (Cabot 5001 slurry + 2% H$_2$O$_2$) to the linear model defined above. Similar analysis for the small-area EDS data acquired for asperities and pores is shown in Fig. 5.10(b) and Fig. 5.10(c), respectively. For this analysis the nanoabrasive ‘counts’
introduced per polish step is not allowed to vary as a function of relative velocity between the pad and conditioner. However, it is allowed to vary between the XPS, EDS-asperities, and EDS-pores dataset. The former, naturally, due to the difference in scale; the latter two due to the fact that nanoabrasive introduced to asperities and pores may differ.

Overall nanoabrasive retention (XPS data) for the pad section exposed to ‘high relative velocity’ conditioning was best described by a nanoabrasive removal efficiency of $0.050\pm0.004$. The ‘low relative velocity’ conditioning data was best described by a nanoabrasive removal efficiency of $0.047\pm0.004$. These efficiencies are statistically identical. Nanoabrasive retention (EDS data) at asperities exposed to ‘high relative velocity’ conditioning was best described by a nanoabrasive removal efficiency of $0.057\pm0.002$. The ‘low relative velocity’ conditioning data from asperities was best described by a nanoabrasive removal efficiency of $0.055\pm0.002$. These efficiencies are also statistically identical. The corresponding nanoabrasive removal efficiencies from best fits of the linear model to the EDS data acquired from open pores were $0.037\pm0.007$ for ‘high relative velocity’ conditioning and $0.053\pm0.004$ for ‘low relative velocity’ conditioning. These values are statistically distinct at the 1-sigma level and point to a relative velocity dependence of nanoabrasive removal from pores. The value for $R_o$ (the nanoabrasive introduced/cycle) for the asperity (EDS) nanoabrasive data was $685\pm103$ while the same value for the pore nanoabrasive data was $851\pm201$. The 1 sigma values are high in keeping with the large experimental variation of the data. The relative values are reasonable in that the nanoabrasive accumulation in pores would be expected to exceed that of asperities.
Figure 5.10. Curve fitting (solid lines) of aluminum (Cabot 5001 slurry + 2% H₂O₂) XPS and EDS data (triangular symbols) using the linear model. (a) Curve fitting with XPS data (b) Curve fitting with EDS data taken on asperities. (c) Curve fitting with EDS data taken inside open pores. For all analyses n=30 and γ=0.75. Ro was considered as a shared parameter for both high and low relative velocity pad sections.
Although, this linear model is consistent with some of the general aspects of nanoabrasive removal data at asperities and inside open pores, its overall agreement with the data is marginal even considering the large experimental variations observed. Most importantly, a strictly linear model does not describe the nominal time-dependence of the nanoabrasive retention as measured through EDS and XPS. Therefore, to more accurately reflect the experimental data and provide more insight into nanoabrasive removal mechanisms, a non-linear model is needed. Two such non-linear models are developed. One model is based on ‘time independent’ removal efficiency and the other is based on a ‘time dependent’ removal efficiency.

5.3.2: Non-linear Empirical Model (Time Independent Nanoabrasive Removal Efficiency)

The main difference between this non-linear model and the linear model regards the nanoabrasive removal efficiency of the conditioner/slurry system. The model definitions for the other parameters (n, R, R_0, t, γ, N, R_{fin}, R_{n}, R_{f(n-1)} and R_{in}) are the same as defined in the previous section 5.3.1 (linear model).

**Definition for Residual Nanoabrasive Removal**

In this non-linear model, the nanoabrasive removal per pad turn (during conditioning step) is not constant in contrast to the linear model. Nanoabrasive removal efficiency (η) in this model represents the fractional removal of nanoabrasive present on the pad surface for a given pad rotation. Therefore, the nanoabrasive left on the pad surface due to a previous pad rotation has a great impact on the removal of residual
nanoabrasives from the pad surface. The efficiency $\eta$ is also considered independent of conditioning time. But the value of $\eta$ is certainly a function of pad/conditioner relative speed, conditioning downforce, pad/conditioner cross-section area (probability) and nanoabrasive composition & suspension as noted for the linear model (previous Section 5.3.1).

**General calculations for residual nanoabrasive removal during any $n^{th}$ polishing cycle:**

*Total initial accumulated nanoabrasive before the start of conditioning step in any $n^{th}$ polishing cycle.* From Equation 5.2 the total initial accumulated nanoabrasive is $R_i_n = R_o + R_{f(n-1)}$, where

- $R_{n} = R_o =$ Residual nanoabrasive introduced by the polishing step in the $n^{th}$ polishing cycle
- $R_{f(n-1)} =$ Residual nanoabrasive on pad surface after the completion of the $(n-1)^{th}$ cycle
- $R_{i_n} =$ Total initial accumulated nanoabrasive present on the pad surface before the start of conditioning step in the $n^{th}$ polishing cycle

*Total removed nanoabrasive from pad surface by the conditioner after completion of conditioning step (by utilizing $N$ pad’s turns) in any $n^{th}$ polishing cycle.* After the polishing step the ex-situ conditioning step of the $n^{th}$ cycle will start to remove the nanoabrasive, therefore,

Nanoabrasive (counts/pad area) removed after pad’s 1

$\eta R_{i_n}$

Nanoabrasive (counts/pad area) resident on pad after pad’s 1


\[ R_{1n} = R_{in} \cdot \eta R_{in} = (1-\eta) \times R_{in} \]

Nanoabrasive (counts/pad area) removed after pad’s 2\textsuperscript{nd} turn during conditioning:
\[ \eta \times \{(1-\eta) \times R_{in}\} \]

Nanoabrasive (counts/pad area) resident on pad after pad’s 2\textsuperscript{nd} turn during conditioning:
\[ R_{2n} = [(1-\eta) \times R_{in}] - [\eta \times \{(1-\eta) \times R_{in}\}] = (1-\eta)^2 \times R_{in} \]

Nanoabrasive (counts/pad area) resident on pad after pad’s 3\textsuperscript{rd} turn during conditioning:
\[ (1-\eta)^3 \times R_{in} \]

Nanoabrasive (counts/pad area) resident on pad after pad’s \( N \)\textsuperscript{th} turn during ex-situ conditioning:
\[ R_{Nn} = (1-\eta)^N \times R_{in} \]

\( N = \gamma t \) (according to Equation 5.1). Furthermore, \( R_{Nn} = R_{fn} \). Thus,
\[ R_{Nn} = R_{fn} = (1-\eta)^{\gamma t} \times R_{in} \] \[ \text{................................. (5.6)} \]

Further, define
\[ A = (1-\eta)^{\gamma t} \] \[ \text{................................. (5.7)} \]

For the case of the experiments presented here, \( N = 0.75t \). So, Equation 5.7 can be written as
\[ R_{fn} = (1-\eta)^{0.75t} \times R_{in} = A \times R_{o}. \]

**Calculations for residual nanoabrasive removal during 1st polishing cycle (n=1):**

**Polishing Step:**
The nanoabrasive (counts/area) introduced by polishing step of 1\textsuperscript{st} cycle is \( R_n = R_1 = R_{o} \).
The nanoabrasive present on the pad surface due to previous, \((n-1)\textsuperscript{th}\), polishing cycle is \( R_{f(n-1)} = 0 \). Therefore, the initial nanoabrasive present on pad surface just before the start of the conditioning step in the 1\textsuperscript{st} polishing cycle will be \( R_{i_n} = R_{i_1} = R_{o} + 0 = R_{o} \).
**Conditioning Step:**

