Material Removal Mechanism during Copper Chemical Mechanical Planarization Based on Nano-Scale Material Behavior

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Comparison of the experimentally measured electrochemical corrosion rate and the physical material removal rate (MRR) revealed that during copper chemical mechanical planarization (CMP) most of the copper was removed mechanically by interaction with sliding abrasive particles. The mechanism for mechanical removal of copper was explained by considering literature values of the properties of copper at the nano-scale. Although the force applied on the copper by abrasive particles may be insufficient to initiate plastic deformation, friction between moving abrasive particles and copper reduces the maximum Hertz pressure required for plasticity. Crystallographic defects and a copper surface roughened by repetitive abrasions and chemical attack further lower the local threshold for plastic deformation, leading to selective plastic deformation of copper at weakened regions. The plastically deformed copper is then removed by a mechanism similar to cutting, releasing free debris that is subsequently dissolved by the oxidizer and/or complexing agent in the CMP slurry. Hardness values obtained from AFM tip scratching experiments on chemically treated copper predicted the MRR behavior during CMP well. In contrast, hardness values obtained by nanoindentation, where the applied force and the tip diameter were much larger than those during AFM tip scratching, yielded poor predictions of the MRR.

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Chemical mechanical planarization (CMP) of copper is the key technology for the multilevel metallization of interconnects during the manufacture of integrated circuits. Excess copper is deposited on the surface of a silicon wafer, then the topography of the wafer is smoothed through selective material removal to yield a planar structure for subsequent deposition of the next level of dielectric and metal. During copper CMP, the wafer is abraded with a rotating CMP pad while supplying slurry containing various chemical additives such as oxidizers, complexing agents, inhibitors, surfactants and abrasive particles.

To predict the material removal rate (MRR) during copper CMP, earlier modeling studies relied on models developed for oxide CMP.1–6 Material was considered to be removed by abrasion by abrasive particles that are trapped between a wafer and pad asperities while sliding on the surface being polished. The chemical additives in the slurry were considered to react with the surface of a wafer to soften the material2,3,6–8 or dissolve physically dislodged material.1 In contrast, Kaufmann et al. proposed a synergistic model for metal CMP that attributes material removal during CMP of metals to the cyclic removal of the passive layer on the surface of a metal through mechanical abrasion by abrasives and pad asperities, and subsequent active oxidative dissolution of the metal from the resulting exposed regions, until the passive layer has been regenerated.9 This model implicitly assumed that the passive layer was thick enough that the underlying unoxidized metal was not removed by abrasion. Tripathi et al. proposed a quantitative model similar to Kaufmann’s by postulating a quasi-steady state where the overall rate of removal of passivating material and the overall rate of growth of passivating material are balanced, giving a constant overall MRR during copper CMP.10 In this model abrasives and pad asperities were considered to only remove the passive layer from the surface of copper, thereby exposing underlying metal that then underwent oxidative dissolution into the slurry. Choi et al. subsequently suggested that at steady state during CMP using an acidic slurry containing benzonitriloacel (BTA) and glycine, Cu(I)BTA and Cu(I)BTA2 form only a fraction of a monolayer on average, partly protecting the surface of a wafer from dissolution.11 In this model, removal of the passive layer contributed only a small portion of the electrochemically measured MRR; most of the electrochemically measured MRR was due to active dissolution of copper. Both Tripathi et al. and Choi et al. considered the material removal during copper CMP to be mostly due to the electrochemical oxidation of the copper while the protective material is repetitively removed by the abrasives, and copper is dissolved from exposed regions.

To the point of fact, though, measurable amounts of copper have been reported to be removed during polishing even when the slurry contains no chemical additives other than deionized water and abrasive particles, implying that copper can be removed directly from the surface through mechanical interactions with the abrasive particles.12–14 Material removal through exclusively mechanical mechanisms has been understood to be due to abrasion of copper metal at the surface of a wafer. In this frame of understanding, enhanced material removal in the presence of chemical additives in the slurry has been attributed to the formation of porous, soft or weakly adhering surface layers on the surface of copper.15–17 Yet hardness measurements by indentation of copper that has been previously exposed to chemical additives have shown contradicting results.18 Although the postulated soft surface layer would explain the increased MRR in the presence of chemical additives, no correlation between the hardness of the surface layer and the MRR has been found.13,18

Despite the earlier efforts, quantitative approaches to modeling the material removal behavior during copper CMP have not been successful to date because the relative contributions of each mechanism have not been unambiguously determined. Also, the response of copper to the force applied by the abrasives has yet to be successfully related to the material removal behavior. In the current paper, the relative contribution of mechanical and electrochemical mechanisms was determined by comparing MRR and corrosion rates during copper CMP. A novel mechanical material removal mechanism based on the hardness of copper at very small length scales is proposed to explain the substantial amount of material removal that was not measured as the corrosion rate.

