

Material Removal By Chemical Mechanical Polishing-A Review

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ABSTRACT

Polishing, the most expensive machining processes, in terms time and labor costs depending on the required surface finish, optic size, and amount of surface roughness from preceding machining operations. A material could remain on the polishing system for hours to days. Thus, attempting to understand the underlying mechanisms and basic science associated with the polishing process is crucial to, in turn, develop methods and procedures to reduce cost, trim schedule, and bolster performance. With an increased need for low surface roughness optics, as in x-ray and enhanced ultra-violet applications, it is imperative to understand the impacts of changing system variables. This paper reviews mechanism of chemical-mechanical polishing (CMP), to provide some interlinking data that can be used to many fundamental aspects of the CMP mechanism, in turn can predict process responses, e.g., material removal rate, non-uniformity across the wafer, dielectric erosion and metal dishing. This review will provide a new platform for further investigation in CMP mechanism of material removal.

Keywords : Chemical Mechanical Polishing, material removal rate, non-uniformity , dielectric erosion and metal dishing

1 INTRODUCTION

The polishing process is referred to as an art form, rather than a strict scientific discipline. As there is no one set theory that can describe the polishing process outcomes are difficult to predict. For many years, researchers have attempted to predict the underlying mechanism responsible for the polishing of glass, metals, and composites. The ability to polish objects, regardless of intended purpose, has existed for thousands of years. In ancient times, the 'shiny' surfaces generated from polishing were most assuredly more decorative than functional for these early civilizations. Lu, et al [1], examined highly polished corundum axe fragments found at an ancient Chinese settlement at Zhejiang Yuhang Wujiabu, circa 2500 BC. They found through Atomic Force Microscopy (AFM) that the surface roughness was on the order of a few nanometers. Over the past 4500 years, humankind has only increased in polishing ability on the order of several nanometers. As the human race developed, surface quality transformed from decorative to an essential function for certain applications, namely the telescope. In the 17th century, scientist Galileo contributed to the body of astronomical discoveries. Researches like Miniati, et al [2], have used modern measurement techniques to study lenses of this era and found that they were of superb quality for the time, having only minor features present on the polished surfaces. Copper and silicon polishing has been of key interest over the last twenty years due to the necessity of the polishing process in the manufacture of integrated circuit chips. The majority of polishing, however, still lies in the realm of glass and glass-ceramic substrates which are used in a vast amount of applications, from optics for lithographic machines to mirrors and lenses for laser

systems.

1.1 POLISHING PROCESS:

It is possible to generate super smooth/super finishing surfaces by various processing techniques such as Loose abrasive polishing, fixed abrasive grain polishing technique, Chemical Mechanical Polishing, Deterministic Micro grinding, Chemical etching, Ion plasma etching techniques either individually or combination of these techniques or modification of the individual process.

Chemical-mechanical polishing (CMP) has been widely used in polishing glass and ceramic surfaces as well as in planarizing semiconductor wafers. CMP mechanisms can offer guidance to the control and optimization of the polishing processes. The chemical-mechanical synergy plays a key role in the CMP process and has been a subject of much research in recent years. The complexity of current microelectronic devices demands global planarity at different metallization levels. Chemical mechanical polishing (CMP) has the capability of achieving such stringent requirements over a step height of several microns. Since the introduction of the new technology in the 80s, the CMP provides advantages of defect reduction, wide windows for etching and lithography and yield improvement. Planarization is usually performed by CMP. Chemical-mechanical polishing (CMP) has been widely used in the semiconductor manufacturing processes for interlevel dielectrics and metal layer planarization. Among several postulated CMP mechanisms is the chemistry-assisted mechanical abrasion. During a typical CMP process, a rotating wafer is pressed against a rotating polishing pad while polishing slur-

ry containing the chemical reagents and abrasive particles flows between the wafer and the pad. CMP causes material removal by rotating a polishing pad against the wafer in the presence of liquid slurry.

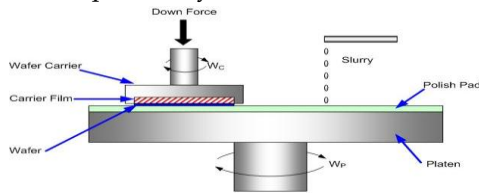


Fig.1 chemical-mechanical polishing

The work is held on a rotating carrier (holder) while the face being polished is pressed against a resilient polishing pad attached to a rotating platen disk. Slurry with abrasive material held in suspension is dripped onto the rotating platen during polish. The carrier and platen rotate at variable speeds. The process removes material at the surface through a combination of mechanical and chemical action. A typical process goal is to achieve “global” planarization (across tens of mm) by preferential removal of “high” material. CMP needs fewer steps compared to deposition/ etchback. Furthermore, CMP uses nontoxic substances, has a good removal selectivity, and a good rate control[3].