According to Equation 5.6, the nanoabrasive resident on the pad’s surface after completion of the conditioning step of the 1\textsuperscript{st} polishing cycle will be, \( R_{f1} = (1-\eta)^{\gamma t} \times R_i = (1-\eta)^{\gamma t} \times R_o = A \times R_o. \)

**Calculations for residual nanoabrasive removal during 2\textsuperscript{nd} polishing cycle (n=2):**

**Polishing Step:**

The nanoabrasive (counts/area) introduced by the polishing step of the 2\textsuperscript{nd} polishing cycle, \( R_n = R_2 = R_o. \) The nanoabrasive present on the pad surface due to the previous polishing cycle (1\textsuperscript{st} cycle) is \( R_{f(n-1)} = R_{f1} = (1-\eta)^{\gamma t} \times R_o. \) Therefore, the total initial nanoabrasive present on the pad surface just before the start of the conditioning step in the 2\textsuperscript{nd} polishing cycle will be (according to Equation 5.2) \( R_{i2} = R_{i1} = R_o + (1-\eta)^{\gamma t} \times R_o = \{1 + (1-\eta)^{\gamma t}\} \times R_o. \)

**Conditioning Step:**

According to Equation 5.6, the nanoabrasive resident on the pad’s surface after completion of the conditioning step of the 2\textsuperscript{nd} polishing cycle will be:

\[ R_{f2} = (1-\eta)^{\gamma t} \times R_{i2} = (1-\eta)^{\gamma t} \times \{1 + (1-\eta)^{\gamma t}\} \times R_o \]

\[ R_{f2} = A \times \{1+A\} \times R_o \]

\[ R_{f2} = A \times R_o \times (1+A) \]

where, \( A = (1-\eta)^{\gamma t}. \)

**Calculations for residual nanoabrasive removal during 3\textsuperscript{rd} polishing cycle (n=3):**

**Polishing Step:**

The nanoabrasive (counts/area) introduced by the 3\textsuperscript{rd} polishing cycle is \( R_n = R_3 = R_o. \) The nanoabrasive present on the pad surface due to the previous polishing cycle (2\textsuperscript{nd} cycle) is
\( R_f^{(n-1)} = R_{f2} = (1-\eta)^{\gamma t} \times [\{1 + (1-\eta)^{\gamma t}\} \times R_o]. \) Therefore, the total initial nanoabrasive present on the pad surface just before the start of the conditioning step in the 3\(^{rd}\) polishing cycle will be (according to Equation 5.2) \( R_{i3} = R_{i3} = R_o + (1-\eta)^{\gamma t} \times [\{1 + (1-\eta)^{\gamma t}\} \times R_o] = R_o + (1-\eta)^{\gamma t} \times R_o + (1-\eta)^{2\gamma t} \times R_o. \)

**Conditioning Step:**

According to Equation 5.6, the final nanoabrasive resident on the pad surface after the completion of the conditioning step of the 3\(^{rd}\) polishing cycle will be:

\[
R_{fi} = (1-\eta)^{\gamma t} \times R_{i3} = (1-\eta)^{\gamma t} \times [R_o + (1-\eta)^{\gamma t} \times R_o + (1-\eta)^{2\gamma t} \times R_o]
\]

\[
R_{fi} = (1-\eta)^{\gamma t} \times R_o \times [1 + (1-\eta)^{\gamma t} + (1-\eta)^{2\gamma t}]
\]

\[
R_{fi} = A \times R_o \times [1 + A + A^2]
\]

\[
R_{fi} = A \cdot R_o \cdot (1+A + A^2)
\]

**Calculations for residual nanoabrasive removal during n\(^{th}\) polishing cycle:**

Combining the above results, the final nanoabrasive resident on the pad surface after the completion of the n\(^{th}\) polishing cycle is \( R_{fn} = A \cdot R_o \cdot (1+A + A^2 + A^3 + \ldots + A^{n-1}). \) This result can be rewritten as \( R_{fn} = A \cdot R_o \cdot [(1 - A^{(n-1)+1})/(1-A)] \) or:

\[
R_{fn} = (1-\eta)^{\gamma t} \times R_o \times \left[ \frac{1-(1-\eta)^{n\times\gamma t}}{1-(1-\eta)^{\gamma t}} \right] \tag{5.8}
\]

Equation 5.8 represents the general formula for the non-linear empirical model. For our experiments, \( n = 30 \) and \( \gamma = 45/60 = 0.75. \) Therefore, equation 5.8 can be written as:

\[
R_{fn} = (1-\eta)^{0.75t} \times R_o \times \left[ \frac{1-(1-\eta)^{22.5t}}{1-(1-\eta)^{0.75t}} \right] \tag{5.9}
\]
A representative plot based on this nonlinear empirical formula (Equation 5.9) is shown in Fig. 5.11 to illustrate the retention removal trend as a function of conditioner time per conditioning step.

![Non-linear Model](image)

**Figure 5.11.** Retention of nanoabrasives as a function of ‘conditioner time per conditioning step’ per the nonlinear model described above. Arbitrary values of efficiency \((\eta = 0.3)\) as well as of nanoabrasive retention \((R_0 = 700,000)\) were used in Equation 5.9 for purposes of illustration. Also, \(n = 30\) and \(\gamma = 0.75\).

Figures 5.11 and 5.12 show that ‘proportional removal’ – nanoabrasive removal per cycle which is proportional to the initial nanoabrasive present – yields a power-law behavior to the nanoabrasive retention as a function of conditioning time per step. The data plotted in Fig. 5.12(b) based on this model suggests that, like the linear model, a sufficient minimum conditioning time is required to avoid accumulation of nanoabrasives.
Trends based on ‘Time Independent’ Non-linear Model: $\eta \neq \eta(t)$

(a) Plots illustrate the effect of removal efficiency on the nanoabrasive retention. Right graph is a magnified portion of the section of the left graph. Here, $n = 30$, $\gamma = 0.75$ and $R_o = 700,000$. (b) Plots show the effect of the number of polishing cycles on nanoabrasive retention ($\eta = 0.3$, $\gamma = 0.75$ and $R_o = 700,000$). The dotted line represents nanoabrasive introduced by a single Cu polishing step.
Figure 5.13 shows fitting results of the experimental XPS and EDS data for alumina retention (Cabot 5001 slurry + 2% H₂O₂) to the non-linear model (time independent nanoabrasive removal efficiency) described above. For this analysis the nanoabrasive ‘counts’ introduced per polish step is not allowed to vary as a function of relative velocity between the pad and conditioner (as with the linear model). However, it is allowed to vary between the XPS, EDS-asperities, and EDS-pores dataset. The former, naturally, due to the difference in scale; the latter two due to the fact that nanoabrasive introduced to asperities and pores may differ.