Experimental

Electrochemical corrosion rate and MRR during CMP of copper were compared to determine the dominant material removal mechanisms during the process.

In situ electrochemical measurement.—The electrochemical material removal (corrosion rate) of copper was evaluated by measuring the current density at a copper electrode while polishing using the
apparatus shown in Figure 1. A three electrode electrochemical cell, housed in a glass beaker, was assembled on the table bed of a high precision machine tool (Matsuura MC-510VSS), which rotated the working electrode at high speed with high precision. The working electrode was a copper tube (99.99% purity from McMaster-Carr) with a 2 mm difference between the outer and inner diameters, so as to minimize the variation of sliding velocities relative to the CMP pad across the annulus. The copper tube was embedded in insulating epoxy, exposing an annulus at the bottom of the electrode, with a cross sectional area of 0.46 cm². A saturated calomel reference electrode (SCE) was placed in a Luggin capillary 5 mm from the copper electrode. The counter electrode was platinum mesh. The slurry contained 2 wt% alumina particles (primary diameter 20 nm, median aggregate diameter 150 nm), 0.01 M glycine, 0.01 M BTA, 0.1 mM Cu(NO₃)₂ and 0.5 wt% H₂O₂ in deionized (DI) water at pH 4. A different slurry containing 4 wt% alumina particles, 0.01 M glycine, 0.01 M BTA, 0.1 mM Cu(NO₃)₂ and 1 wt% H₂O₂ in DI water at pH 4 was used only during the potentiodynamic scans for testing the efficacy of polishing at removing the protective material on the surface of copper (Figure 2). A piece of IC1010 (Rohm and Haas) pad was fixed horizontally on the bottom of the beaker. The pressure applied to the copper surface was measured with a load cell (TUF-010-025-S from Loadstar Sensors) placed under the beaker. Before each run the electrode was polished using the apparatus, to maintain a consistent surface roughness. It was then washed with DI water and any remaining oxide on the copper surface was reduced by holding at −1.2 V (SCE) for 60 seconds while polishing the working electrode. Potentiodynamic polarization was conducted by scanning the potential from −0.8 V (vs. SCE) to 0.8 V (or 1.0 V) at a rate of 5 mV/s, to estimate the corrosion rate of copper during CMP. The corrosion rate was evaluated from the measured potentiodynamic curves using the linear polarization resistance technique \(^{20}\) and Faraday’s law.

**Copper CMP**—A 4 inch blanket copper wafer underwent CMP using a POLI-500 CMP machine (GNP Technology). The blanket copper wafer had a 1000 nm thick layer of copper electrochemically deposited on a thin Ta and Cu seed layer. The CMP pad (IC1010) was broken-in initially, and then conditioned for 30 seconds using a diamond conditioner (supplied from GNP Technology) between each run. During conditioning deionized water was passed at 300 ml/min; the slurry (composition as above) was supplied at 100 ml/min during CMP of copper. The applied pressure and sliding velocity of a wafer over the CMP pad were varied from 2 psi to 6 psi, and 0.5 m/s to 1.25 m/s, respectively. CMP was performed for three minutes for each test, and the MRR was evaluated by measuring the sheet resistance of the remaining copper at 21 points.

CMP of the copper blanket wafer was also performed using a slurry containing only 4 wt% of alumina abrasives and 0.3 mM sodium oleate in DI water. The surfactant sodium oleate was added to prevent excessive frictional force between the wafer and the pad during the process.\(^{19}\) It did not affect the measured MRR. The pH of the slurry was not controlled; the natural pH of the alumina suspension was about pH 4. The sliding velocity was 0.75 m/s and the applied down pressure was 4 psi. The wafer was weighed before and after two minute CMP runs five times using an electronic balance (Sartorius A200S) to evaluate the MRR. The MRR was evaluated by averaging the MRRs from three runs of CMP.

**Results**

Figure 2 shows the influence of polishing on the electrochemical behavior of copper. Abrasion had little impact on the cathodic current at potentials lower than −0.3 V (SCE), but significantly increased the oxidation rate at higher potentials, resulting in both a lower corrosion potential and a corrosion rate (evaluated using the linear polarization resistance technique\(^{20}\)) that was about an order of magnitude higher than that observed under static conditions. This demonstrates the efficacy of BTA as a corrosion inhibitor. It also shows that abrasion by the abrasives removed the protective material, CuBTA, on the copper surface, thereby allowing more rapid oxidation at the exposed surfaces.