2. MATERIAL REMOVAL RATE

Of the different theories available, the experiments presented herein will address two broad categories, chemical and mechanical removal mechanisms. Specifically, the influence of polishing slurry pH and abrasive particle size and concentration on material removal rates (MRR) and surface finish investigated will be reviewed. It is important to attempt to understand these mechanisms because an understanding leads to process improvement.

In 1991 Kaufman et al. [4] published a paper on the mechanism of polishing tungsten-covered silicon wafers. The mechanism postulated was chemistry-aided mechanical abrasion. The material removal was illustrated as a sequential process of formation and removal of a surface layer with reduced hardness. A softened surface film was first created by chemical reactions between the tungsten and slurry chemicals and then, removed by abrasive plowing of slurry particles. The dynamical process continued until the material at the wafer surface was removed.

Tesar et al [5], studied the effects of pH on the resulting surface finish. The study found that silica polishing with Hastilite PO brand ceria slurry produced higher MRR and better surface finishes at a pH of 4 versus a pH of 7. When silica was polished with Opaline (a higher purity ceria slurry) at pH 4, the removal rate was much lower, but the surface finish was nearly exactly that achieved with Hastilite at pH 4. Regardless of the removal rates, the work showed that higher quality silica surface finish could be achieved with low pH ceria slurry.

Cumbo, et al [6], studied pH effects on the polishing of fused silica, BK7 borosilicate glass and SF6 dense flint glass. Particle

size and zeta potential measurements were made of three different commercial slurries (CeO₂, m-ZrO₂, and n-Al₂O₃) used in a slurry recirculation polishing system. It was shown that, with the exception of the CeO₂/SF₆ combination, the maximum removal rate occurred at the conditions where the particle pzc was closest to the slurry pH (i.e. pH 7 for CeO₂, pH 4 for ZrO₂, and pH 10 for Al₂O₃). It was shown that removal rate predictions with the chemical tooth model did not always correlate with experimental results when the glasses were subject to solutions that were corrosive to the glasses (i.e. acidic to neutral for SF₆ and neutral to basic for BK7).

In the paper by [7] the polished surfaces of wafers and pads were examined using an optical microscope, Scanning electron microscope, atomic force microscope, and other surface analysis techniques. The material, chemical, mechanical and lubricating properties between polishing slurry, a semiconductor wafer, and a polishing pad determined the controllability and quality of CMP. For semiconductor wafers, the material removal rate, surface roughness, the number of defects, and the surface flatness were the benchmarks of CMP performance. The amount of the observed chemical effect in this by adding citric acid was increased by 133% and the chemical reaction played an important role. Common defects on a tungsten wafer after polishing were edge defects, pits, and scratches. An electrochemical reaction combined with surface non-uniformity of pads and asperity contacts under high pressure were the possible reasons for the formation of pits. The properties vs. performance relationships of polishing pads, slurries and wafers were investigated and found that plastic deformation predominates the wear mechanisms of both wafer and pad materials. However, during conditioning, abrasive wear played a major role in the wear mechanism, in polishing, fatigue and rolling phenomena. In both conditioning and in polishing, cutting action was found. In polishing, the cutting was on a nano-scale, comparable with the diamond size.

Semi-ductile grinding followed by simple mechanical polishing is an economical process for producing a mirror-like surface for hard and brittle Pyrex. In [8] a fine-grit resinoid-bonded diamond wheel was used to generate large amounts of ductile streaking to improve the surface quality and reduce the polishing time. The ground samples were polished with diamonds and cerium oxide to analyse the effect of the abrasives, the polishing pad and the pressure on the surface produced. The microstructure of the ground sample was investigated using a scanning electron microscope whilst the polished surface was analysed using an atomic force microscope. The results of this study as much as 85% of ductile streaks found on the ground surface and cerium oxide polishing produced the reflective mirror-like surface with very few scratches as compared to diamond polishing. The results showed that cerium oxide smooths the surface from 74.3 to 8.7 nm within 2 min of polishing, whilst diamond polishing required about 3.5 min to smooth the surface from 58.83 to 16.6 nm with very few fine hair-line scratches. The presence of ductile streaks not only shortened the polishing time but also improved the surface roughness to the nanometric range of 53–82 nm.