In terms of nanoabrasive removal efficiencies obtained from best fits to the XPS and EDS data (Fig. 5.13), this non-linear model (similar to linear model) is consistent with the general aspects of nanoabrasive removal. Compared to the linear model, this nonlinear model provided a better fit to the EDS-asperity data (Fig. 5.13(b)). However, the model provided a poorer quantitative fit to the XPS and EDS-pore data as can be seen clearly in terms of the increased $\chi^2$ and decreased $R^2$ ‘goodness of fit’ parameters. More troubling, however, is the unreasonably large values of $R_o$ demanded by this approach (larger than the value predicted by the linear model by roughly a factor of $10^3$). Based on direct SEM imaging of conditioned and non-conditioned asperities and pores this factor seems extremely unrealistic. (By way of comparison with the linear model, this nonlinear model analysis did not yield statistically distinct values of $\eta$ as a function of relative pad/conditioner velocity.)
Curve Fitting with ‘Time Independent’ Non-linear Model: $\eta \neq \eta(t)$

Figure 5.13. Curve fitting (solid lines) of experimental alumina retention data (Cabot 5001 slurry + 2% H$_2$O$_2$) to the time independent non-linear model. (a) Results for XPS data. (b) Results for EDS data from asperities. (c) Results for EDS data from open pores. The values of $n$ and $\gamma$ were 30 and 0.75, respectively. $R_0$ was considered as shared parameter for both high and low relative velocity pad sections.
To address these shortcomings it is necessary to develop a model which maintains a reasonable value for retention at shorter conditioning times yet displays the crossover or ‘transition regime’ behavior that was experimentally observed. A simple empirical approach to incorporate these features in the nonlinear model is to insert a time-dependence to the efficiency, $\eta$. Clearly, this increases the number of free parameters into the analysis which calls into question the model’s validity considering the number of experimental data points. However, it is justified as a means to more thoroughly explore the experimental data and guide the design of future experiments or models. Intuitively, a time-dependent efficiency may reflect an initial conditioner/pad contact time required to loosen the agglomerated, stuck and/or trapped nanoabrasive particles on the pad surface. So, it is not difficult to imagine that removal efficiency might significantly increase after a certain initial period of conditioning time. On the basis of this type of argument, a new non-linear empirical model is developed and applied in the next section to quantitatively describe the experimental data.

5.3.3: Non-linear Model (Time Dependent Nanoabrasive Removal Efficiency)

In this non-linear model it is considered that the nanoabrasive removal is a function of conditioning which exhibits a rapid rise after some characteristic time. The specific time dependent efficiency is defined below.

Definition for nanoabrasive removal function (f):

Previously, the removal efficiency, $\eta$, was defined per turn (rotation) of the pad when undergoing conditioning. This efficiency represented removal which was either
fixed (linear model) or proportional to the amount of nanoabrasive resident on the pad (nonlinear model with time-independent removal efficiency). Neither model is capable of representing nanoabrasive removal mechanisms which may be activation-based, e.g. mechanical breakdown of agglomerates or two-step mechanisms based on pad roughening. Since the characteristic time at which the removal begins to increase may occur between or within conditioning steps a more general function is defined:

$$\eta' = \frac{1}{1 + \exp(\lambda \times (t_0 - t))}$$  \hspace{1cm} (5.10)

where, $\lambda$ is a characteristic rate constant, $t_0$ is a characteristic activation time, and $t$ is the conditioning time. The choice of the exponential functional dependence here is, to a certain extent, arbitrary. The activation time, $t_0$, represents the length of initial conditioning required to promote substantial removal of residual nanoabrasive. The rate constant, $\lambda$, is related to the time period over which this removal increases.

As with the previous models the parameters for the removal efficiency are expected to be dependent on pad/conditioner relative speed, conditioner downforce, pad/conditioner cross-section area (probability) and nanoabrasive suspension.

Definition for the nanoabrasive removal function for the total conditioning step:

In contrast to the nonlinear model discussed in the previous section, the nanoabrasive removal for this model is not calculated per pad rotation during the conditional step, but per the step as a whole. This reflects the fact that ‘activation’ may occur at any point during the step. Consequently, for the $n^{th}$ polishing cycle, the final nanoabrasive ($R_{fn}$) that is resident on the pad surface after the completion of conditioning
step can be written in terms of total initial nanoabrasive \((R_{in})\) present on the pad surface just before the start of conditioning.

\[
R_{fn} = R_{in} - \eta' R_{in} = (1-\eta') R_{in} \tag{5.11}
\]

According to equation 5.2, we know that total residual nanoabrasive present on the pad surface at the start of the conditioning step of the \(n^{th}\) polishing cycle is

\[
R_{in} = R_o + R_{f(n-1)}
\]

And

\[
R_n = R_o = \text{Residual nanoabrasive introduced by a Cu polishing step in } n^{th} \text{ polishing cycle}
\]

\[
R_{f(n-1)} = \text{Total residual nanoabrasive present on pad surface at the end of the } (n-1)^{th} \text{ polishing cycle}
\]

**Calculations for residual nanoabrasive removal during 1\textsuperscript{st} polishing cycle (n=1):**

**Polishing Step:**

The nanoabrasive (counts/area) introduced by the polishing step of the 1\textsuperscript{st} cycle is \(R_n = R_1 = R_o\). The nanoabrasive present on the pad surface due to the previous polishing cycle – the (n-1)\textsuperscript{th} cycle – is \(R_{f(n-1)} = 0\). Therefore, the total accumulated nanoabrasive present on pad surface just before the start of conditioning step in the 1\textsuperscript{st} polishing cycle will be (according to equation 5.2)

\[
R_{in} = R_{i1} = R_o + 0 = R_o.
\]

**Conditioning Step:** According to Equation 5.11 the final nanoabrasive that is left on the pad surface after the completion of the conditioning step of 1\textsuperscript{st} polishing cycle will be

\[
R_{f1} = (1-\eta') \times R_{i1} = (1-\eta') \times R_o.
\]
Calculations for residual nanoabrasive removal during 2\textsuperscript{nd} polishing cycle (n=2):

\textit{Polishing Step:}

The nanoabrasive (counts/area) introduced by the polishing step of the 2\textsuperscript{nd} polishing cycle is \( R_n = R_2 = R_o \). The nanoabrasive present on the pad surface due to the previous polishing cycle (1\textsuperscript{st} cycle) is \( R_{f1} = (1-\eta') R_o \). Therefore, the total initial nanoabrasive present on the pad surface just before the start of the conditioning step of the 2\textsuperscript{nd} polishing cycle will be (according to Equation 5.2) \( R_{i2} = R_o + R_{f1}= R_o + (1-\eta') R_o = (2-\eta')R_o \).

\textit{Conditioning Step:}

According to Equation 5.11, the final nanoabrasive that is resident on the pad surface after the completion of the conditioning step of the 2\textsuperscript{nd} polishing cycle will be \( R_{f2} = (1-\eta')R_{i2} = (1-\eta') \times (1+1-\eta')R_o = [(1-\eta')+(1-\eta')^2]R_o \).

Calculations for residual nanoabrasive removal during 3\textsuperscript{rd} polishing cycle (n=3):

\textit{Polishing Step:}

The nanoabrasive (counts/area) introduced by the 3\textsuperscript{rd} polishing step = \( R_o \). The nanoabrasive present on the pad surface due to the previous polishing cycle (2\textsuperscript{nd} cycle) is \( R_{f2} = [(1-\eta')+(1-\eta')^2]R_o \). Therefore, total initial nanoabrasive present on the pad surface just before the start of the conditioning step in the 3\textsuperscript{rd} polishing cycle will be (according to Equation 5.2) \( R_{i3} = R_o + R_{f2} = [1+(1-\eta')+(1-\eta')^2]R_o \).