Figure 3 compares the MRR measured from CMP experiments and the corrosion rates evaluated from potentiodynamic curves during polishing. The electrochemically measured corrosion rate is the sum of the rate of removal of the protective material and the overall dissolution rate at the surface (because copper must be oxidized before it interacts with BTA to form protective material). The corrosion rates were less than 1% of the total MRR measured in CMP experiments for all conditions shown in Figure 3. Similar results were reported by Jindal et al. using slurries containing hydrogen peroxide, glycine and abrasives.\(^{21}\) This implies that almost all of the material removal during CMP was attributable to direct mechanical removal, rather than to electrochemical dissolution or removal of the protective layer. It also suggests that the material removed during copper CMP is not limited to the weak and soft surface layer as postulated previously.\(^{2,15–17}\) Note that the evaluated corrosion rates might have underestimated the total oxidation rate of copper if hydrogen peroxide acted via a Fenton-type mechanism that yielded hydroxyl radicals, which are strong oxidizers. This is because the oxidation through this mechanism is not measured electrochemically.

The MRR measured from the CMP experiments using a slurry containing only alumina abrasives and sodium oleate was 9 nm/min, which was lower than the MRR for the slurry containing H₂O₂, glycine, BTA and Cu(NO₃)₂ but not insignificant compared to the corrosion rates. Other researchers also observed substantial MRRs.
when copper was polished with DI water containing only abrasive particles.\textsuperscript{13-14}

From those observations, it is apparent that most of the total MRR during copper CMP must be due to the mechanical removal of metallic copper. Removal of the material by the CMP pad material itself was not considered because CMP without abrasive particles yielded negligible MRR.\textsuperscript{13} The linear increase in total MRR with applied pressure and sliding velocity seen in Figure 3 contrasts with the near constant corrosion rate of about 0.2 nm/min, providing further support for direct mechanical removal of significant amounts of the copper. It should be noted that the chemical additives used in the slurry enhanced the overall MRR, as observed from the significant difference in the MRRs obtained using the slurry containing chemicals and that using the slurry with only abrasives and a small amount of surfactant. The probable mechanism for the MRR enhancement is discussed in detail below.

\section*{Discussion}
To explain the significant contribution of the mechanical material removal during copper CMP, a novel material removal mechanism based on the material response of copper at nano-scale is proposed starting from the traditional material removal models by abrasion. The literature regarding the onset of plasticity of copper has been extensively reviewed because the material property of copper at such small scale has hardly been employed to explain the material removal behavior during CMP despite its relevance.

\textbf{Model for material removal by abrasion.—}Applying the material removal mechanism for oxide CMP, many researchers have considered that material is removed mechanically from the surface of a wafer during copper CMP by abrasive particles trapped between a wafer and pad asperities. The abrasive particles are considered to slide on the surface of a wafer while plastically deforming the surface, piling up dislodged material along the trajectory of the sliding abrasives to form shallow trenches. This dislodged material is then removed by chemical additives in the slurry\textsuperscript{4} or by another abrasion.\textsuperscript{5} Some researchers have also argued that material is cut from the surface by sliding abrasive particles, with detached material becoming debris.\textsuperscript{3} Regardless of whether the dislodged material becomes debris or piles up, plastic deformation of copper has generally been assumed. Although there are some variations in the representation of the number of abrasive particles that are involved in the ploughing or abrasion of the copper wafer, \( n_{\text{ab}} \) estimation of the forces exerted by the abrasives, \( f_{\text{ab}} \), calculation of the depth of the trenches, \( h_{\text{c}} \), and the portion of the deformed copper that contributes to the MRR \( K_{\text{e}} \), the MRR predicted by this mechanism is generally expressed as:

\[
MRR = K_{\text{e}} \frac{n_{\text{ab}} A_{i} v}{A_{w}}
\]

where \( A_{i} \) is the cross sectional area of the trench generated on the copper by the indentation of the sliding abrasive, \( v \) is the sliding velocity of the wafer over the pad and \( A_{w} \) is the area of the wafer surface. The equation gives the MRR as a unit of thickness removal per unit processing time. The cross sectional area of a trench generated on the wafer surface by a sliding abrasive can be expressed as:

\[
A_{i} \approx \frac{h_{w} w_{ab}}{2} = \frac{\sqrt{2} f_{\text{ab}}^{3/2}}{\pi^{3/2} r_{\text{ab}} H_{w}^{3/2}}
\]

where \( r_{\text{ab}} \) is the average radius of the abrasive particles, \( H_{w} \) is the hardness of a wafer, \( h_{w} \) the depth of the indentation, \( w_{ab} = \frac{f_{\text{ab}}}{\sigma_{\text{ab}} H_{w}} \), and \( w_{ab} \) is the width of the trench, \( w_{ab} = \frac{2}{\sqrt{2} f_{\text{ab}} h_{w}} \). Then Equations 1 and 2 give the MRR during CMP to be:

\[
MRR = \frac{\sqrt{3}}{\pi^{3/2}} K_{\text{e}} \frac{n_{\text{ab}} f_{\text{ab}}^{3/2} v}{r_{\text{ab}} H_{w}^{3/2} A_{w}}
\]