The effect of influence of silica slurry was studied by [9] for

interlayer dielectric CMP in the alkaline region to accelerate the chemical corrosion process of plasma enhanced tetraethylorthosilicate (PETEOS). Si ions were dissolved to the point where it would adversely affect the colloidal stability of the silica particles. Under alkaline conditions above pH 9, silica solubility sharply increased and the silica layer was dissolved with the formation of silicic acid and subsequently, ionized silicate species that resulted in a decrease of surface potential due to electrical double layer compression. As the silica surface was modified with water soluble polymer, Passivation resulted in a well-dispersed suspension at pH 11. The surface potential decreased above pH 9 and resulted in an increase in the stability of silica particles dispersed in the alkaline region. The field evaluation of silica suspensions were tested using an industrial CMP machine, which showed an increase in removal rate upon passivation. Micro scratches on wafers with the modified slurry were reduced and the removal rate in CMP processing was increased.

A study of the chemical mechanical polishing (CMP) of thin copper films using fixed-abrasive pads is presented in [10]. The composition of the polishing solution which consisted of hydrogen peroxide as oxidizer and complexing and buffering agents, was optimized by investigating the impact of both the oxidizer concentration and the pH of the solution on the polishing characteristics of copper. Experimental results showed that the optimized polishing solution has a pH of 3 and a hydrogen peroxide concentration of 15 vol%. The resulting optimum polishing solution gave a high removal rate (>300 nm/min), good uniformity (standard deviation 3%) and a very high selectivity for the oxide removal rate (>100:1). The dependence of the removal rate of copper on the geometry was also studied for different feature sizes and various pattern densities. The geometry dependency was considerably less in the slurry-free process than in the conventional slurry CMP. The good polishing results for patterned wafers included a small amount of dishing, a smooth copper surface, a fast planarization and relatively easy post-CMP cleaning. The fixed-abrasives technique proved to be promising alternative for copper CMP.

The friction and thermal phenomenon was investigated by [11] to verify the effect of temperature on the material removal mechanism in chemical mechanical polishing (CMP). Slurry property changes were also studied with respect to temperature change and the rate of temperature change. The polishing of various materials, temperature measurement by way of infrared ray camera, frictional force measurement and real contact area measurement experiment were conducted. The results showed that the contact area increased with temperature, which was caused by the decrease of asperity hardness due to the temperature elevation. The pH of the slurry dropped with temperature rise and the particle size increased over the range of 50–60 C. From the results of the experiments, they concluded that the material removal mechanism in CMP under the effect of temperature was dominated by an increase in the importance of chemical parameters rather than mechanical ones. The friction coefficient and polishing temperature were changed significantly during the first stage of polishing

stating that the first polishing period as an important factor in influencing WIWNU. Furthermore, the removal rate did not remain constant during the polishing process and this had an effect on the within wafer non-uniformity (WIWNU).

In this paper[12], various facility factors on the CMP process defects were investigated. For the improvement of the CMP process, deionized water (DIW) pressure, purified nitrogen (PN_2) gas, point of use slurry filter, and high spray bar were installed. Experimental results showed that DIW pressure and PN_2 gas factors were not related to removal rate, but closely related to the edge hot spot on a patterned wafer. Also, the filter installation in a CMP instrument could remarkably reduce the defects after CMP processing. It was shown that the slurry filter played an important role in the determination of pad lifetime. However, since the slurry filter cannot completely prevent defect-causing particles from entering the system, the installation of the high spray bar of deionized water with high pressure was proposed.