\textit{Conditioning Step:}

According to Equation 5.11, the final nanoabrasive that is resident on the pad surface after the completion of the conditioning step of the 3\textsuperscript{rd} polishing cycle will be \( R_{f3} = (1-\eta')R_{i3} = [(1-\eta')+(1-\eta')^2+(1-\eta')^3]R_o \).
Calculations for residual nanoabrasive removal during $n^{th}$ polishing cycle:

By comparing the results for the first three cycles we can generalize the result for the residual nanoabrasive resident on the pad after the $n^{th}$ cycle.

\[ R_{fn} = [(1-\eta') + (1-\eta')^2 + (1-\eta')^3 + \ldots + (1-\eta')^{n-1} + (1-\eta')^n]R_o. \]

\[ R_{fn} = (1-\eta')[1 + (1-\eta') + (1-\eta')^2 + \ldots + (1-\eta')^{n-2} + (1-\eta')^{n-1}]R_o. \]

From the definition given in Equation 5.10 and the formula for the sum of a geometric series this can be expressed as:

\[ R_{fn} = e^{\lambda(t_o - t)} \times \left[ 1 - \frac{1}{(1 + e^{\lambda(t-o)})^n} \right] \times R_o \quad \text{.......................................................... (5.12)} \]

But in our case, $n=30$

Therefore, the final nanoabrasive retention on pad surface after completion of 30 polishing cycles (30 polishing and conditioning steps)

\[ R_{30} = e^{\lambda(t_o - t)} \times \left[ 1 - \frac{1}{(1 + e^{\lambda(t-o)})^{30}} \right] \times R_o \quad \text{.......................................................... (5.13)} \]

Representative plots for efficiency and nanoabrasive retention based on this model are shown in Fig. 5.14. The plots show the ‘time dependent’ nanoabrasive removal efficiency ($\eta' = 1/(1+e^{\lambda(t-o)})$) and its effect on residual nanoabrasive removal for various model parameters.

Firstly, $\eta'$, is restricted to be less than or equal to 1 at all times. The value of $t_o$ is effectively a ‘turn-on’ time, after which $\eta'$ becomes significant (Fig. 5.14(a)), while $\lambda$ represents a rate associated with the rise of $\eta'$ (Fig. 5.14(b)). The effect of a time-
dependent removal efficiency on the time-dependence of nanoabrasive removal in this model is illustrated in Figs. 5.14(c-e). As shown in Fig. 5.14(c) the value of \( t_0 \) dictates the conditioning time at which substantial nanoabrasive removal occurs. The value of \( \lambda \) determines how rapidly the nanoabrasive retention decreases (Fig. 5.14(d)). Figure 5.14(e) illustrates the variation of nanoabrasive retention with the number of cycles. This model better represents the experimental observations regarding nanoabrasive retention in CMP pads. Firstly, it reproduces the ‘transition regime’ discussed at the beginning of this section and schematically illustrated in Fig. 5.8. Secondly, the nanoabrasive retention at times less than \( t_0 \) remains bounded (Fig. 5.14(e)) in contrast to the power-low behavior noted for the previous nonlinear model that incorporated a fixed nanoabrasive removal efficiency. Although the number of model parameters has been increased, this empirical model displays key features observed experimentally.
`Time Dependent’ Non-linear Model: $\eta' = \eta'(t)$

Figure 5.14. Plots based on non-linear nanoabrasive retention model (time dependent efficiency). (a) Nanoabrasive removal efficiency, $\eta'$, vs. conditioner time for different values of $t_o$ (characteristic conditioning time for which $\eta'$ becomes significant). Here, $\lambda = 0.5$. (b) Nanoabrasive removal efficiency, $\eta'$, vs. conditioner time for different values of $\lambda$. Here, $t_o = 20s$. (c) Nanoabrasive retention vs. conditioner time for different values of $t_o$ for $n=30$ and $\lambda =1$. (d) Nanoabrasive retention vs. conditioner time for different values of $\lambda$ for $n=30$ (e) Nanoabrasive retention vs. conditioner time for different number of polishing cycles. Where, $\lambda=1$ and $t_o = 25s$. For plots in ‘c’,‘d’ & ‘e’ $R_o = 700,000$. 

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Results of the analysis of the XPS and EDS nanoabrasive retention data (Cabot 5001 slurry + 2% H₂O₂) by the retention model illustrated in Fig. 5.14 are shown in Figures 5.15-5.17. To realistically apply this model in light of the additional efficiency parameter, three sets of analyses were undertaken for different combinations of variable parameters. During this analysis a variation in Rₒ as a function of relative pad/conditioner velocity was considered. This variation was not presented above for the previous two models as it was presumed independent of the pad/conditioner relative velocity. A preliminary analysis of varying Rₒ was carried out for the previous two models, but the fitting results did not justify its consideration. It was introduced here to reflect conditioning-induced variations in nanoabrasive accumulation in the pad.

XPS and EDS data analysis was carried for three sets of parameter constraints. **Constraint condition 1:** A single value of λ is chosen to simultaneously fit both the ‘high’ and ‘low’ pad/conditioner relative velocity data (i.e. the parameter is shared while fitting both data sets). In contrast, distinct values of both tₒ and Rₒ are used to fit the ‘high’ and ‘low’ pad/conditioner relative velocity data. **Constraint condition 2:** A single value of Rₒ is chosen to simultaneously fit both the ‘high’ and ‘low’ pad/conditioner relative velocity data. In contrast, distinct values of tₒ and λ are used to fit the ‘high’ and ‘low’ pad/conditioner relative velocity data. **Constraint condition 3:** Single values of λ and Rₒ are chosen to simultaneously fit both the ‘high’ and ‘low’ pad/conditioner relative velocity data (i.e. both parameters are shared while fitting the two data sets). In contrast, distinct values of tₒ are used to fit the ‘high’ and ‘low’ pad/conditioner relative velocity data sets.
1. **Overall trends**: For the three data sets (XPS, EDS-asperities, EDS-pores) each set of constraints results in a fitted curve which reproduces the rapid transition from nanoabrasive accumulation to nanoabrasive removal. For the XPS, EDS-asperities, and low relative velocity EDS-pores datasets, the ‘turn-on’ time, $t_o$, averaged across all constrained fits was 26s. For the high relative velocity EDS-pores data the ‘turn-on’ time, $t_o$, averaged across all constrained fits was 35s. *This latter value reflects the persistence of nanoabrasive retention in pores at high pad/conditioner relative velocity.* The average value of the transition rate, $\lambda$, across the XPS, EDS-asperities, and low relative velocity EDS-pores datasets was $0.6\text{s}^{-1}$. (Since no substantial nanoabrasive removal ‘transition’ was observed for the high relative velocity EDS-pores dataset, the value of $\lambda$ for those data is not relevant.) The average value of $R_o$ for the EDS-asperities data was $243\pm19$. The average value of $R_o$ for the EDS-pores data was $371\pm48$ (both are in units of EDS ‘counts’).

*Taken together these overall trends indicate that, on average, 26s of conditioning is required to substantially clear the pad of nanoabrasive – at least as well as can be reasonably achieved by the conditioner.* However, the experimental data do show that removing nanoabrasive from within open pores would require additional conditioning depending on the relative velocity of the pad and the conditioner. This will be discussed further at the end of this section.

