The efficiency of a pad asperity and abrasives embedded between the asperity and wafer at removing the protective material on the surface of copper (removal efficiency) during chemical mechanical planarization (CMP) was determined experimentally using current densities from in situ electrochemical measurements while polishing with a slurry containing BTA. The removal efficiency was insensitive to the pressure and sliding velocity, but was dictated by the pad surface topography parameters and abrasive concentration in the slurry. An analytical estimate was derived by comparing the trajectories of a pad asperity and the abrasives embedded in the asperity. Comparison of the experimental and analytical estimate suggests that the asperities are deformed enough by the embedded abrasives to contact the surface of copper at abrasive concentrations up to 1 wt%. At higher concentrations up to 5 wt%, the asperities deflected to a lesser amount, making the force exerted on the copper increase. At these higher concentrations, some of the copper interacting with the squeezed abrasives was plastically deformed, yielding higher removal efficiency than when elastically deformed. The removal efficiency can be used as a standard metric for assessing the material removal ability of various consumables such as slurry, CMP pad and pad conditioner.

The presence of a protective surface layer is crucial for attaining planar wafer surfaces during copper CMP; this ensures that the wafer does not dissolve congruently, but rather that topographically protruding regions are removed selectively. Inhibitors such as BTA are typically added to the slurry to protect the recessed regions from being dissolved. While the formation of the protective layer has been studied widely, the removal of this layer is less understood; instead, studies of the removal of materials have focused on the copper itself, studied widely, the removal of this layer is less understood; instead, studies of the removal of materials have focused on the copper itself, based on the study of oxide CMP. To address this gap in knowledge, the present paper quantitatively analyzes the removal of the protective materials during copper CMP. The fraction of the protective material removed by the abrading action of a pad asperity on which numerous abrasive particles are embedded is defined as removal efficiency. The removal efficiency of a CMP pad was evaluated experimentally and analytically and the two compared.

Experimental

In situ electrochemical measurements were made during polishing using the apparatus shown in Figure 1 connected to a Gamry G300 Potentiostat. A three electrode electrochemical cell, housed in a table of a vertical machining center tool (Matsuura MC-510VSS). Cross-section of the copper working electrode is shown in the upper left.
plastic beaker, was constructed on the table 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. The surfaces of the copper electrode were insulated by epoxy except the bottom, where electrochemical reactions occurred and the corresponding current density was measured. The counter electrode was platinum mesh, placed under the polishing pad parallel to the copper electrode. A saturated calomel reference electrode (SCE) was placed in a Luggin capillary, and the tip of the capillary was located between the polishing pad and the counter electrode. An IC1010 (Rohm and Haas) CMP pad, through which four equispaced holes (4.76 mm diameter) were machined along the trajectory of the contact by the copper electrode (Figure 2), was fixed to the bottom of the beaker. The purpose of the through holes on the CMP pad was to reduce the uncompensated resistance between the working electrode and the counter electrode and facilitate the delivery of slurry to the region between the working electrode and the pad. The pad was maintained parallel to the open surface of the copper electrode to ensure a uniform pressure distribution across the copper during polishing. The polishing slurry contained 5 wt% alumina particles (primary diameter of 20 nm and a median aggregate diameter of 150 nm, from Cabot Corporation) and 0.01 M glycine in deionized water (DI water), with or without 0.01 M benzotriazole (BTA). The pH of the slurry was adjusted to 4 using acetate buffer. All potentials are reported with respect to the SCE.

The pressure applied on the copper surface was adjusted by vertically moving the axis of the machine tool; the position was numerically controlled as precisely as one micrometer. The load applied during polishing was measured by a load cell (TUF-010-025-S from Loadstar Sensors) placed under the electrochemical cell. The sliding velocity of the copper surface over the polishing pad was adjusted by varying the rotational speed of the working electrode.

The copper electrode was potentiodynamically polarized from −0.8 V to 0.8 V at a scan rate of 5 mV/s. The copper electrode was conditioned at −0.8 V for 30 seconds before each scan to remove any oxides on the surface. In situ IR compensation was not applied because of the noise in the output data. Scans were obtained while rotating or not rotating the copper electrode. Several scans made for each condition confirmed good reproducibility.

The CMP pad was conditioned before each experiment with a diamond conditioner (GNP Technology) while irrigating with DI water. The exposed surface of the copper working electrode was polished for 30 seconds before each experiment with an IC1010 CMP pad using the same slurry specified above to flatten the entire surface including the epoxy insulating layer, followed by additional polishing using a commercial CMP slurry for 30 seconds to reduce the topography of the copper surface. The electrode was then immediately rinsed with DI water. Any remaining oxide on the copper surface was reduced by polarizing at −1.5 V for 5 seconds followed by −1.2 V for 10 seconds while abrading the working electrode on the pad. The potential was then stepped up to 0.6 V and the current was measured for 10 seconds while polishing. In situ IR compensation was applied using an integrated function of the potentiostat. Since the experimental results were highly dependent on whether the surface of the copper electrode and the top surface of the pad were truly parallel, this was ensured throughout the measurements. Figure 2 shows the pad surface after CMP when the bottom of the copper was well aligned with the top surface of the pad. The uniform annular trajectory of the copper electrode demonstrates that the exposed surface of the copper electrode interacted with a corresponding annulus of the pad. Polishing was conducted with different down pressures and sliding velocities while maintaining the potential of copper at 0.6 V. The same experiments were repeated, while exerting a down pressure but holding the electrode stationary, to compare with the data for the rotating electrode. Experiments were repeated at least three times for each condition.