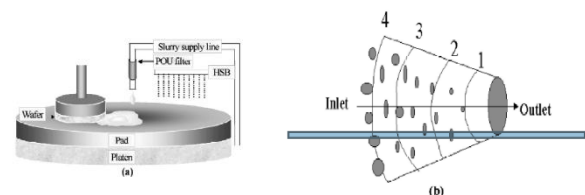


Fig 2 (a) Schematic diagram of modified CMP polisher using in this experiment, (b) schematic diagram of POU slurry filter, The effects of polishing pressure and abrasive on the chemical mechanical polishing of blanket and patterned aluminum thin films were investigated in [13]. The CMP process experiments were conducted using a soft pad and slurry mainly composed of acid solution and Al_2O_3 abrasive. It was found that the abrasive concentration as well as the abrasive size and the polishing pressure have a significant effect on the performance of Al CMP. The result of the blanket film showed that, as the concentration of abrasive in the slurry increased, surface roughness deteriorated but waviness improved. The planarity of the patterned Al films was slowly improved by the CMP when the widths of the gaps between the patterns were relatively small. When planarizing the patterned Al film by CMP, more polishing time was required, the surface produced was rougher. To acquire good flatness and moderate surface roughness of Al thin films, the abrasive concentration was set relatively high and the polishing pressure as low as possible. An attempt was made to find the optimum CMP process conditions by which the patterned Al thin film could be planarized with a fine surface. The most satisfactory film surface was obtained when the applied pressure was low (10 kPa) and the abrasive concentration was relatively high (5 wt. %). Suphantharida and Osseo-Asare [14] studied zeta potential effects and silica adsorption on ceria solutions. The experiments did not use polishing slurries, rather solutions of ceria particles with varying amount of silicate ions added to determine end effects. However, the experiments were directly

comparable to the conditions found in polishing. Several interesting observations were made in this paper. First, it was shown that the zeta potential curves shift left with increasing concentrations of silicate ions in the pH range of 2-12. This shift showed that the pzc of the ceria particles, with increased addition of silicate ions, approached that of silica. For this to occur there would have to be substantial accretion of silicate ions on the ceria surfaces. Another important observation was that maximum adsorption was found to take place near pH 9. At this level, both the silicate ions and ceria particles would be negatively charged and would be expected to repel one another. Thus, it was rationalized that the two species must be chemically bonding, versus bonding through charge forces. This observation suspected that the maximum removal rates would occur at pH 9 versus the chemical tooth prediction of pH 6.8.

In this paper [15] chemical mechanical polishing (CMP) of aluminum and photoresist using colloidal silica-based slurry was investigated. The effects of varying slurry pH, silica concentration and oxidizer concentration on surface roughness and removal rate were investigated in order to determine the optimum conditions for those parameters. Using these optimum conditions silica-based CMP was compared with conventional CMP, which uses alumina-based slurry. In the Al CMP, the micro-scratches were small and the removal rates were large when the slurry pH was 2-4 and the oxidizer H₂O₂ concentration was 1-3 vol. %. The micro-scratch size and removal rate increased as the abrasive concentration in the slurry increased. In the PR CMP, the micro-scratch and removal rate generally increased as the slurry pH and abrasive concentration increased. The optimum CMP conditions from the colloidal silica based slurry experiments and the optimum CMP were compared with the alumina-based slurry CMP. The results of the CMP of the aluminum with the colloidal silica-based slurry were good, but the CMP of the photoresist were not. The colloidal-based silica slurry produced a desirable fine Al surface with few micro-scratches, but produced a photoresist surface with many micro-scratches.

Abiade and Choi [16] studied pH effects on the polishing of silica thin films deposited on a silicon substrate. In this work, zeta potential of the ceria based slurries was measured along with the respective polishing rates. It was found that maximum material removal occurred at pH ~ 6, which was also the measured iep of the ceria slurry. Low removal rates were generated in acidic conditions and intermediate removal rates were obtained at basic conditions. The higher removal rates at the elevated pH levels were attributed to the enhanced dissolution of the silica in the corrosive environment

In this study, influential factors that control the removal rates are elucidated by [17] based on the relative importance of interaction between abrasive particle and the film to be polished. Particles with varying bulk and surface properties were used to obtain the removal rate selectivity for copper and Ta. For copper slurry (1-5 wt.% of hydrogen peroxide, 0-1 wt.% of glycine, 0-1 mm of benzotriazole, and other additives, barrier slurry contains 1-6% abrasive particles and 0-0.1% surfactant such as polyvinyl alcohol) that contains both oxidizer and

complexing agent, the rapid dissolution of abraded materials levitated the demand for surface adsorption. Polish rates of both Cu and Ta increased with increasing surface area of silica abrasives. The experimental results obtained from this investigation helped in formulation of slurry for a metal with desirable removal rate as well as surface quality. In addition, the assistance from A Rodel Suba IV polyurethane pad in absorbing the abraded materials further lowered the defects. It was found that the Ta material removal rate had direct correlation with the effective hydroxyl content on the surface of abrasive particles. The material removal rate and surface quality of copper, was heavily influenced by the hardness of the abrasive particle and the presence of oxidizer/complexing agent. The surface treatment that removed some of the surface hydroxyl groups reduced the Ta material removal rate. The difference in removal mechanism for copper and tantalum was explained with the distribution of the abraded materials between spent slurry and pad.