2. **General comparison of curve-fitting approaches**: Based purely on the reduced chi-squared parameter ($\chi^2/(\text{degrees of freedom})$), constraint condition 1 provides the best fit to the XPS (wide-area) nanoabrasive retention data. The value of the reduced chi-
squared for constraint condition 1 was 0.026 compared to 6.31 and 5.74 for constraint conditions 2 and 3, respectively. (Note: The value of the reduced chi-squared reflects the simultaneous fitting of BOTH the low relative velocity and high relative velocity data). This behavior was also observed for the EDS-asperities (local) nanoabrasive retention data fits which yielded reduced chi-squared values of $1.82 \times 10^4$, $2.23 \times 10^5$, and $7.75 \times 10^5$ for constraint conditions 1, 2, and 3, respectively. For these two experimental data sets (XPS and EDS-asperities) constraint condition 1 clearly describes the data more accurately. Although these models contain a relatively large number of variable parameters compared to experimental data points, the order of magnitude difference in the reduced chi-squared values between condition 1 and conditions 2, 3 is compelling.

In contrast, the reduced chi-squared values yielded from curve fitting of the EDS-pores dataset with the three constraint conditions is not conclusive. Constraint conditions 1, 2, and 3 for this dataset yield chi-squared values of $4.39 \times 10^6$, $5.54 \times 10^6$, and $2.89 \times 10^6$, respectively. This simply reflects the large experimental variation of that dataset and the fact that the data for the high relative pad/conditioner velocity data did not see a substantial reduction for increased conditioning time. Still, constraint condition 3 may be considered suitable for open pores based on the chi-squared values. This is discussed in more detail below.

3. Interpretation of XPS and EDS-asperities dataset analysis for constraint condition 1:
Based on the fit results for constraint condition 1 in Figs. 5.15 and 5.16 we can conclude that the average ‘turn on’ time for nanoabrasive removal, $t_o = 25.8 \pm 0.3$s. Moreover, at the pad surface (i.e. not deep within the pores) this value is NOT DEPENDENT on the pad
conditioner relative velocity. The nanoabrasive removal transition rate derived from the XPS data was $\lambda_{XPS} = 0.82\pm0.02s^{-1}$. The same value derived from the EDS-asperities data was $\lambda_{EDS-Asp} = 0.52\pm0.07s^{-1}$. These are similar, but statistically distinct at the 1-sigma level and imply that the nanoabrasive removal only becomes appreciable as the conditioning time/cycle approaches 24-25s.

An intriguing result of the data analysis for the XPS and EDS-asperities data for constraint condition 1 is that both datasets imply that $R_o$ (nanoabrasive introduced/cycle) depends on the relative pad/conditioner velocity. From Figs. 5.15(a) and 5.16(a) the best-fit values of $R_o$ for the low relative velocity data and the high relative velocity data are statistically distinct at the 3-sigma level. Considering that this is the case for BOTH the XPS and EDS-asperities datasets and that BOTH those datasets are preferentially sensitive to the surface (asperities) of the pad, it is logical to assume that this is related to pad surface morphology. Figure 5.1(b) shows that pad asperities exposed to high relative velocity pad conditioning have increased surface roughness. Based on this simple comparison, it is not unlikely that conditioning actually affects $R_o$ (nanoabrasive introduced/cycle) due to a permanent change in the local pad morphology. This is also supported by the observation in Chapter 2 (section 2.1.5) that slurry flow and its thickness increases with increasing the surface roughness.

4. Interpretation of EDS-pores dataset analysis: As noted in point #2 above, no constraint condition resulted in a comparatively superior fitted curve to the EDS-pores dataset. As noted, this reflects the large experimental variation of that dataset and the fact that the data for the high relative pad/conditioner velocity data did not see a substantial reduction
for increased conditioning time. It is assumed that longer conditioning at higher relative pad/conditioner velocity would result in more substantial nanoabrasive removal. Considering $R_o$ is sensitive to surface roughness as discussed in point #3 above and that overall pad surface roughness due to micro-scale pores does not change with increasing relative velocity (Fig. 5.1(a)), it is likely that constraint 3 is more appropriate to describe the EDS-pore dataset. Moreover, reduced chi-squared value for constraint condition 3 is slightly less compared to conditions 1 & 2. From the fitting results, it is clear that higher nanoabrasive retention ($R_o$) is introduced inside open pores compared to asperities. This is consistent with the observation that porous pads introduce more particle defectivity on wafers compared to non-porous pads as noted in Chapter 2 (Section 2.1.3). Moreover, pores retain nanoabrasives much like a filter (Section 2.2.1 & 2.3.3). In terms of $\lambda$, the values of $\lambda_{EDS-Asp}$ and $\lambda_{EDS-pore}$ are statistically the same. It appears that the value of $\lambda$ is somewhat independent of pad morphology (asperities and pores) for the same type of pads. Putting aside the curve fitting analysis for the moment, the experimental data in Fig. 5.17 imply that a lower pad/conditioner relative velocity can be more effective in reducing nanoabrasive retention in pores. This may be related to the differences in local pad-deformation rates as the conditioner disk moves across the pad. However, there is not sufficient data presented here or in the technical literature to explore such effects. This experimental observation is an excellent candidate for further research.
Figure 5.15. Results of analysis with the non-linear model (time dependent nanoabrasive removal efficiency) on XPS nanoabrasive retention data by using different fixed (constant) parameters for both low and high pad/conditioner relative velocity sections: (a) For shared $\lambda$; (b) For shared $R_o$; (c) For shared $\lambda$ & $R_o$. Triangular symbols represent the data points and solid lines represent the fitted curves.
Curve Fitting with ‘Time Dependent’ Non-linear Model: $\eta' = \eta'(t)$

![Diagram](image)

Figure 5.16. Results of analysis with the non-linear model (time dependent nanoabrasive removal efficiency) on EDS-asperity nanoabrasive retention data by using different fixed (constant) parameters for both low and high pad/conditioner relative velocity sections: (a) For shared $\lambda$; (b) For shared $R_o$; (c) For shared $\lambda$ & $R_o$. Triangular symbols represent the data points and solid lines represent the fitted curves.
Curve Fitting with 'Time Dependent’ Non-linear Model: $\eta' = \eta'(t)$

(a) For shared $\lambda$; (b) For shared $Ro$; (c) For shared $\lambda$ & $Ro$; Triangular symbols represent the data points and solid lines represent the fitted curves.

Figure 5.17. Results of analysis with non-linear model (time dependent nanoabrasive removal efficiency) on EDS open pore nanoabrasive retention data by using different fixed (constant) parameters for both low and high pad/conditioner relative velocity sections.
5.4: Comparative Analysis of Nanoabrasive Retention in ANW, JSR and Cabot 5001 Cu CMP Slurries

In this section the retention of nanoabrasive in a polyurethane CMP pad will be compared between the three different slurries for which data was presented in Chapter 4: Cabot 5001 commercial Cu slurry, ANW baseline Cu slurry, and JSR commercial Cu slurry. This comparative analysis focuses on a single conditioning time per step (per relative velocity region) of the pad of 20s for the ANW and JSR slurries. This conditioning time per step was reduced by 1s in comparison with the corresponding parameter used for the Cabot slurry to ensure that the conditioning resided within the respective transition regimes for the ANW and JSR slurries (see Fig. 5.8). To facility a more representative comparison, an interpolation of the Cabot nanoabrasive retention data was carried out to correct for this difference in conditioning time per cycle and was based on the analysis of Section 5.3.3.