Equivalently, the equation can be expressed based on the interaction of a single pad asperity, copper and abrasive particles between them as

\[
MRR = \frac{\sqrt{3}}{\pi^{3/2}} K_{\text{e}} \frac{n_{\text{ab}} f_{\text{ab}}^{3/2} r_{\text{contact}}}{r_{\text{ab}} H_{w}^{3/2} a_{\text{ui}}}
\]

where \( n_{\text{ab}} \) is the number of abrasives that plastically deform the copper while squeezed between a pad asperity and the copper, \( r_{\text{contact}} \) is the areal ratio of real contact between a wafer and a CMP pad and \( a_{\text{ui}} \) is the average contact area of a pad asperity and copper. Note that \( n_{\text{ab}} \) is considered to be influenced by the concentration and the size of the abrasive particles in the slurry, the ionic strength of the slurry, the zeta potential of the abrasive particles (which determines the degree of agglomeration), the zeta potential of the wafer surface and pad asperities, and the interval between consecutive interactions of a given site on the copper surface with pad asperities, which in turn depends on the surface topography of the pad, down pressure and the sliding velocity, \( f_{\text{ab}} \), depends on \( n_{\text{ab}} \), the amount to which trapped abrasive particles deflect the pad asperities, the surface topography of the pad and the down pressure. The hardness of the wafer, \( H_{w} \), depends on the processing and consumables variables as discussed later.

Unfortunately, the model based on mechanical abrasion has not been successful when applied to copper CMP, yielding MRR values that are two or three orders of magnitude higher than those experimentally observed. Numerous hypotheses have been proposed to address
Material properties of copper at the nano-scale.—Hardness at more relevant length scales can be obtained from experiments or atomistic simulations of nanoindentation where the indentation depth is of the order of nanometers and the load is of the order of tens or hundreds of nano-Newton as summarized in Table I. The maximum shear stress in the copper during load controlled nanoindentation at the onset of the plasticity was approximated as the theoretical shear strength of the material, suggesting that plastic deformation is due to homogeneous nucleation of dislocations at the subsurface of the indented area. Other researchers have used similar criteria to filter out the size of the abrasive particles participating in the material removal. It has also been argued that only a portion of the material dislodged by the sliding abrasives is actually removed. Zhang et al. suggested that only a portion of dislodged material becomes loose debris that contributes to material removal. However, it is well known that indentation hardness shows a size effect, with larger indenter size or indentation depth yielding lower apparent indentation hardnesses. As the indented volume decreases the probability of crystallographic defects being present under an indenter decreases, leading to enhanced resistance to plastic deformation. Therefore the material properties at more relevant length scale are required to understand the deformation of copper induced by interaction with abrasive particles.

### Table I. Maximum shear stress in copper during nanoindentation at the onset of plasticity

| Method                  | Maximum shear stress (GPa) | Evaluation methods | Indenter radii (nm) |
|-------------------------|---------------------------|--------------------|---------------------|
| Suresh et al.            | 10.7                      | Nanoindentation experiments | 50                  |
| Chen et al.              | 8.5                       | Nanoindentation experiments | 50                  |
| Ziegenhain et al.        | 7.8-11.2 (100)            | MD simulations of nanoindentation | 8                   |
| (111)                    |                           |                     |                     |
| Sarav et al.             | 8.5                       | MD simulations of nanoindentation | 3                   |

**Figure 4.** Length scales during the interaction between an abrasive particle and the copper during CMP.

This discrepancy. Luo and Dornfeld devised a concept of “active abrasives”, particles that are large enough to be squeezed between the pad asperities and the wafer to reduce the number of abrasives participating in the material removal. Other researchers have used similar criteria to filter out the size of the abrasive particles participating in the material removal. It has also been argued that only a portion of the material dislodged by the sliding abrasives is actually removed. Xie et al. suggested that only a portion of dislodged material becomes loose debris that contributes to material removal. Che et al. asserted that the material dislodged by a scratching event is removed only when it is involved in another scratching event based on the experimental observations of material removal by micro-scale scratches.