In [18], chemical mechanical polishing (CMP) of polycarbonate(PC) and poly-methyl methacrylate (PMMA) substrates was investigated. Four types of slurry fumed silica polishing slurry containing ammonium hydroxide, Mazin SRS1 and SRS3 are colloidal silica polishing slurry for stock removal applications, Okamoto Simlox A1136 slurry, designed for removal of polymeric materials were tested. CMP of the polymers was performed by varying two key process parameters, namely table speed and head load while other parameters were kept constant. The slurry suitable for polishing PC and PMMA was then chosen, and further CMP experiments were carried out under different process conditions. Experimental results showed that increasing table speed or head load increased the material removal rates of the polymers. The MRRs and surface roughness of PC were found to be much higher than those of PMMA due to different material hardness, regardless of the types of slurry used. Simlox slurry was found to be suitable for CMP of the two polymers. Polished PMMA and PC surfaces had nanometer-order surface roughness heights, acceptable to most MEMS. Analysis of variance was also carried out, and it was found that the interaction of head load and table speed had a significant (95% confidence) effect on surface finish of polished PMMA. On the other hand, table speed had a highly significant (99% confidence) effect on surface finish of polished PC.

The effect of the process variables such as turn table speed, head speed, down force and back pressure on copper CMP were investigated in [19] Using a design of experiment (DOE) to achieve desired the removal rates and non-uniformity. A better understanding of the interaction behavior between the various parameters and the effect on removal rate, non-uniformity and ETC (edge to center) were achieved by using the statistical analysis techniques. The type L8 orthogonal array of process variables was used in order to apply the DOE regarding removal rate, non uniformity, and ETC. Polishing of all the test materials was executed using the G&P POLI-500CE CMP polisher [20]. An IC-1400 k-groove polyurethane pad (Rodel Co.) was used for the polishing pad. The basic equipment condition such as the positions of conditioning and slur-

ry flow for CMP process scarcely affected the process results. However, the change in CMP process variables provided substantial effects on non-uniformity and ETC within removal rate and wafer. When the down force was at the level of 300 psi, relatively low non-uniformity and ETC were obtained. When the turntable speed was at 100 rpm, the level of non-uniformity and ETC was relatively high, but high level of removal rate was observed as well. At this point, optimal changes in process variables were attainable. The optimized process variables obtained by DOE method considering the interaction effect of process parameters were 300 psi of down force, 98 psi of back pressure, 100 rpm of turntable speed, and 50 rpm of head speed. In order to confirm the optimized condition achieved from the response optimizer of the design of experiment, the polishing experiment was employed under the optimal condition. The result based on the response optimizer from MINITAB™, removal rate and non-uniformity of copper was improved predominantly, from, 910.8nm/min and 16.6% to 1152.0 nm/min and 10.2%. It also confirmed the improvement in selectivity of copper to tantalum from 87.24 to 125.22. With increase in pressure, removal rate tended to increase contingent to the relative speed. The optimal variables were effective in improving the removal rate, the non-uniformity and the selectivity. The Preston equation was in accordance with the result: removal rate was proportional to the relative rate of pad and its pressure.

The effect of the contact nominal pressure on the surface roughness and sub-surface deformation in chemical mechanical polishing (CMP) process has been investigated by [21]. The experimental results showed that a better surface quality can be obtained at the lower pressure and the thickness of sub-surface deformation layer increased with the increase of the pressure. This process not only introduced amorphous transformation, but also a silicon oxide layer on the top surface with a thickness of 2-3nm. The atomic structure of the material inside the damage layer changed with the normal pressure. Under a higher pressure (125 kPa), there were few crystal grain packets surrounded by the amorphous region in which the lattice was distorted and a narrow heavy amorphous deformation band with the average thickness of 2-3nm appeared on the deformation region side of the interface. Under lower pressure (25-100 kPa), an amorphous layer only was observed.