Direct comparisons of the XPS data between all three datasets is straightforward since the difference in sensitivity factors between characteristic Si and Al photoelectron emission is accounted for in the XPS data analysis software. However, direct comparisons of the EDS data between the three datasets require relative normalization of EDS spectra for the respective nanoabrasive particles. A simple relative normalization procedure is outlined in Section 5.4.1. Direct comparison of the normalized XPS and EDS datasets for nanoabrasive retention is discussed in Section 5.4.2. Section 5.4.3 comments on the relative nanoabrasive retention in light of the models presented in section 5.3.3.
5.4.1: Monte Carlo Simulation Results:

5.4.1.1: Comparison of Aluminum X-rays Intensities from Alumina Films of Different Thicknesses on Polyurethane Substrates

Monte Carlo simulations were run to determine the x-ray intensities of Al K lines from alumina films (50 nm and 100 nm thick) on a polyurethane substrate. These results were used to provide a first-order approximation of quantitative EDS comparison of nanoabrasive retention on the surface of CMP pad (at asperities and inside open pores) from ANW and Cabot slurries. Details about the Monte Carlo simulations can be found in Chapter 3 (Section 3.5.3).

Monte Carlo simulations (Fig. 5.18) showed that emitted x-ray intensities of aluminum K lines increased by a factor of 2.09 on increasing Al₂O₃ film thickness from 50 nm to 100 nm on the surface of a polyurethane substrate. Although extrapolation of this result from a blanket film to adsorbed nanoabrasive particles is highly nontrivial, it is reasonable to employ it to aid in qualitative comparisons of the data. If this trend is extrapolated to alumina particles of a given diameter it is expected that a residual film of Cabot nanoabrasive (70 nm diameter) would yield a 46% increase in EDS counts compared to a comparable residual film of ANW nanoabrasive (50 nm diameter). Clearly, this assumption ignores issues related to agglomerates or uniform coverage, but it is reasonable to first order.

To facilitate comparisons with the JSR nanoabrasive retention data (also 50 nm diameter) the Cabot EDS data is normalized compared to the ANW EDS data. That is, the EDS Al spectra from pad samples containing Cabot nanoabrasive were normalized by a factor of 1.46. The effects of this normalization are shown in Fig. 5.19.
Figure 5.18. Monte Carlo simulation results of x-ray intensities from Al in 50 nm and 100 nm thick alumina films on polyurethane substrates.

Figure 5.19. Cabot alumina retention vs. conditioner downforce and pad/conditioner relative velocity: (a) Raw and normalized EDS Al data at pad asperities; (b) Raw and normalized Al EDS data at open pores. Normalization is with respect to ANW slurry particle diameter.
5.4.1.2: Monte Carlo Simulation Results: Comparison of Aluminum and Silicon X-rays Intensities from Alumina and Silica Films on Polyurethane Substrates

Monte Carlo simulations were also run to determine the emitted x-ray intensities of silicon and aluminum K lines from silica and alumina films of 50 nm thickness on a polyurethane substrate. These results were used to provide a first order approximation of quantitative EDS comparison of silica (JSR slurry) and alumina (ANW slurry) nanoabrasive retention on the surface of the CMP pad at asperities and inside open pores. Details about the Monte Carlo simulations can be found in Chapter 3 (Section 3.5.3).

Monte Carlo simulations (Fig. 5.20) showed that the x-ray intensity signal from Si was 83% of the x-ray signal emitted from Al. Although extrapolation of this result from a blanket film to adsorbed nanoabrasive particles is highly nontrivial, it is reasonable to employ it to aid in qualitative comparisons of the data. Since the JSR silica nanoabrasive and ANW alumina nanoabrasive have the same nominal diameter (~50nm) no correction is presumed for effective thickness. Clearly, this assumption ignores issues related to agglomerates or uniform coverage, but it is reasonable to first order.

To facilitate comparisons the JSR EDS data is normalized compared to the ANW EDS data. That is, the EDS Si spectra from pad samples containing JSR nanoabrasive were normalized by a factor of 0.83. The effects of this normalization are shown in Fig. 5.21.
Figure 5.20. Monte Carlo simulation of emitted Si and Al x-rays (K lines) from 50 nm thick silica and alumina films, respectively, on polyurethane substrates.

Figure 5.21. JSR silica retention vs. conditioner downforce and pad/conditioner relative velocity: (a) Raw and normalized EDS data of Si at pad asperities; (b) Raw and normalized EDS data of Si at open pores in pad. Normalization is with respect to ANW slurry particle diameter and composition.
5.4.2: Comparison of Nanoabrasive Retention for ANW, JSR and Cabot 5001 Cu Slurries

Utilizing the conditioning time per step interpolation for the Cabot 5001 nanoabrasive retention data, and the EDS intensity normalization for the Cabot and JSR nanoabrasive retention data, a direct comparison of nanoabrasive retention between the Cabot 5001, ANW and JSR Cu slurries is summarized in Fig. 5.22. A few general trends are briefly noted here. More detailed discussions are summarized in the sections below.

Firstly, The Cabot 5001 slurry exhibited notably higher nanoabrasive retention across all XPS and EDS datasets. Loading of the Cabot slurry is ostensibly higher (~ 1 wt%) compared to the ANW slurry (0.44 wt%), but not the JSR Si slurry (~ 2 wt%). And particle loading is difficult to correlate with retention due to dilution effects. Likewise, both Cabot and JSR nanoabrasives exhibited nontrivial amounts of retention at the pad center for selected datasets. This implies some level of retention that may not be directly related to wafer polishing.

5.4.2.1: Comparison of XPS Nanoabrasive Retention Analyses

As noted previously, XPS measurements sample a larger area as compared with EDS data. However, XPS is a primarily a surface probe and may not accurately reflect complex agglomerates or areas of high coverage. Still, the XPS data in Fig. 5.22(a) clearly show that the larger alumina nanoabrasives in the Cabot slurry exhibit a greater degree of retention compared to the ANW and JSR slurries. Based on XPS results, higher pad/conditioner relative velocities and conditioner downforces are more effective at removing alumina based nanoabrasives independent of nanoabrasive diameter. The
situation is reversed for the silica nanoabrasive in JSR, however. Figure 5.22(a) implies that lower pad/conditioner relative velocities and conditioner downforces are more effective at removing silica-based nanoabrasives. There is no a priori reason to expect such an inverse relationship based on the composition of the particle. This is discussed further below.

5.4.2.2: Comparison of EDS Nanoabrasive Retention Analyses at Asperities

The EDS data from pad asperities presented in Fig. 5.22(b) primarily support the XPS data in Fig. 5.22(a). Regarding the alumina nanoabrasive it is clear that the Cabot nanoabrasive retention at pad asperities is more than quadruple that of the ANW nanoabrasive retention regardless of the relative pad/conditioner velocity or conditioner downforce. Since nanoabrasive retention at asperities was more closely related to local asperity roughness for alumina it is likely that the particle size and/or chemical additives characteristic of the Cabot 5001 slurry promote greater adhesion and/or agglomeration of alumina at asperities. Although the composition of the ANW baseline slurry is precisely known, the additive package for the Cabot slurry is not publicly available to confirm this speculation.