**Results**

Figure 3 shows the efficacy of BTA at protecting the surface of copper over the entire potential range of the scan. At anodic potentials the oxidation rates of the copper were nearly two orders of magnitude lower when the slurry contained BTA, compared to the rates measured in the absence of BTA. Consistent with the experimental observations of Tripathi et al., BTA also suppressed the current density at cathodic potentials, corresponding to reduction of oxygen, albeit less markedly. When the copper electrode slid over the CMP pad at 0.5 m/s under 24.8 kPa (3.6 psi) of down pressure, the current densities increased about two orders of magnitude in the anodic region, approaching the oxidation rates observed for the stationary electrode in the absence of BTA, demonstrating the efficacy of the abrading action in removing the protective layer on the surface of the copper.

---

**Figure 2.** IC1010 CMP pad with four machined holes after CMP of copper. Oxidized copper remained on the surface of the pad leaving an annular trajectory. Slurry, which appears white, remains on the left two holes.

**Figure 3.** Potentiodynamic polarization scan of copper electrode in a pH 4 slurry containing 0.01 M glycine and 5 wt% alumina abrasives with or without 0.01 M BTA. Scanned from −0.8 V to 0.8 V at 5 mV/s. Polishing, when used, was done with a sliding velocity of 0.5 m/s under 24.8 kPa (3.6 psi) of down pressure.
Note that the current densities in the cathodic region also increased when the copper was polished in the presence of BTA. This implies that the inhibition by BTA at cathodic potentials was induced by physical adsorption of BTA and the abrading actions by pad asperities and abrasives easily removed the weakly sorbed layer of BTA from the surface.

Figure 4 shows a typical chronoamperometry curve when the potential of copper was stepped up to an anodic potential, 0.6 V (SCE) while the copper electrode was polished. The current density decreased rapidly before stabilizing at a quasi-steady state after two seconds; thus the values for the first two seconds were excluded when evaluating the average current densities for each experimental condition. The initial decay of the current density (see the inset of Figure 4) was attributed to the adsorption of BTA on the oxide-free surface of copper despite the abrading action of the polishing pad. Capacitive charging of the macroelectrode was not considered because it was finished by 0.05 seconds in the absence of BTA (see filled circles in Figure 5) and the protective layer on the surface of copper would further reduce the time for the capacitive charging in the presence of BTA. After the initial decay of the current, a quasi-steady state was reached where the current densities were nearly constant, implying that the overall fraction of sites occupied by BTA remained constant, although the exact location of the occupancy would change as the asperities swept the surface of the copper. The noise of the measured current densities was due to the rotation of the copper electrode; the frequency of the noise exactly matched that of the rotation.

Figure 5 compares the decrease in the current densities over time for micro- and macro-electrodes, both of which were stationary, in a pH 4 aqueous solution containing BTA and glycine. It also shows that in the absence of BTA (upper curves) the current densities were almost constant after about 0.1 s. In the acquisition of the data shown in Figure 5, 5 wt% of alumina abrasives was added to the solutions used for the macro-electrode, whereas no abrasive was present in the tests using the microelectrode. Although stationary, the macro-electrode was in contact with the perforated CMP pad during the potential-step chronoamperometry measurements, to allow comparison with the currents measured during polishing. It was of interest to compare the data obtained using a macro-electrode in the polishing slurry used in this work with the data obtained by Tripathi et al. using a micro-electrode in the same aqueous solution, but without added alumina particles, because the adsorption kinetics of BTA for this case were known. Because of the different geometries, the current densities for the micro-electrode at any given time were about 22.7 times larger than those for the macro-electrode (see inset of Figure 5). To aid the comparison the data for the micro-electrode were scaled down by a factor of 22.7 in the main plot of Figure 5. It is clear that, with this correction, the relative magnitudes of the current densities in the absence and the presence of BTA coincided for the macro- and micro-electrodes over a protracted time period.

The differences in geometry between the micro- and macro-electrodes leads to much better mass transport for the microelectrode, which is surrounded by a spherical region of electrolyte into which oxidized products can be transported. In contrast, the configuration of the copper macro-electrode parallel to the platinum counter electrode, separated by perforated CMP pad, yielded a restricted electric field and poorer ability for oxidized products to be transported from the electrode. Despite the difference in the magnitude of the oxidation rates for the two types of electrode, the intrinsic mechanism for passivation would be unchanged. Therefore, the approach used by Choi et al. of considering the fractional coverage of the copper by Cu(O)BTA complexes as a function of time was adopted to examine the material removal efficiencies from the measured current densities. Figure 6 shows the average steady-state current densities of copper during polishing with different down pressures or sliding velocities. It is clear that the current densities in the absence of BTA, where protective material was not expected to form, were insensitive to the down pressure and sliding velocity. In contrast, the current densities in the presence of BTA, where some sites on the copper were expected to be protected, were always significantly lower than those in the absence of BTA, but increased steadily with down pressure and sliding velocity. This suggests that increasing pressure and velocity increased the amount of protective material removed from the surface of copper by the pad asperities and the abrasives embedded between the asperity and the copper or allowed less time for protective material to be adsorbed on the surface of copper, leaving more sites unprotected.