Pad flattening ratio (PFR) was investigated as a non-destructive pad surface analysis method on the IC1000 K groove pad during silicon dioxide chemical mechanical planarization by [22]. A series of marathon polishing runs were performed under ex-situ diamond disc pad conditioning, ex-situ high-pressure micro jet (HPMJ) pad conditioning and no pad conditioning methods where PFR analysis was performed to estimate the amount of pad surface flattening or glazing under these conditions. With no conditioning, PFR increased rapidly to 40% indicating severe glazing. With ex-situ diamond disc pad conditioning, the PFR remained below 5% after 37-wafer polishing, constant below 12% at the end of 50-wafer polishing, suggesting a rough and stable pad surface for polishing, while with ex-situ HPMJ conditioning it increased

gradually and stabilized at the value of about 23%. Real-time friction force was measured during polishing and the general trend showed that the coefficient of friction was inversely proportional to the PFR value. When the PFR value was less than 10%, the ex-situ diamond disc and HPMJ pad conditioning gave a higher silicon dioxide removal rate compared with no pad conditioning, suggesting that the extent of pad flatness and glazing was not the only factor to affect the removal rate in this region. When the PFR value was larger than 10%, the removal rate decreased linearly with the increase of the PFR, indicating the extent of pad flatness and glazing had a dominant effect on the removal rate. A linear relationship was observed between the silicon dioxide removal rate and the coefficient of friction. The PFR technique provided a good qualitative analysis on the extent of flatness and glazing of the pad surface and was consistent with the SEM analysis. In the future research, the correlation between the PFR value and the exact percentage of the pad surface that is flattened or glazed during CMP processes shall be investigated to provide an accurate quantitative pad surface analysis

DL-aspartic acid as a removal rate selectivity enhancer for shallow trench isolation chemical mechanical polishing slurries was investigated over a pH range by [23]. The effects of downward pressure, rotational speed of the turntable as well as the ceria abrasive loading were also examined. When DL-aspartic acid was used as an additive, ceria based slurries exhibited a high selectivity in the pH range of 4 to 5. A comparison of the pKa values of the amino acid with the variation of the selectivity with the pH indicated that, the form of amino acid plays a vital role in determining the polishing behavior. At low pH values both the oxide and the nitride polishing were suppressed in the presence of DL-aspartic acid and at high pH values, there was no strong suppression of the oxide and the nitride removal rates. At a given additive concentration, an increase in the ceria abrasive concentration increased the oxide and the nitride removal rates. The high selectivity was observed only for the slurries based on ceria abrasives and not for the slurries with other abrasives. In the high selectivity pH regime, increasing the pressure adversely affected the selectivity, while changing the rotational speed does not strongly influence the selectivity. Select experiments were also conducted with other types of abrasives with and without the additive. A comparison of the pKa values of the amino acid with the variation of the selectivity with pH indicates that the form of amino acid plays a vital role in determining the polishing behavior and the selectivity. The results strengthen the hypothesis that chemically active sites on ceria surface may be blocked by certain forms of the amino acids in select pH range, which resulted in a high selectivity.

In this study [24], the effects of chemical additives in silica (SiO₂)-based slurry on the removal rate of the tungsten film were investigated. Design of experiments was carried out to understand how the chemical adjustments influence the polishing parameters. As an experimental result, the static etch rate (wafer weight loss) and the oxidizer decomposition rate as a function of chemical additives were measured. Carboxylic acid addition increased the dissolution rate opposite to ferric

nitrate addition which softened the oxidation. Specific concentration of dicarboxylic acid was necessary to control the stability of H_2O_2 . Operating results through statistical analysis (Fischer-Snedecor's test) showed that addition of chemical components significantly influenced the oxidation of tungsten but also influenced the slurry stability (H_2O_2 decomposition). Slurry stability was expected to increase with mixed surfactant addition. Driving both numerical analysis and static experiments with concentrated after being used slurry, the authors could obtain oxidation conditions very close to those of the operational slurry by chemical adjustment. The tungsten removal efficiency and the stability of slurry used could be controlled by adjusting iron catalyst and complexing agent concentration.

The Paper [25] investigates the effects of oxidizer concentration, pH and slurry flow rate on the material removal rate (MRR) in chemo-mechanical polishing (CMP) of Si (100) wafers. The CMP was carried out in alkaline slurry using alumina and ceria particles of a normal diameter 50 nm with hydrogen peroxide and de-ionized water. Abrasive concentration of 2.5% Vol NaOH and HCl were applied to adjust the pH value. It was found that the applications of the two particle materials lead to very different results. When using the alumina particles, the MRR initially decreased with increasing the slurry pH value until pH= 9. The application of the ceria particles increased the MRR before the pH of the slurry reaches 10. It was concluded that in the former, the effect was due to the particle agglomeration and the contact angle decrease of the oxidizer slurry with the wafer surface; whereas in the latter it was caused by the particle agglomeration and the modification of trivalent ceria ions. The influence of the slurry flow rate and oxidizer concentration, regardless of the particle type, was found to be similar with flow rate is 70 ml/min, optimal oxidizer concentrations were 0.4% and 1% for Al_2O_3 and CeO_2 slurries respectively. A higher flow rate or a higher oxidizer concentration brought about a greater MRR before reaching a plateau. Many of these were interpreted by an adhesive removal mechanism on the molecular scale.