In contrast to alumina, silica nanoabrasive retention at pad asperities exhibits at inverse sensitivity to pad/conditioner relative velocity and conditioner downforce. Higher values of relative velocity and downforce arguably promote increased retention. This agrees with the XPS dataset discussed above.
Figure 5.22. Comparison of nanoabrasive retention for the three slurries investigated. (a) Wide area XPS data (Al or Si at%); (b) EDS analysis of Al or Si at pad asperities; (c) EDS analysis of Al or Si at open pores in pad. Note: The Si EDS data in (b) and (c) has been corrected via Monte Carlo modeling as described in the text for a more representative comparison with the Al EDS data. The Cabot EDS data has been normalized for collection time.
5.4.2.3: Comparison of EDS Nanoabrasive Retention Analyses at Open Pores

The EDS data in Fig. 5.22(c) likewise show heightened retention in open pores of Cabot alumina compared to ANW alumina and JSR silica. This is completely consistent with the XPS data in Fig. 5.22(a). In terms of conditioning downforce and/or pad/conditioner relative velocity, the decrease in alumina nanoabrasive retention of ANW slurry, inside open pores, exhibited an opposite trend compared to alumina nanoabrasive retention of Cabot 5001 slurry (Fig. 5.22(c)). Although the variation in the data prohibits any firm conclusion, similar trends were also observed in the ESEM and SEM images discussed in chapter 4 (Fig. 4.4 and Fig. 4.20). This may be tied to the more frequent observation of nanoabrasive agglomeration for the case of Cabot 5001. Although the intrinsic colloidal suspension stability of the Cabot slurry may be reduced compared to that of the ANW slurry due to particle size effects, it is more likely that the various additives in the Cabot slurry drive this agglomeration.

The behavior of silica retention in open pores mirrors that of the ANW alumina. Silica retention is substantially smaller than the retention of Cabot alumina. Silica retention in open pores also exhibits an inverse sensitivity with respect to pad/conditioner relative velocity and conditioner downforce as compared with the alumina retention. This effect is only marginally larger than the error bars associated with individual data points so there is little justification for speculation.

Overall, the data of Fig. 5.22 enable two primary conclusions. Firstly, the Cabot alumina nanoabrasive exhibits substantially more retention in the CMP pad compared to the ANW slurry alumina. Secondly, the removal mechanisms of alumina and silica by
pad conditioning are notably different. Residual alumina abrasive can be more effectively removed with higher pad/conditioner relative velocities. Residual silica abrasive can be more effectively removed with lower pad/conditioner relative velocities.

5.4.3: Discussion of Nanoabrasive Retention of ANW Alumina and JSR Silica with Respect to Empirical Nanoabrasive Removal Models

Assuming that the empirical model presented in Section 5.3.3 is representative of conditioner-induced nanoabrasive removal, the data in Fig. 5.22 can be interpreted in terms of relative nanoabrasive removal efficiency. In other words the pad conditioning would be expected to exhibit higher removal efficiencies for ANW and JSR nanoabrasives compared to Cabot 5001 nanoabrasives. That observation, however, does not point to any particular mechanism regarding improved efficiency. The most probably mechanism involves nanoabrasive suspension. Residual nanoabrasive removal efficiency is expected to increase with increased suspension of nanoabrasives in the slurry. Agglomerated particles would most likely inhibit transport processes at pad asperities and exhibit higher adhesion at pad asperities. Likewise, agglomerates may resist being transported from open pores due to adhesion with the pore walls.

The ESEM and SEM imaging of post-CMP pad sections in Chapter 4 provided anecdotal examples of higher agglomeration of alumina nanoabrasive from the Cabot slurry as compared to the ANW slurry (and, in some respects, the JSR slurry), but agglomerates were observed for ALL slurries. Specifically, ESEM micrographs in chapter 4 (Fig. 4.20), showed ANW residual alumina nanoparticles inside open pores existed in an agglomerated form at the CMP pad center. So the question remains as to
why the ANW nanoabrasive removal efficiency would be expected to be larger than that of the Cabot slurry. This is likely affected by the ease with which nanoparticles in agglomerated form are re-suspended as a result of conditioning. Note that agglomerates of ANW alumina were observed via ESEM from a pad section that underwent 10 lbs conditioning downforce with a 0.59 m/s pad/conditioner relative velocity (Fig. 4.20). In contrast to this, ANW residual alumina nanoabrasives were in a more suspended form rather than agglomerated form at higher conditioning downforce (18 lbs) and relative velocity (1.07 m/s) as shown in Fig. 4.20 (c). This may imply that conditioner mechanics are more effective at dispersing agglomeration of ANW. The same kind of observation (agglomeration breaking due to mechanical force) has also been made by Bahar et. al. 7 They found through analysis of particle size distribution of slurries collected from pad surfaces after polishing, that dry aggregation and flocs (both added into supplied slurry) were broken down during polishing processes under the applied normal and shear forces. Similarly, ESEM micrographs taken at asperities (Fig. 4.19) showed ANW alumina nanoabrasive was in agglomerated form at CMP pad center. In contrast, residual nanoabrasive of ANW slurry existed in a relatively suspended (less agglomerated) form for both pad sections exposed to 10 lbs (0.59 m/s) and 18 lbs (1.07 m/s) conditioning downforce (pad/conditioner relative velocity). Since the direct physical interaction of the conditioner with the nanoabrasives at the asperities of CMP pad can exert large force on agglomerates, even the smaller 10 lbs conditioner downforce may be sufficiently effective to break the soft agglomeration. As a result, due to direct contact and more particle suspension (higher nanoabrasive removal efficiency), less retention of ANW nanoabrasives at pad asperities of low pad/conditioner relative velocity pad section (10
lbs conditioning downforce) was observed as compare to open pores of same pad section. Likewise, it can be inferred that the conditioner downforces and relative velocities studied here are less effective at breaking Cabot nanoabrasive agglomerates, leading to lower nanoabrasive removal efficiency.

There is less clarity regarding retention of the JSR silica nanoabrasive. As shown in Fig. 5.22 silica nanoabrasive retention increased from low pad/conditioner relative velocity pad section (10 lbs conditioning downforce) to high pad/conditioner relative velocity pad section (18 lbs conditioning downforce). This was observed for ALL data analyzed (XPS and EDS at asperities and inside open pores). Silica retention for low conditioner downforce (10 lbs) and low pad/conditioning relative velocity (0.59 m/s) was not only close to the silica retention at pad center but also was the least retention yet determined for all other experiments with alumina based slurries. Returning to nanoabrasive suspension, one possibility is that this silica slurry resisted agglomeration formation more effectively under exposed areas of wafer for lower downforce and relative velocity. As mentioned in chapter 2 (literature review) the surface of silica abrasive particles has a higher number of hydroxyl groups than other abrasives such as alumina, ceria, titania, and diamond (Section 2.3). Additionally, higher amounts of copper (~48%) in the form of oxide adsorbed onto the silica as compared to alumina (8%) as described in Section 2.3.3. Moreover, most of the silica abrasive particle based slurries show sensitivity to shear stress application, i.e. shearing can cause silica particle agglomeration (Section 2.3.3). ESEM micrographs taken on pad surface for silica retention of JSR slurry showed agglomeration/aggregation at various points across the pad surface.
On the basis of this discussion it is possible that the higher relative velocity/higher downforce conditioning of the pad in the presence of silica actually promoted silica nanoabrasive agglomeration (or was less effective in mechanically breaking silica agglomerates). This is an attractive scenario in terms of the data of Fig. 5.22 and may serve to explain certain differences with the alumina data. However, a new generation of experiments must be designed to identify such nanoscopic mechanisms. This would be important future work to pursue.