Discussion

Evaluation of the removal efficiencies from the experimental results.—Recalling the concept of a quasi-steady state, it is reasonable to assume that the steady current seen during polishing corresponds to a state in which the rate of removal of the protective material on copper is balanced by the rate of formation of new protective material. The removal of protective material by an asperity would be nearly instantaneous, whereas the protective material, Cu(II)BTA, reforms comparatively gradually, until the next interaction with another
The average duration of contact by a pad asperity on a given point on the copper, \( t_{as} \), was estimated assuming circular asperity and copper contacts:

\[
  t_{as} \leq \frac{d_{as}}{v}
\]

where \( d_{as} \) is the average diameter of the circular contacts between the asperities and copper and \( v \) is the sliding velocity of the wafer over the pad. Equation 1 gives a maximum because the duration of the contact varies with the wear distances\(^1\) across the circular contact, as shown in Figure 8.

The growth of the protective material on the copper surface is dependent on the coverage ratio, or fraction of occupied sites immediately after interaction with a pad asperity, characterized as \( \theta_0 \) in Figure 9, and the interval until the subsequent contact by another asperity, defined as \( t_{tas-as} \) in Figure 9. Throughout the following analysis, a fraction of a monolayer of the protective material is assumed to be formed on the surface of copper during CMP, on the basis of the findings of Choi et al.\(^3\) A complete monolayer of protective material is taken as a coverage ratio of unity.

The average time interval between two consecutive interactions of a given point on the surface of copper with asperities, \( t_{tas-as} \), can be determined by equating it with the time required to completely sweep the surface of the copper wafer by the asperities:

\[
  N_{as} d_{as} v t_{tas-as} = A_w \quad \text{or} \quad t_{tas-as} = \frac{A_w}{N_{as} d_{as} v}
\]

where \( N_{as} \) is the number of asperities that contact the surface of a wafer, \( d_{as} \) is the average diameter of the circular contact areas between asperities and a wafer and \( A_w \) is the surface area of a wafer. The number of asperities that contact the surface of a wafer is calculated by the following expression:

\[
  N_{as} = \frac{r_{contact} A_w}{d_{as}}
\]

where \( r_{contact} \) is the ratio of real area of contact between a CMP pad and a wafer to the nominal contact area and \( d_{as} \) is the average contact area of an asperity contacting the copper. Thus, assuming a circular contact area between an asperity and a wafer the time interval between consecutive contacts by asperities at a point on the surface of copper is determined as:

\[
  t_{tas-as} = \frac{\pi d_{as}}{4 v r_{contact}}
\]

where \( r_{contact} \) is an increasing function of the down pressure\(^6,7\) and \( d_{as} \) can either increase or stay constant with the down pressure. Both can be experimentally characterized using confocal reflectance interference contrast microscopy (C-RICM)\(^8\) or dual emission laser induced fluorescence (DELIF).\(^8\)

Once the experimentally observed average oxidation rate of copper is known, \( v_0 \) and \( t_{tas-as} \) can be determined from a plot of the oxidation rate of copper as a function of time elapsed since a bare surface of copper was raised to an anodic potential as illustrated in Figure 9. Since the measured oxidation rate, \( v_{measured} \), is the average of the current densities from the entire surface of the copper where some...
Table I. Removal efficiencies and BTA coverage ratios on the surface of copper during CMP under different experimental conditions. Pad topography parameters were from Elmufdi et al.6

| Condition | Down Pressure (kPa) | Sliding Velocity (m/s) | Pad topography parameter | \( t_{as-as} \) (ms) | \( \theta_0 \) | \( \theta_0 + t_{as-as} \) | \( \eta \) |
|-----------|---------------------|------------------------|--------------------------|-------------------|---------|-----------------|---------|
| 1         | 12.4                | 0.5                    | SPD-01                   | 8.71              | 0.530   | 0.505           | 0.841   |
| 2         | 24.8                | 0.25                   | CG-181060               | 4.35              | 0.820   | 0.566           | 0.790   |
| 3         | 24.8                | 0.5                    | CG-181060               | 8.31              | 0.0803  | 0.267           | 0.833   |
| 4         | 24.8                | 0.75                   | SPD-01                   | 2.90              | 0.532   | 0.505           | 0.748   |
| 5         | 24.8                | 1                      | SPD-01                   | 5.54              | 0.0479  | 0.217           | 0.798   |
| 6         | 37.2                | 0.5                    | SPD-01                   | 2.18              | 0.566   | 0.514           | 0.723   |
| 7         | 49.6                | 0.5                    | SPD-01                   | 2.18              | 0.545   | 0.509           | 0.722   |
| 8         | 62                  | 0.5                    | SPD-01                   | 1.74              | 0.340   | 0.443           | 0.689   |
| 9         | 86                  | 0.5                    | CG-181060               | 3.33              | 0.0368  | 0.195           | 0.746   |

Figure 9. Evaluation of \( t_0 \) from known \( t_{as-as} \), measured oxidation rate and the curve of the coverage ratio over time.
where \( \eta \) is the removal efficiency of the protective material on the surface of the copper.