The paper [26] introduces the preparation of silane (including γ -aminopropyl triethoxysilane (APTS)/methyl trimethoxysilane (MTMOS) modified SiO_2 particles and their application on final polishing of silicon wafer. The siloxane groups in the silane and hydroxyl groups on the surface of the silica particle generated hydrolysis condensation reaction, which changed the surface chemical properties of silica particles. The modified silica particles were characterized by Particle Size/Zeta Potential Analysis, Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Research results demonstrated that APTS and MTMOS-modified particles had better dispersion stability than unmodified particles which conformed to the results of zeta potential. In addition, the average size and size distribution of MTMOS-modified particles were almost close to those of unmodified particles, while APTS-modified particles tend to form the aggregation among particles. Polishing experiments showed that MRR of the slurry with modified particles increased comparing with that with unmodified par-

ticles, resulting from readily carrying off of polishing debris because of permeability of silane. The modified particles provided better surface quality of silicon wafer than unmodified particles, in that the soft coating of modified particles decreased mechanical damage so as to improve surface quality; particularly, the wafer surface of non-visible defects and lower Ra and PV were observed by the slurry with MTMOS-modified particles.

Novel PS/ SiO_2 core-shell nano-composite abrasives with smooth surface and controllable size were successfully synthesized by [27]. Monodisperse silica-coated polystyrene (PS) nano-composite abrasives with controllable size were prepared via a two-step process. Monodisperse positively charged PS colloids were synthesized via polymerization of styrene by using a cationic initiator. In the subsequent coating process, silica formed shell on the surfaces of core PS particles via the ammonia-catalyzed hydrolysis and condensation of tetraethoxysilane. Centrifugation/ waterwash / 03redispersion cycle process or surface modification or addition surfactant was needed in the whole process. The morphology of the abrasives was characterized by scanning electron microscope. Transmission electron microscope and energy dispersive X-ray analysis results indicated that silica layer was successfully coated onto the surfaces of PS particles. Composite abrasive has a core-shell structure and smooth surface. The chemical mechanical polishing performances of the composite abrasive and conventional colloidal silica abrasive on blanket copper wafers were investigated. The root mean square roughness decreased from 4.27 nm to 0.56 nm using composite abrasive. The PS/ SiO_2 core-shell composite abrasives exhibited little higher material removal rate, better surface quality than silica abrasives under the same polishing conditions.

The material removal mechanism of chemical mechanical polishing was simplified as a single nanoparticle scratching the surface of a Cu film based on contact mechanics that relates the size of scratches to the applied force. Scratch experiments were carried out by [28] for Cu-blanket wafers comprised multiple layers (from top): 1.5 μ m-thick Cu film, 25-nm-thick TaN film, 550-nm SiO_2 film, and a Si substrate. The scratch depths were controlled to below 150 nm, which is one tenth of the Cu film thickness (1.5 μ m) [19], to avoid the substrate effect using an atomic force microscope with a SiO_2 spherical tip with a radius of 400 nm at low normal forces under three environmental conditions, namely air, deionized (DI) water, and slurry. The slurry comprised 5.5 wt% phosphoric acid, 1.8 wt% ethylenediamine, 1.8 wt% ammonium hydrogen citrate, 0.3 wt% benzotriazole, 0.1 wt% KOH, 0.5 wt% hydrogen peroxide, 1 wt% SiO_2 abrasive particles with mean particle size of 110 nm, and 89 wt% DI water. It had a pH value of 5.72 and a viscosity of 3.6 cP. The scratches were produced with constant normal forces ranging from ~ 6 μ N to ~ 37 μ N in the z-direction, a lateral scratching speed of ~ 1 μ m s⁻¹. Six scratches, each 4 μ m long, were produced for each of the applied normal forces. The direction of the scratches, x-direction is perpendicular to the longitude direction of the cantilever, y-direction. The experimental results showed that the scratch