However, this modeling approach has shown clear limitation in predicting the MRR trend when the influence of chemical additives is considered. Nano- or micro-indentation experiments have been employed to estimate the hardness of copper during CMP exposed to various chemical environments. However, it is not been successful to date to predict the MRR because the indentation load and depth and the size of an indenter were larger than those appropriate for CMP (Figure 4). It is well known that indentation hardness shows a size effect, with larger indenter size or indentation depth yielding lower apparent indentation hardnesses. The indented volume decreases the probability of crystallographic defects being present under an indenter decreases, leading to enhanced resistance to plastic deformation. Therefore the material properties at more relevant length scale are required to understand the deformation of copper induced by interaction with abrasive particles.
Influence of crystallographic defects.—Some regions of a copper film on a wafer during CMP may have a high dislocation density, voids, vacancies, impurities and grain boundaries resulting from the previous deposition, lithography and etching processes. These regions of high crystallographic defect density may be plastically deformed by abrasive particles sliding on the surface of the wafer, leaving an even higher defect density in the copper, as predicted with MD simulation. The crystallographic defects lower the shear strength of copper because they facilitate activation of the dislocation source or function as sites for heterogeneous nucleation of dislocations. MD simulations predicted that vacancies in otherwise perfect Fe crystals and Ni crystals reduced the stress required for plasticity. Dislocations did not nucleate at the vacancies but interacted with them during subsequent motion so as to reduce the shear strength of the materials. Static atomistic simulations of nanoindentation on (111) Cu crystal planes and MD simulations of nanoindentation on Ni showed that the hardness was also reduced by voids in the crystal. The cutting and thrust forces during nanomachining of single crystalline copper were also reduced by voids. Nanoindentation experiments on a single crystal of tungsten showed that the load for plasticity decreased as the dislocation density in the crystal increased. Simulations of nanomachining of copper showed that dislocations nucleate near the surface of the workpiece and emit into the crystal. When machining was conducted at previously scratched regions with high defect densities, the cutting load was decreased. Also, atomistic simulation of nanoindentation of Cu and Mo at grain boundaries predicted that lower contact stresses were required for plasticity than required in the interior of perfect crystals.

Influence of roughness.—In addition to the crystallographic defects in copper the surface roughness on the surface also reduces the threshold of the plasticity. Chemical additives used in CMP slurries have been reported to change the surface topography of copper. In addition, the nano-scale scratches or trenches generated by sliding abrasive particles further roughen the surface. Crystallographic defects make copper more susceptible to chemical attack, which exacerbates the roughness on the surface. Surface roughness that is smaller than the size of an indenter has been observed to induce plasticity by facilitating the nucleation of dislocations near the surface. Since the abrasive particles used in CMP on the order of tens of nanometers in size, are larger than the scale of roughness of the wafer after CMP, on the order of a nanometer or less, dislocations would be expected to nucleate at the surface when the wafer interacts with sliding abrasive particles. Simulations and experiments of nanoindentation have shown the influence of surface roughness on the shear strength of various materials including copper. Atomistic simulations of nanoindentation on Cu showed a significant decrease in the load needed to nucleate dislocations when indented near surface steps. Similar behavior was predicted for the (111) faces of Au. Nanoindentation experiments on Au showed a 45 percent reduction in yield stress when indented near surface steps.

Table II. Depth of scratches by an AFM tip, surface roughness, and hardness values of copper samples exposed to aqueous solutions containing different chemicals. Indentation hardness along with the depth of scratches and the surface roughness were from Liao et al. and the AFM tip scratching hardness was estimated in this work from the depth of scratches by an AFM tip.

|                | 5 wt% H₂O₂ | 5 wt% H₂O₂ and 1 wt% glycine | 5 wt% H₂O₂, 1 wt% glycine and 0.1 wt% BTA |
|----------------|------------|-----------------------------|-----------------------------------------|
|                | Not treated | pH 4                        | pH 10                                   | pH 4          | pH 10          | pH 4                  | pH 10                  |
| Depth of scratches by AFM (nm) | 6.61       | 12.89                       | 11.78                                   | 37.57         | 29.05          | 9.35                  | 15.2                   |
| Surface roughness (nm) | 10         | 17.9                        | 12                                      | 85.5          | 185.3          | 12.3                  | 20.3                   |
| Indentation hardness (GPa) | 2.21-2.71  | 2.68-3.64                   | 2.53-4.63                               | 2.99-8.35     | 2.59-4.16      | 3.11-5.89             | 2.16-2.38              |
| AFM tip scratching hardness (GPa) | 11.9       | 6.12                        | 6.70                                    | 2.10          | 2.72           | 8.44                  | 5.19                   |
most dramatically the hydrogen peroxide-glycine solution, whereas the measured nanohardness values evaluated from the indentation experiments were only slightly changed, either positively or negatively. The insensitivity of the nanohardness to the chemical treatment has also been reported by other researchers.\textsuperscript{13,18} The slight change of the nanohardness has been attributed to the oxide layer on the surface of copper.\textsuperscript{15,18}

