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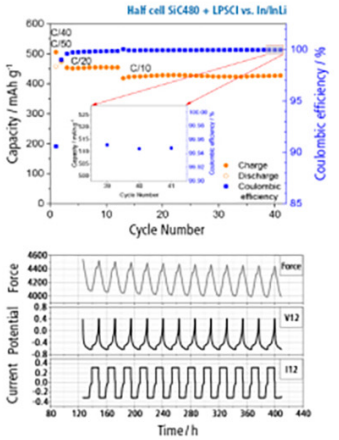
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Use of Slurry Colloidal Behavior in Modeling of Material Removal Rates for Copper CMP

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The effects of slurry chemistry through measured particle aggregate size distribution data were incorporated into the model of chemical mechanical planarization (CMP) of Luo and Dornfeld to predict material removal rate (MRR). This model was able to predict the trends of MRR for copper CMP as observed experimentally from the literature, such as the highest MRR for an alumina slurry with H_2O_2 in the range of 2–3.6 wt % and 0.1 M glycine. The model was also used to predict MRR for slurries that contained a combination of common additives.
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Chemical mechanical planarization (CMP) is a complex process involving numerous parameters such as wafer down pressure, wafer velocity, slurry chemistry, and abrasive particle, pad, and substrate characteristics. In addition to these variables, chemical interactions between the slurry, pad, and wafer affect CMP performance, making it difficult to understand and, therefore, to model. Most existing models of CMP focus on a specific aspect of the process. Although chemical action can modify the surface removal rates with or without abrasion, there has been little modeling of the chemical aspects of CMP. Our research has investigated the colloidal behavior of copper CMP slurries through the measurement of zeta potential and particle agglomerate size distribution.[1,2] The objective of this study was to incorporate experimentally measured agglomerate size data as a function of slurry chemistry into an existing model of CMP of Luo and Dornfeld[3] to predict material removal rate (MRR) for copper and compare the predictions to experimental polishing results from the literature.

The most widely used and well-known model of CMP is Preston's equation in which the material removal rate (MRR in nm/min) is a linear function of both wafer down pressure (P in Pa) and relative linear velocity (v in cm/s)[4]

$$\mathrm{MRR} = K_p P v \quad [1]$$

where K_p (in Pa^{-1}) represents the effects of the other variables and depends upon the chemical system.[4] Preston's equation is based on concepts derived from mechanical polishing,[4] but fails to provide insight into the interactions of the process even from a mechanical point of view, such as effects of particle size, particle concentration, pad characteristics, etc. Furthermore, many experimental results show a nonlinear relationship between polishing rate and pressure and velocity.[3,5]

Boning's model, which is widely used in industry, leverages Preston's equation for various wafer pattern densities over the entire wafer surface to predict MRR, but still does not address other nonmechanical CMP factors.[6] There are a few models that focus on the chemical aspects of CMP. Stein's heuristic model describes the role of surface chemistry of the colloids.[7] Gutman et al. developed a two-step reaction-based model that correlated the removal rate as a function of the active chemical species in the slurry.[8] Gokis and Kistler proposed a synergistic model that incorporates both chemical and mechanical aspects of CMP and shows that the chemical action cannot be separated from the mechanical removal.[9] Oliver has provided a summary of models for metal CMP.[10]

Luo and Dornfeld developed a comprehensive model of CMP that includes down pressure, velocity, wafer hardness, pad hardness, pad roughness, abrasive size, and abrasive geometry to calculate material removal rate.[3] Their simplified model equation for material removal rate is

$$\mathrm{MRR} = \rho_w N V + C_o \quad [2]$$

where ρ_w is the density of the wafer, N is the number of active abrasives, V is the volume of material removed by a single abrasive, and C_o is the material removal rate due to chemical etching, which is usually negligible compared to the overall material removal rate.[3]

The model assumes a solid-solid contact mode (rather than a hydrodynamic mode) with plastic contact at the wafer-abrasive interface, elastic contact at the pad-abrasive interface, a normal distribution of abrasives, and periodic roughness of the pad surface.[3] The interaction between the chemical and mechanical effects is through a fitting parameter H_w, which represents the dynamic hardness of the wafer surface in the model.[3]