profiles and applied forces depend on the surface material properties and the scratch environments. As the applied force increased, the scratch depth increased due to more energy being provided to remove excess material. If the surface material properties were considered to be the same in the air and DI water environments, the resistance from the liquids reduced the applied force on the Cu film surface, thus leading to a smaller scratch depth in the DI water environment. Without considering the liquid resistance (in the DI water and slurry environments), the passivation layer reduced the material strength and hardness of the Cu film surfaces, increasing the scratch depth in the slurry environment. The COF and wear rate for the material removal mechanism were evaluated by the combination of surface plowing and shearing under a single-particle scratch. Since less force is applied to plow Cu film surfaces in liquids due to the resistance and buoyancy force. The coefficient of friction (COF) in an air environment was ~205% and ~356% larger than those in DI water and slurry environments, respectively, at a given scratch depth. The difference in the COF was due to the effect of buoyancy force in the liquids. The COFs in liquid environments depend on the surface properties of the Cu films. The COF in the slurry environment was smaller than that in the DI water environment at low scratch depths. In general, the wear rates of the Cu film surfaces in the three environments increased with the applied normal force or scratch depth. The wear rates in the air environment and in the DI water environment were smaller than that in the slurry environment. The wear rate for scratches in the air environment was almost the same as that in the DI water environment at a given scratch depth, since the surface properties of the Cu films were almost identical and the same amount of shearing and plowing force was required to perform material removal. For a given force, the scratch depth in a slurry environment is significantly larger than that in a DI water environment, which was due to the slurry chemically interacting with the Cu film surface to generate a soft passivation layer.

In this paper [29], an empirical expression $MRR = MRR_0 \exp(-kC_{BTA}) + MRR_M$ was proposed based on the experimental data for material removal rate of copper chemical mechanical polishing containing BTA as inhibitor. The UNIPOL-1502 polishing machine (China Shenyang Kejing Instrument Co., Ltd) was used to polish the blank copper disk (2 in, 99.99%). The blank copper disk was polished with a FKN polishing pad under the constant conditions of processing pressure 0.5psi, rotating speed 80r/min, and slurry-supplying rate 60 mL/min. Every CMP process was performed for 5min. The slurry used in the copper CMP process was composed of 2wt% fumed silica as abrasive (mean particle size 50nm), 2wt% H_2O_2 as oxidizer, 0.1-0.3wt% glycine as chelating ligand, 0-600ppm benzotriazole (BTA) as corrosion inhibitor and deionized water. The slurry was adjusted by phosphoric acid to pH=3.6. The specimen before and after polishing were ultrasonically rinsed in deionized water (DI) for 2min, dried by N_2 , and then measured by a FA1004 electronic balance. The parameters of this expression were the initial chemical corrosion rate (MRR_0), the corrosion

inhibition efficiency (k) and the mechanical abrading rate (MRR_M). It was found that the proportional coefficient k could qualitatively reflect the inhibition efficiency of BTA under different conditions based on the simulating results about the given data in literatures. Based on the experimental results under different glycine concentrations in this paper, the same k value was obtained, which revealed that the formation of Cu-BTA film cannot be affected by the glycine concentration. In addition it is of interest that the empirical expression can also be used to uncover the low inhibition efficiency of uric acid in Cu-CMP process. Future work has to be done in regard to the application of this proposed empirical MRR expression

3 CONCLUSIONS

CMP is a very complicated process in which both mechanical and chemical factors play an important role. Some mechanisms can explain a certain type of CMP process but not others. Fundamental and deep understanding of the CMP mechanism is desirable to characterize, optimize and model the process. Considerable research effort has been devoted to developing a model for the CMP material removal mechanism. The consumable parameters from slurry chemicals, including the oxidizer concentration, slurry PH value and slurry buffering agents to the nano-scale slurry abrasives, including the abrasive materials, size distribution, pad parameters including pad materials and topography play important roles in the material removal in CMP. An implication of the model is that the effects of the consumable parameters should be evaluated under a comprehensive frame work, considering the competition among different interactions. CMP is in a very early stage of modeling since even the physical effects are not yet completely clear. Programs which work with the existing models are not available. From the modeling point of view the flow of the slurry seems to be the most difficult question since the behavior of the fluid and the mechanical effects are not completely understood. For modeling purposes of the entire CMP process, a completely three-dimensional simulation would be necessary. CMP of new materials for micro electromechanical system (MEMS) applications and its modeling are becoming interesting topics. These kinds of research will lead to a more predictable and reliable CMP process for the next generation of IC fabrication. Making improvements in the CMP process to reduce the surface defects is an important engineering challenge.

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