Poor correlation between the nanohardness measured with nanoindentation experiments and the MRR\textsuperscript{13,18} was presumably due to an effect of size on hardness, which was not recognized by the original authors. As discussed above, material properties at very small length scales differ from those at larger length scales. The load applied during AFM tip scratching, about 2.48 μN, was up to three orders of magnitude smaller than that used for the nanoindentation experiments, up to 2500 μN. Also, the tip diameter, 20 nm, was nearly an order of magnitude smaller than that for indentation, 100 nm. Thus the plastic zone created by an AFM tip was very small, and would have contained few dislocations. At this length scale, where very few dislocations are near the AFM tip before indentation, the dislocations responsible for the onset of plasticity may have been nucleated homogeneously, requiring a shear stress as high as the theoretical shear stress. Plastic deformation of copper sample that was not exposed to the chemicals is considered to occur this way.

The hardness of copper at this small length scale was also affected by the surface roughness of the testing samples exposed to different chemical environments. As shown in Table II, the scratches made by an AFM tip were deeper with increasing surface roughness. While the original authors attributed the deeper scratches to weaker adhesion of the roughened surface material to the substrate, the increase in the depth of the scratches clearly demonstrated that the increased surface roughness reduced the hardness of the surface material; the plasticity was initiated by heterogeneous nucleation of dislocations or the activation of dislocation sources at surface steps, voids, vacancies or impurities created by the chemical treatment. Moreover, since a given copper sample was scratched repeatedly by the AFM tip to give 2 × 2 μm\textsuperscript{2} of scratched area, the region would have contained additional defects from the scratching events that facilitated heterogeneous nucleation of more dislocations. It might be argued that the changes after treatment with chemical additives reflected the mechanical properties of different oxidized surface layers, rather than changes in the underlying copper. However, copper oxides such as CuO, which have been suggested to be formed upon exposure to H\textsubscript{2}O\textsubscript{2},\textsuperscript{16} are much harder than pure copper,\textsuperscript{16,67} and hence would not appear to explain the greater susceptibility to scratching.

To confirm that the deformation of the untreated copper sample was due to homogeneous nucleation of dislocations, the maximum shear stress induced in the copper during AFM tip scratching was evaluated. Assuming the Tresca yield criterion, the maximum shear stress, τ\textsubscript{max}, induced in the copper by scratching was evaluated using:

\[
\tau_{\text{max}} = 0.30 p_0 \]  \hspace{1cm} [5]

where \(p_0\) is the maximum Hertz pressure, given by:\textsuperscript{47}

\[
p_0 = \frac{6 f_{\text{tip}} E^* v^2}{\pi^3 r_{\text{tip}}^2} \]  \hspace{1cm} [6]

where \(f_{\text{tip}}\) and \(r_{\text{tip}}\) are the force exerted by the AFM tip and its radius, respectively; \(E^* = \left(\frac{1-v^2}{E_1} + \frac{1-v^2}{E_2}\right)^{-1}\), where \(E\) and \(v\) are the elastic modulus and Poisson’s ratio, respectively and the subscripts 1 and 2 denote the contacting materials, in this case copper (\(v_1 = 0.33\) and \(E_1 = 132\) GPa) and the silicon AFM tip (\(v_2 = 0.27\) and \(E_2 = 163\) GPa), respectively. Under the applied load the maximum shear stress induced in the copper calculated using Equations 5 and 6 was about 9.4 GPa, exceeding the theoretical shear stress of copper at this length scale. As a result, the scratches on the untreated copper sample may be attributed to either homogeneous or heterogeneous nucleation of dislocations.

The hardnesses of copper samples estimated on the basis of the depth of scratches made by the AFM tip are summarized in Table II. The hardness values differ from those measured by nanoindentation, provided by Liao et al.\textsuperscript{16} because of the discrepancy in the length scales at which the hardness was measured. Note that Liao et al.\textsuperscript{16} neither calculated the hardness of copper based on the AFM tip scratching tests nor related the depth of scratches with the MRR during CMP. The hardnesses evaluated for copper samples that had previously been exposed to chemical solutions were considerably smaller than that of untreated copper, suggesting heterogeneous nucleation of dislocations. The hardnesses were lowest for the roughest samples, e.g. when the copper sample was pre-exposed to aqueous solution at pH 4 or 10 containing 5 wt% H\textsubscript{2}O\textsubscript{2} and 1 wt% glycine, further supporting the hypothesis that the heterogeneous nucleation of dislocations was responsible for the reduction in hardness induced by these conditions.