**Analytical prediction of the removal efficiency.**—The removal efficiency was predicted analytically to compare with the removal efficiencies evaluated from the experimental data. The response of the protective material on the surface of copper, Cu(I)BTA, to the sliding abrasive particle is modelled as a sequence of events: (1) the abrasive particle leaves a new trajectory only when its sliding area had no overlap with the trajectory of the first abrasive particle, reducing the probability of the second abrasive removing protective material to the abrasives. Rolling of the embedded abrasives was not considered. If considered, it might reduce the evaluated removal efficiency because of the shorter moving distance than during sliding as illustrated in Figure 12. Since most of copper interacting with the sliding abrasives during CMP undergoes elastic deformation, Hertz contact theory was used to obtain the pressure induced in the copper by the force transmitted through the copper because it is very soft and thin.

The width of the sliding trajectory of an asperity was calculated by summing the expected widths of the sliding trajectories of the individual abrasives:

\[
w_{\text{as}} = (w_{\text{ab}})_1 + (w_{\text{ab}})_2 + (w_{\text{ab}})_3 + \ldots + (w_{\text{ab}})_{n_{\text{ab}}}
\]

where \( (w_{\text{ab}})_i \) is the expected width of the sliding trajectory of the \( i \)-th abrasive particle. The expected width of the sliding trajectory of the second abrasive is reduced by the probability that it overlaps with the trajectory of the first abrasive. Figure 11 shows that the second abrasive can leave a new trajectory only when its sliding area had no overlap with the trajectory of the first abrasive particle, reducing the probability of the second abrasive removing protective material to

\[
1 - \frac{w_{\text{as}}}{w_{\text{ab}}}.
\]

The same argument was applied to the remaining abrasives to determine the cumulative width of the sliding trajectories of all embedded abrasives.

It was assumed that the removed protective material did not redeposit on the surface of the copper; if it did, this would lower the removal efficiency. It was also assumed that the ability of abrasives to remove the protective material was not affected by the adherence of the removed protective material to the abrasives. The rolling of the embedded abrasives was not considered. If considered, it might reduce the evaluated removal efficiency because of the shorter moving distance than during sliding as illustrated in Figure 12. Since most of copper interacting with the sliding abrasives during CMP undergoes elastic deformation, Hertz contact theory was used to obtain the pressure induced in the copper by the force transmitted through the copper and the shape of the contact area. The width of the sliding trajectory of the first abrasive particle was estimated using Hertz contact theory as follows:

\[
(w_{\text{ab}})_1 = 2\sqrt{\frac{\kappa_{\text{as}}}{h}}
\]

where \( h \) is the penetration depth of an abrasive particle into elastically deformed copper, which is also determined using Hertz contact theory:

\[
h = \frac{3f_{\text{ab}}}{4E\tau_{\text{ab}}^{2/3}}
\]

where \( f_{\text{ab}} \) is the force transmitted by an abrasive to a wafer, \( E^* = \frac{1-v^2}{E_1} + \frac{1-v^2}{E_2} \).
or compress the double layer enough to eliminate the electrostatic repulsion between the particles.\textsuperscript{15,16} Henfeldt et al.\textsuperscript{17} estimated the force required to break up the agglomerates using the equations developed by Brown et al. to calculate the shear strength of a powder.\textsuperscript{18} Using their analysis, the lower and upper bounds of the force required to break up an agglomerate 20 nm in diameter were only 70 pN and 0.9–4 nN, respectively. These forces are nearly three orders of magnitude smaller than the force transmitted to an embedded abrasive (discussed below), suggesting that any agglomerates that may have been present in the slurry during the experiments would have been broken up when squeezed between an asperity and copper. Therefore, it was assumed in the following analysis that only individual abrasive particles were present in the area between asperities and copper.

Slurry containing abrasive particles wets the CMP pad and was present between the pad and the wafer during the CMP process. Neglecting any forces that could influence the spatial distribution of abrasives around the pad asperities, such as electrostatic and van der Waals interaction between abrasive particles and the pad material, the local concentration of abrasive particles in the slurry squeezed between the pad and the copper was assumed to be identical to that in the bulk slurry, $c_{ws}$, which is expressed as a ratio of the weight of abrasives to the total weight of the slurry. Further, assuming that the abrasive particles were rigid spheres with uniform radius, $r_{ab}$, the number of abrasive particles that are embedded between an asperity and copper, $n_{ab}$, is determined as:

$$n_{ab} = \frac{3c_{ws}r_{ab}\rho_{slurry}}{2\pi r_{ab}^3\rho_{ab}}$$

where $\rho_{slurry}$ and $\rho_{ab}$ are the density of slurry and abrasives, respectively. It was assumed that the number of embedded abrasives maintained a steady state in which abrasives in the slurry were continuously drawn into and discharged from the gap between the asperities and the copper as the wafer slid over the pad. The assumptions employed in this analysis are similar to those by Che et al.,\textsuperscript{19} Zhao et al.,\textsuperscript{20} and Bastawros et al.\textsuperscript{21} The estimated number of abrasive particles embedded into an asperity is listed in Table II for various concentrations of abrasives in the slurry.