References:


CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1: Conclusions

Quantitative microscopic and spectroscopic analyses on IC1000 CMP pads revealed that considerable CMP slurry nanoabrasive was retained at pad asperities and open pores that contacted the wafer during Cu CMP in comparison to pad surfaces which were exposed to the slurry but did not come in contact with the wafer. This confirms that the Cu CMP process is primarily responsible for nanoabrasive retention on the pad surface. In general, nanoabrasive retention was higher inside open pores compared to asperities. This retention was investigated as a function of CMP pad conditioning parameters and for various commercial (Cabot alumina-based, JSR silica-based) and non-commercial (ANW alumina-based) CMP Cu slurries.

With respect to the effect of CMP pad conditioning on pad surface roughness, profilometry analysis showed that the overall surface and pore morphologies of the pad do not change with CMP pad conditioning, although the surface roughness of pad asperities is increased. The increase in the surface roughness of asperities primarily resulted from an increase in the pad/conditioner relative velocity, and was less dependent on the increase in the conditioning downforce. This increase in the surface roughness of asperities by increased pad conditioning was identified as the primary mechanism of nanoabrasive removal at pad asperities for all the slurries investigated. This appeared true as pad conditioning was found effective in reducing the alumina and silica nanoabrasive
retention as a function of conditioning parameters. The relative efficiency of pad conditioning in the removal of residual nanoabrasive from CMP pad asperities was strongly dependent on slurry composition. Removal of residual nanoabrasive from open pores of the CMP pad was also investigated and was likewise dependent on pad conditioning parameters and slurry composition.

Nanoabrasive retention at CMP pad asperities and open pores was found to be a strong function of conditioning time but a weak function of conditioner downforce and pad/conditioner relative velocity. In general, pad/conditioner relative velocity played a more important role in residual nanoabrasive removal compared to conditioner downforce. This dependence of residual alumina nanoabrasive removal on pad/conditioner relative velocity became more prominent for open pores for Cabot 5001 commercial Cu CMP slurry. That is, lower pad/conditioner relative velocities were more favorable to remove nanoabrasive retention from open pores of pad surface. However, in case of a non-commercial alumina slurry (ANW slurry) higher pad/conditioner relative velocity and conditioning downforce was also effective. This was possibly due to the increased effectiveness of conditioner mechanics in dispersing ‘soft’ agglomerates of ANW alumina.

In terms of nanoabrasive particle size, the ANW alumina (~50 nm diameter) and JSR silica (~50 nm diameter) nanoparticles showed substantially smaller retention (both at asperities and open pores) compared with the retention of Cabot alumina (~70 nm diameter). It was concluded that the smaller nanoabrasive particle sizes promoted better particle suspension at higher conditioning downforce and pad/conditioner relative velocity and resulted in lower residual nanoabrasive retention on the pad surface and in
open pores. Still, the effects of slurry chemical additives could not be ruled out as the exact compositions of the Cabot and JSR slurries were proprietary. Silica retention for low conditioner downforce and low pad/conditioning relative velocity was the lowest for any of the slurries studied for this work. The removal mechanisms of alumina and silica by pad conditioning were notably different. Silica retention increased with increasing pad/conditioner relative velocity and conditioning downforce at both asperities and open pores.

For the Cabot 5001 Cu CMP slurry three semi-empirical models were developed for quantitative analysis of the spectroscopic nanoabrasive retention data. The 3rd model (non-linear model with time-dependent removal efficiency) was by far the most effective in accurately describing the XPS and EDS datasets (for asperities and open pores) from Cabot 5001 alumina slurry in comparison to the 1st model (linear model with constant retention removal) and 2nd model (non-linear model with time-independent removal efficiency). The ‘time-dependent non-linear model’ (3rd model) reproduced the ‘transition regime’ behavior observed experimentally for nanoabrasive removal via pad conditioning. It also provided reasonable behavior for nanoabrasive retention in the ‘accumulation’ and ‘removal’ regimes as discussed in Chapter 5. This 3rd model was also capable of representing nanoabrasive removal mechanisms which may be activation-based, e.g. mechanical breakdown of agglomerates or two-step mechanisms based on pad roughening. For the XPS, EDS-asperities, and low relative velocity EDS-pores datasets, the ‘turn-on’ time, t₀, for the onset of residual nanoabrasive removal via pad-conditioning averaged across all constrained fits was 26s. For the high relative velocity EDS-pores data the ‘turn-on’ time, t₀, averaged across all constrained fits was 35s. This latter value
reflects the persistence of nanoabrasive retention in pores at high pad/conditioner relative velocity. Taken together these overall trends indicate that, on average, 26s of conditioning is required to substantially clear the pad of nanoabrasive – at least as well as can be reasonably achieved by the conditioner. Moreover, at the pad surface (i.e. not deep within the pores) this value is NOT DEPENDENT on the pad conditioner relative velocity. But the value of $R_o$ (nanoabrasive introduced by polishing step) on the asperities depends on the pad/conditioner relative velocity and it is due to a permanent change in the local pad morphology. The average value of $R_o$ for the EDS-asperities data was lower compared to the value of $R_o$ for the EDS-pores data.

Several other aspects of the Cu CMP process were also evaluated with respect to nanoabrasive retention. Regarding the effect of pad aging, Cu polishing results showed reduced MRR, increased scratching, increased contamination (particle adhesion) and higher surface roughness on the surface of the Cu wafer that was polished with the ‘expired’ CMP pad as compared to the ‘unexpired’ CMP pad. Similarly, higher alumina nanoabrasive retention was observed on the surface of the ‘expired’ CMP pad as compared to ‘unexpired’ CMP pad. Regarding oxidizer concentration, Cabot alumina (mixed with 6 % H$_2$O$_2$) showed more alumina retention and agglomeration (particularly inside open pores) and also lower MRR compared to Cabot 5001 (mixed with 2% H$_2$O$_2$). Regarding the presence of Cu on the CMP pad asperities or in open pores, no Cu retention on pad surface was determined for JSR silica, ANW alumina and Cabot alumina (2% H$_2$O$_2$) slurries. Cu retention on pad surface was only determined for Cabot alumina (6% H$_2$O$_2$).
6.2: Future Directions

Further work with designing experiments for lower conditioning times (< 15 seconds) will be helpful to see how retention decreases with increasing conditioning time and this will help to further validate and improve the modeling. This work can also be utilized for the investigation in terms of nanoabrasive retention vs. CMP performance (MRR, WIWNU) and wafer surface quality (roughness, scratches and particle adhesion).

For silica slurry, experiments such as silica retention vs. conditioning downforce, pad conditioner relative velocity, and location of pad section (from pad center) at areas of the pad exposed to polishing will be helpful to fully understand the retention mechanism of silica nanoabrasives. This study can also be utilized to quantify the relationship between slurry retention and agglomeration. Moreover, to further explore residual nanoabrasive removal mechanisms inside open pores, additional nanoabrasive retention experiments vs. pad/conditioner relative velocity will be helpful. Detailed investigation of nanoabrasive retention vs. pad life experiments can also be helpful to understand nanoscopic mechanisms (in nanoscale web-like pores) as observed and to determine how pad aging can affect the slurry retention, agglomeration and CMP performance. This study will also help to determine pad lifetimes most relevant to nanoabrasive retention.