**Prediction of MRR.**—The MRRs predicted for copper CMP using slurries at pH 4 or 10 containing 5 wt\% H\textsubscript{2}O\textsubscript{2} and 3 wt\% of alumina abrasives, and the same slurries containing an additional 1 wt\% glycine, were evaluated from Equation 3 and the hardness values in Table II. The relative magnitudes of the MRRs for the different conditions were determined from Equation 3 by which the MRRs during copper CMP are inversely proportional to the 3/2 power of the hardness at the surface of copper, for constant size of abrasive particles, sliding velocities and down pressures. The predicted rates are graphically compared with the experimental data of Jindal et al.\textsuperscript{13} in Figure 5. It was assumed that the number of abrasive particles participating in material removal was unaffected by the presence of glycine and the pH of the slurry. The degree of agglomeration has not been reported for such solutions, and since both pH values are well-removed from reported values for the PZC of alumina, it is reasonable to assume significant electrostatic repulsion between particles. The electrochemical portion of the MRR was also neglected because, as discussed earlier, it was miniscule compared to the mechanical portion. It was also assumed that the presence of alumina abrasives did not influence the hardness of copper at nano-scale. The predictions based on the AFM tip scratching tests agreed well with the experimental observations while those based on the nanohardness obtained from deep indentation tests by Liao et al.\textsuperscript{16} were poorly correlated, even in the trends. This poor correlation is not due to ignoring the effect of direct
dissolution of copper, because even the highest dissolution rates seen in the presence of glycine were insignificant compared to the MRR during CMP.

Note that there is a huge difference in the duration of exposure of a given surface element of copper to chemicals during Liao et al.’s experiments and during CMP. During CMP itself, the probability that a given location on a wafer is contacted by abrasive particles held under a pad asperity during interaction between the asperity and the wafer is defined as the removal efficiency. The removal efficiency during CMP has been determined to be smaller than unity, meaning that a given point on a wafer during CMP is contacted less than once during CMP. During CMP itself, the probability that a given surface element of copper to chemicals during Liao et al.’s experiments and during CMP. During CMP itself, the probability that a given location on a wafer is contacted by abrasive particles held under a pad asperity during interaction between the asperity and the wafer is defined as the removal efficiency.

The hardness of copper in Table III was taken from Table II for the consumable and processing variables listed in Table III for copper CMP, Equations 3, 4 and 7 predicted a MRR of 500 nm/min if one percent of the copper that is contacted by abrasive particles held between the copper and pad asperities then becomes either free debris or is piled up while still located on the wafer surface after abrasion. The hardness of copper in Table III was taken from Table II for the case where 5 wt% H2O2 and 1 wt% glycine was added to the slurry. The oxidation of free debris will not be measured in electrochemical tests. Considering that the measured corrosion rates were insignificant compared to the total MRR during CMP, it is suggested that (a) most of the copper removed is first detached, forming metallic debris or (b) pile-up copper was not readily dissolved by the oxidizer during the in situ electrochemical measurements and the CMP experiments. In fact this explanation aligns well with the experimental observations and the scratch intersection based material removal mechanism proposed by Che et al., despite the clear difference in the length scales of the scratches made on the wafer.

The finding that the parameter \( K \) would be expected to be larger than two during CMP implies that the amount of copper removed through a cutting mechanism may be only a fraction of the plastically deformed copper, depending on the parameter \( K \), making the coefficient \( K_{cr} \) in Equation 3 smaller than unity. For example, for the consumable and processing variables listed in Table III for copper CMP, Equations 3, 4 and 7 predicted a MRR of 500 nm/min if one percent of the copper that is contacted by abrasive particles held between the copper and pad asperities then becomes either free debris or is piled up while still located on the wafer surface after abrasion. The hardness of copper in Table III was taken from Table II for the case where 5 wt% H2O2 and 1 wt% glycine was added to the slurry.

### Table III: Typical consumables and process variables during copper CMP.

| Parameter | Value |
|-----------|-------|
| \( r_{contact} \) | 0.1% |
| \( a_{as} \) | 10 \( \mu \)m² |
| \( r_{ab} \) | 10 nm |
| \( H_w \) | 2.1 GPa |
| \( \tilde{h}_{ab} \) | 1000 |
| \( f_{ab} \) | 100 mN |

As the penetration depth increases, the rate of deformation of copper or the parameter \( K \) changes from a no-wear state (\( K \leq 0 \)), through a ploughing state (\( K \approx 0–2 \)), and a ploughing dominant cutting state (\( K \approx 2–8 \)), to a cutting dominant cutting state (\( K \geq 8 \)). The scratching depth data reported by Liao et al. yielded values of \( K \) ranging from 9.35 to 37.6 when the copper samples were exposed to the chemicals. The \( K \) value reduced to 6.61 when copper was untreated with the chemicals. This implies that the untreated copper sample was mostly ploughed, with some material being removed by cutting, while the scratching on the chemically treated copper samples resulted in cutting, with some ploughing as illustrated in Figure 6.