### Force applied on an abrasive

The force applied on an abrasive particle that is embedded between an asperity and copper was estimated by evaluating the upper and lower extreme situations where pad asperities are deformed by the embedded abrasive particles as shown in Figure 13. Note that pad asperities will be deformed by the applied force in preference over the abrasives and copper because the pad material has a much lower elastic modulus and hardness than copper and abrasives. The upper bound of the estimated force is obtained when the pad asperity is not deflected enough to contact the surface of the copper (Figure 13a). Thus the force applied to the asperity is supported only by the embedded abrasives. The upper bound of the estimated force on an abrasive, $f_{ab-lb}$, is then:

$$f_{ab-lb} = f_{as}/\tilde{n}_{ab}$$

where $P$ is the nominal down pressure applied on a wafer. Using the values used in this work, the average force per asperity was 0.2 mN or 0.5 mN when pad surface topography parameters for SPD-01 or CG-181060 conditioners, respectively, were used.

### Number of abrasive particles embedded between an asperity and copper

Alumina abrasives may agglomerate when the pH of a slurry, the ionic strength or additives in a slurry lower the zeta potential

$$n_{ab} = \frac{3c_{ws}r_{ab}\rho_{slurry}}{2\pi r_{ab}^3\rho_{ab}}$$

where $\rho_{slurry}$ and $\rho_{ab}$ are the density of slurry and abrasives, respectively. It was assumed that the number of embedded abrasives maintained a steady state in which abrasives in the slurry were continuously drawn into and discharged from the gap between the asperities and the copper as the wafer slid over the pad. The assumptions employed in this analysis are similar to those by Che et al.,\textsuperscript{19} Zhao et al.,\textsuperscript{20} and Bastawros et al.\textsuperscript{21} The estimated number of abrasive particles embedded into an asperity is listed in Table II for various concentrations of abrasives in the slurry.

### Force applied on a pad asperity

The force applied on pad asperity—The insensitivity of removal efficiencies to the down pressure in Figure 10 could be explained if the average area of an asperity-copper contact was independent of the down pressure. Although this may seem counterintuitive, and indeed is invalid if considering the contact area of a specific asperity, it is worth recalling that during copper CMP the number of asperities contacting a wafer is a small fraction of the total number of asperities. Hence the Gaussian distribution of asperity heights\textsuperscript{13} can be approximated to an exponential distribution, which results in the number of abrasive particles embedded between an asperity and copper, $n_{ab}$, as determined as:

$$n_{ab} = \frac{3c_{ws}r_{ab}\rho_{slurry}}{2\pi r_{ab}^3\rho_{ab}}$$

where $\rho_{slurry}$ and $\rho_{ab}$ are the density of slurry and abrasives, respectively. It was assumed that the number of embedded abrasives maintained a steady state in which abrasives in the slurry were continuously drawn into and discharged from the gap between the asperities and the copper as the wafer slid over the pad. The assumptions employed in this analysis are similar to those by Che et al.,\textsuperscript{19} Zhao et al.,\textsuperscript{20} and Bastawros et al.\textsuperscript{21} The estimated number of abrasive particles embedded into an asperity is listed in Table II for various concentrations of abrasives in the slurry.

$$f_{ab-lb} = f_{as}/\tilde{n}_{ab}$$

where $P$ is the nominal down pressure applied on a wafer. Using the values used in this work, the average force per asperity was 0.2 mN or 0.5 mN when pad surface topography parameters for SPD-01 or CG-181060 conditioners, respectively, were used.

$$n_{ab} = \frac{3c_{ws}r_{ab}\rho_{slurry}}{2\pi r_{ab}^3\rho_{ab}}$$

where $\rho_{slurry}$ and $\rho_{ab}$ are the density of slurry and abrasives, respectively. It was assumed that the number of embedded abrasives maintained a steady state in which abrasives in the slurry were continuously drawn into and discharged from the gap between the asperities and the copper as the wafer slid over the pad. The assumptions employed in this analysis are similar to those by Che et al.,\textsuperscript{19} Zhao et al.,\textsuperscript{20} and Bastawros et al.\textsuperscript{21} The estimated number of abrasive particles embedded into an asperity is listed in Table II for various concentrations of abrasives in the slurry.

$$f_{ab-lb} = f_{as}/\tilde{n}_{ab}$$

where $P$ is the nominal down pressure applied on a wafer. Using the values used in this work, the average force per asperity was 0.2 mN or 0.5 mN when pad surface topography parameters for SPD-01 or CG-181060 conditioners, respectively, were used.
abrasive particle, in general, can be written as:

$$f_{ab-int} = f_{as} \left( \frac{\pi \eta_{ab}^2}{\pi \eta_{ab}^2 \eta_{ab} + 4 \eta_{as-def}^2} \right)$$  \hspace{1cm} [17]$$

where $\eta_{as-def}$ is the contact area between copper and the asperity that is deformed by the embedded abrasives.