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**Figure 6.** Material removal mechanism at the abrasive scale during copper CMP.

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**Material removal mechanism at abrasive scale.**—As discussed above, the hardness of copper is locally reduced by increases in crystallographic defect density during CMP. At some sites, repetitive abrasions reduce the local hardness sufficiently that the site undergoes plastic deformation, as illustrated in Figure 6. At other sites on the copper where the local hardness remains higher than the stress induced by the abrasion, the only material that would be removed by an abrasive particle would be protective material on the surface of the copper. Thus not all of the abrasive particles sliding across the surface of a wafer while squeezed between the pad asperities and the wafer would actually plastically deform copper. Defining a ratio \( K^* \) this is expressed as:

\[
\begin{align*}
n^*_ab &= K^* n_{ab} & \text{or} & \quad n^*_ab &= K^* n_{ab} \\
\end{align*}
\]

where \( n_{ab} \) and \( n^*_{ab} \) are the number of abrasive particles sliding across the surface of a wafer while squeezed between the pad asperities and the wafer and the number of abrasives that plastically deform the copper among them, respectively. \( \tilde{h}_{ab} \) and \( \tilde{n}_{ab} \) are the equivalent quantities based on the interaction between a single asperity and the wafer. The exact mechanism by which the plastically deformed material is removed from the surface is unclear. Earlier studies of the influence of the attack angle of an indenter on the wear process showed that when the attack angle is sufficiently small, only a small fraction of the material dislodged during the wear process becomes detached debris. Yan et al. argued that the deformation of copper by a hemispherical scratching tip can be divided into four categories, depending on a parameter \( K \), which is defined in terms of the radius of the tip and the penetration depth, \( h_w \), into copper:

\[
K = \frac{h_w - 0.07 r_{tip}}{0.07 (r_{tip} - h_w)}
\]

As the penetration depth increases, the rate of deformation of copper or the parameter \( K \) changes from a no-wear state (\( K \leq 0 \)), through a ploughing state (\( K \approx 0–2 \)), and a ploughing dominant cutting state (\( K \approx 2–8 \)), to a cutting dominant cutting state (\( K \geq 8 \)). The scratching depth data reported by Liao et al. yield values of \( K \) ranging from 9.35 to 37.6 when the copper samples were exposed to the chemicals. The \( K \) value reduced to 6.61 when copper was untreated with the chemicals. This implies that the untreated copper sample was mostly ploughed, with some material being removed by cutting, while the scratching on the chemically treated copper samples resulted in cutting, with some ploughing as illustrated in Figure 6.

The ploughed copper contains a higher density of crystallographic defects than the material that has not interacted with the abrasives. The material in these defect-rich regions would be expected to be preferentially oxidized by the oxidizing agent in the slurry, having a higher thermodynamic chemical potential. Oxidation may also involve a Fenton-type mechanism, producing hydroxyl radicals. MD simulation of nano-scale machining showed that material dislodged during nano-machining was removed by chemical dissolution. The copper debris detached during cutting is dissolved by the oxidizing and complexing agents in the slurry. The oxidation of copper on the surface of a wafer is measured as an electrochemical corrosion rate if it dissolves electrochemically by a non-Fenton-type mechanism. The oxidation of free debris will not be measured in electrochemical tests. Considering that the measured corrosion rates were insignificant compared to the total MRR during CMP, it is suggested that (a) most of the copper removed is first detached, forming metallic debris or (b) pile-up copper was not readily dissolved by the oxidizer during the in situ electrochemical measurements and the CMP experiments. In fact this explanation aligns well with the experimental observations and the scratch intersection based material removal mechanism proposed by Che et al., despite the clear difference in the length scales of the scratches made on the wafer.
predicted MRR would be 50 μm/min, which is unrealistically high, and inconsistent with experimental observation.

Conclusions

The majority of material removal during copper CMP is attributed to the removal of copper through abrasion. During CMP, copper can be plastically deformed by mechanical interaction with abrasive particles squeezed between pad asperities and the wafer, even though the shear stress induced in the copper by this interaction may be smaller than the theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength. This happens because friction between the abrasives and copper (a) activates dislocation sources, or (b) nucleates theoretical shear strength.

Acknowledgments

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