The estimated upper and lower bound forces applied to an abrasive for the varied concentrations of abrasives are listed in Table II. The upper bound of the estimated force transmitted to each embedded abrasive particles decreased with increasing concentration of the abrasives, from 3.06 μN or 4.11 μN for 0.5 wt% of abrasives to 0.304 μN or 0.411 μN for 5 wt% of abrasives when pad topography parameters for SPD-01 or CG-181060, respectively were used. In contrast, the lower bound of the estimated force applied to an abrasive was 5.78 nN or 7.80 nN for pad topography parameters for SPD-01 or CG-181060, respectively, regardless of the concentrations of the abrasives.

**Prediction of the removal efficiency.**—Applying this analysis to predict the removal efficiencies using Equation 7 and 8 for the experimental conditions 1 to 8 in Table I, removal efficiencies of 0.208 and 0.582 were obtained for the lower and upper bounds of the estimated forces, respectively when conditioning with an SPD-01 conditioner, assuming that the copper underwent elastic deformation only. If copper was considered to undergo plastic deformation, a removal efficiency of 0.678 was predicted for the upper bound of the estimated force. For a pad conditioned with a CG-181060 conditioner, the predicted removal efficiencies were 0.280 and 0.709 for copper elastically deformed by the lower and upper bounds of the estimated forces, respectively, and 0.844 for copper plastically deformed by the upper bound of the estimated force. Note that all the experimental conditions 1 to 8, other than conditions 1 and 2 for the CG-181060 conditioner, yielded the same experimental removal efficiencies for each conditioning specification because the average area of the asperities and copper contacts was assumed to be invariable. The experimentally determined removal efficiencies shown in Table I ranged between the analytically predicted value for copper elastically deformed by the lower bound of the force and the value for plastically deformed copper, which is physically valid.

To further examine the validity of the analysis, chronomoamperometry measurements were made during polishing with various concentrations of abrasives in the slurry, with other conditions unchanged. Four different abrasive concentrations were used, namely 0.5, 1, 3 and 5 wt% of alumina abrasives in the slurry. The experimental data, analyzed by Equation 7 and 8, for pad topography parameters for either an SPD-01 or CG-181060 conditioner, yield removal efficiencies indicated in Figure 14. The analytical prediction is presented as curves in Figure 14. The upper bound of the estimated force on an abrasive gave two different curves, one for the condition where the copper undergoes plastic deformation and the other for elastic deformation. However, the lower bound of the estimated force gave only a curve for elastic deformation of copper because the indentation depth is only a fraction of the diameter of a copper atom, 0.6 Å or 0.7 Å for pad topography parameters for SPD-01 or CG-181060, respectively, which is too small to initiate dislocations in the crystal lattice and hence plastic deformation.

The width of the trajectories of abrasives when the copper was plastically deformed was calculated using the nanohardness value, 15 GPa, obtained from molecular dynamic (MD) simulation of nanoindentation at appropriate length scales for copper CMP. This value is nearly an order of magnitude larger than the hardness measured by nanoindentation with higher loads and deeper depths due to the significant size effect. The penetration depths caused by the force applied on an abrasive particle, used to determine the widths of the trajectories for different concentrations of abrasives in the slurry, are listed in Table II. The upper bound force estimate gave a penetration depth of the order of 1 nm for plastic deformation, which is of the same order as the roughness after copper CMP. For lower concentrations of the abrasives, the experimentally evaluated removal efficiencies approximated well the analytical predictions for copper elastically deformed by the lower bound of the

---

**Table II.** Number of abrasive particles embedded between an asperity and the wafer, force on an embedded abrasive particle, maximum shear stress and penetration depth induced by the applied force for different concentrations of abrasives. The down pressure, the sliding velocity and the diameter of abrasive were 24.8 kPa, 0.5 m/s and 20 nm, respectively. Pad topography parameters were from Elmufdi et al. a

| $c_{ab}$ (wt%) | Pad topography parameter | $h_{ab}$ (μm) | $f_{ab}$ (upper) (μN) | $f_{ab}$ (lower) (nN) | $\tau_{max}$ (upper) (GPa) | $\tau_{max}$ (lower) (GPa) | $h_{50}$ (upper) (nm) | $h_{50}$ (lower) (nm) | $a_{ab} h_{ab}/r_{ab}$ (%) |
|---------------|--------------------------|----------------|----------------------|----------------------|---------------------------|---------------------------|----------------------|----------------------|--------------------------|
| 0.5           | SPD-01                   | 66             | 3.06                 | 5.78                 | 12.3                      | 1.51                      | 3.6                  | 0.06                 | 0.188                    |
|               | CG-181060               | 133            | 4.11                 | 7.80                 | 13.5                      | 1.67                      | 4.4                  | 0.07                 | 0.190                    |
| 1             | SPD-01                   | 133            | 1.52                 | 5.78                 | 9.71                      | 1.51                      | 2.2                  | 0.06                 | 0.380                    |
|               | CG-181060               | 266            | 2.05                 | 7.80                 | 10.7                      | 1.67                      | 2.7                  | 0.07                 | 0.380                    |
| 3             | SPD-01                   | 399            | 0.507                | 5.78                 | 6.73                      | 1.51                      | 1.1                  | 0.06                 | 1.14                     |
|               | CG-181060               | 798            | 0.684                | 7.80                 | 7.44                      | 1.67                      | 1.3                  | 0.07                 | 1.14                     |
| 5             | SPD-01                   | 665            | 0.304                | 5.78                 | 5.68                      | 1.51                      | 0.77                 | 0.06                 | 1.90                     |
|               | CG-181060               | 1330           | 0.411                | 7.80                 | 6.28                      | 1.67                      | 0.94                 | 0.07                 | 1.90                     |
estimated force, regardless of the assumed pad surface topography parameters. This implies that the pad asperities supported by the abrasives were deformed enough to encapsulate the copper, such that the force applied to the embedded abrasive particles approached the lower bound of the estimate. In contrast, for higher abrasive concentrations the experimentally evaluated removal efficiencies exceeded the prediction for copper elastically deformed by the lower bound force estimate. This suggests that the pad asperities supported by the embedded abrasives were deflected to partly contact the surface of the copper as depicted in Figure 13b. As the concentration of the abrasive particles increased, the portion of the asperity ($a_{asp}$) contacting the wafer decreased, so that a higher force was borne by the abrasives. This behavior would be expected, as the distance between the embedded abrasive particles decreased with increasing concentration of the abrasives. Nevertheless, the separation between the embedded abrasive particles remained much larger than the size of the abrasives; only 1.90% of area was occupied by the abrasive particles held under an asperity contacting the copper when 5 wt% abrasives was used, as indicated in Table II. The conclusion that deflected asperities completely or partly contacted the copper is consistent with the work of DeNardis et al.\textsuperscript{10} and Li et al.\textsuperscript{36} who deduced a contact mode during copper CMP from the slopes of experimentally obtained Stribeck curves. The contact mode during copper CMP was “partial lubrication”, in which abrasive particles present under an asperity, the possibility increases that a region on the surface of copper undergoes multiple abrasions, leading to more sites on the copper that could deform plastically. As a result, the overall removal efficiency by a pad asperity for these cases increased, because the contact area during plastic deformation is higher than that during elastic deformation.

### Conclusions

The efficiencies of abrasive particles that are embedded into a pad asperity in removing protective material from the surface of copper during CMP were determined experimentally and analytically, then compared. The experimentally determined removal efficiencies were insensitive to the down pressure and the sliding velocity, agreeing well with the analytical analysis due to the insensitivity of the average contact area of a single pad asperity and copper to pressure. Comparison of the analytically and experimentally determined removal efficiencies for various concentrations of the abrasives in the slurry suggested that the pad asperities encapsulated the embedded abrasive particles and contacted the surface of the copper at abrasive concentration up to 1 wt%, so that minimum load is exerted to the copper by the abrasives. At higher abrasive concentrations, up to 5 wt%, the fraction of asperity and copper contact decreased, so that higher loads are applied to the copper by the embedded abrasives. With more abrasive particles in the slurry, the frequency of copper and embedded abrasive contacts under a pad asperity increases, increasing the possibility that the interaction will plastically deform the copper. This will eventually increase the contact area between the abrasive particles and the protective material on the copper surface, resulting in more removal of protective material by the abrasives.

In short, the removal efficiency is a function of consumable variables, such as the pad surface topography parameters, determined by the type of pad and the conditioning specification, and the concentration of abrasive in the slurry. The analytical and experimental approaches outlined in this work could be applied to compare the material removal ability of various consumables such as slurry, CMP pads, and pad conditioner, using removal efficiency as a standard metric for comparison. More importantly, the analyses are essential for completing the mechanistic model that predicts the MRR during CMP proposed by Choi et al.\textsuperscript{4} Once the number of abrasive particles that are embedded between a pad asperity and the wafer is known, the analytical solution given in this work can directly evaluate the removal efficiency of a set of consumables and eventually predict the MRR for a given processing and consumables variables. The incomplete portion of the analysis, which is the influence of the slurry chemistry and the processing conditions on the behavior of the abrasive particles, must be understood to estimate the number of abrasive particles squeezed between a pad asperity and copper and hence to complement the mechanistic MRR model.

### Acknowledgments

This work was supported in part by the UC Discovery grant under the IMPACT program, and AMD, Applied Materials, ASML, Cadence, Canon, Ebara, Hitachi, IBM, KLA-Tencor, Magma, Marvell, Mentor Graphics, Novellus, Panoramic, SanDisk, Spansion, Synopsys, Tokyo Electron Limited, and Xilinx, with donations from Photronics and Toppan. This work was also supported by a Lam Research Graduate Fellowship.
References

1. Shantanu Tripathi. 2008, Tribo-chemical mechanisms of copper chemical mechanical planarization (CMP) - Fundamental investigations and integrated modeling. Ph.D. Thesis University of California, Berkeley. Ann Arbor: ProQuest/UMI. (Publication No. 3353284.)

2. S. Tripathi, S. Choi, F. M. Doyle, and D. A. Dornfeld, Mater. Res. Soc. Symp. Proc., 1157, E02 (2009).

3. S. Choi, S. Tripathi, D. A. Dornfeld, and F. M. Doyle, J. Electrochem. Soc., 157, H1153-9 (2010).

4. S. Choi, F. M. Doyle, and D. Dornfeld, Procedia Eng., 19, 73 (2011).

5. S. Choi. 2013, Physicochemical Modeling of Copper Chemical Mechanical Planarization (CMP) Considering Synergies in Removal Materials. PhD thesis, University of California, Berkeley. Ann Arbor: ProQuest/UMI. (Publication No. 3616430.)

6. C. L. Elmufdi and G. P. Muldowney, Mater. Res. Soc. Symp. Proc., 991, 0991-02 (2007).

7. T. Sun, Y. Zhuang, L. Borucki, and A. Philipossian, Jpn. J. Appl. Phys., 49, 066501 (2010).

8. C. Gray, C. Rogers, V. P. Manno, R. White, M. Moinpour, and S. Anjur, Mater. Res. Soc. Symp. Proc., 991, 0991-04 (2007).

9. J. A. Greenwood and J. B. P. Williamson, Proc. R. Soc. Lond. A, 295, 300 (1966).

10. D. DeNardis, J. Sorooshian, M. Habiro, C. Rogers, and A. Philipossian, Jpn. J. Appl. Phys., 42, 6809 (2003).

11. S. Aksou and F. M. Doyle, J. Electrochem. Soc., 149, G352 (2002).

12. K. L. Johnson, Contact Mechanics, p. 90, p. 208, Cambridge University Press, Cambridge, UK (1985).

13. T. Yu, C. Yu, and M. Orłowski, Proceedings of the 1993 International Electron Devices Meetings, IEEE, Washington DC, December, p.35 (1993).

14. T. Sun, L. Borucki, Y. Zhuang, and A. Philipossian, Microelectron. Eng., 87, 553 (2010).

15. R. Ihnfeldt and J. B. Talbot, J. Electrochem. Soc., 153, G948 (2006).

16. R. Ihnfeldt and J. B. Talbot, ECS Trans., 3, 21 (2007).

17. R. Ihnfeldt and J. B. Talbot, J. Electrochem. Soc., 154, H1018 (2007).

18. R. L. Brown and J. C. Richards, Principles of Powder Mechanics, Pergamon, Elmsford, NY (1970).

19. W. Che, Y. Guo, A. Chandra, and A. Bastawros, J. Manuf. Sci. Eng., 127, 545 (2005).

20. Y. Zhao and L. Chang, Wear, 252, 220 (2002).

21. A. Bastawros, A. Chandra, Y. Guo, and B. Yan, J. Electron. Mater., 31, 1022 (2002).

22. G. Ziegenhain, A. Hartmaier, and H. M. Urbassek, J. Mech. Phys. Solids, 57, 1514 (2009).

23. D. Saraje and R. E. Miller, Modell. Simul. Mater. Sci. Eng., 13, 1089 (2005).

24. S. Chang, T. Chang, and Y. Lee, J. Electrochem. Soc., 152, C657 (2005).

25. D. Beguin, S. Chowdhury, and M. T. Laugier, Surf. Coat. Technol., 201, 5804 (2007).

26. Y. M. Soifer, A. Verdyun, M. Kazakevich, and E. Rabkin, Scr. Mater., 47, 799 (2002).

27. R. Ihnfeldt and J. B. Talbot, J. Electrochem. Soc., 155(6), H412 (2008).

28. C. Liao, D. Guo, S. Wen, and J. Luo, Tribol. Lett., 45, 309 (2011).

29. J. G. Swadener, E. P. George, and G. M. Pharr, J. Mech. Phys. Solids, 50, 681 (2002).

30. S. Gu, Y. Huang, W. D. Nix, H. Jiang, F. Zhang, and K. C. Hwang, J. Mater. Res., 19, 3423 (2004).

31. W. D. Nix and H. Gao, J. Mech. Phys. Solids, 46, 411 (1998).

32. Y. Huang, F. Zhang, K. C. Hwang, W. D. Nix, G. M. Pharr, and G. Feng, J. Mech. Phys. Solids, 54, 1668 (2006).

33. G. Feng, A. S. Budiman, W. D. Nix, N. Tamura, and J. R. Patel, J. Appl. Phys., 104, 043501 (2008).

34. N. Chandrasekaran, S. Ramarajan, W. Lee, G. M. Sabde, and S. Meikle, J. Electrochem. Soc., 151, G882 (2004).

35. M. T. Wang, M. S. Tsai, C. Liu, W. T. Tseng, T. C. Chang, L. J. Chen, and M. C. Chen, Thin Solid Films, 308, 518 (1997).

36. Z. Li, K. Ina, P. Lejeune, F. Koshiyama, and A. Philipossian, J. Electrochem. Soc., 152, G299 (2005).