The important relationship for volume removed by an abrasive, V is given by[3]

$$V = dav = \frac{\sqrt{2}}{3}\frac{x^2 E_p}{(bH_w)^{2/3}} P^{1/2} v \quad [3]$$

where x is the average diameter of the active abrasives, d is the penetration depth of the abrasive particle into the wafer, a is the radius of the projected circle of contact between the abrasive and the wafer, and E_p is the Young's modulus of the pad. The parameter $b = \pi D_s^{1/3}(3R/4)^{2/3}$, where D_s is the uniform area density of the spherical contact points of radius R on the pad. The number of abrasives in the wafer-pad interface is calculated from the slurry concentration and dilution ratio with water. The number of active abrasives, N in Eq. 2, is determined by multiplying this total number of abrasives by only a portion of a normal distribution of particles with diameter equal or smaller to $x + 3\sigma$, where σ is the standard deviation. The final model equation, assuming that chemical removal C_o is negligible, is

$$\mathrm{MRR} = C_1[1 - \Phi(3 - C_2 P^{1/3})]P^{1/2} v \quad [4]$$

where

$$C_1 = \rho_w k^2 A_o \frac{2 d_s \rho_s m D_s a l \sqrt{2}}{\rho_a \pi x}\frac{E_p}{(bHw)^{3/2}} \quad [5]$$

$$C_2 = \frac{0.25\left(\frac{4}{3}\right)^{2/3}(x + 3\sigma)\left(\frac{1}{H_P} + \frac{2}{H_W}\right)}{\sigma}\frac{E_P^{2/3}}{b} \quad [6]$$

where $k = 1 + 3\sigma/x$, A_o is the apparent contact area of the pad asperities on the wafer, d_s is the dilution ratio of the slurry to water, ρ_s is the density of the slurry before dilution, m is the concentration of the slurry before dilution, ρ_a is the abrasive density, ρ_w is the wafer material density, 1 is the mean height of a contact asperity, and H_p is the pad hardness. The dependence of MRR on velocity is linear.

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However, the dependence on applied down pressure is more complicated as the normal probability function Φ is a function of $P^{1/3}$; but in general there is a linear dependence for the pressure range of interest.[3] The effect of the slurry chemistry on the wafer surface is characterized by ρ_w and H_w.[3] Chemical reactions on the wafer surface may form a layer with a different hardness than the bulk wafer material.[3] In CMP, this is the layer that is mechanically removed by the abrasive particles.

The number of active abrasives is affected by the pad hardness. For constant pad hardness, a larger contact ratio (smooth pad) results in less material removal due to a smaller force experienced by each abrasive and the volume removed by a single abrasive decreases. The active abrasive number and V are both dependent on wafer hardness, resulting in higher removal rates for a softer wafer surface.[3] Using this model, an optimal abrasive size can be calculated for maximizing material removal rate.[3] Because the slurry is one of the most expensive consumables for CMP, an optimization of abrasive size would be useful. The model is sensitive to variations in the average abrasive diameter and the standard deviation of its size distribution simplified from Eq. 4 as

$$\text{MRR} \propto \frac{(x + 3\sigma)^2}{x^3} \qquad [7]$$

Therefore, for large agglomerate diameter ($x > \sim 750$ nm), MRR will not vary much for small variations in σ. However, for smaller particle (agglomerate) diameters the model will exhibit notable variations in MRR for small variations in σ.

A comparison of predictions of Luo and Dornfeld's model to experimental MRR data for SiO_2 CMP showed good agreement within $\pm 7\%$.[1,3] Also, Luo and Dornfeld's model agrees more closely than does Preston's equation for the given set of experimental data.[3]

The goal of our research was to incorporate the effects of the colloidal behavior of a copper CMP slurry into Luo and Dornfeld's model. In our previous work, colloidal behavior was characterized through the measurement of zeta potential and effective particle size distribution of alumina ($\sim$120 nm diam) as a function of copper CMP slurry chemistry.[1] It was found that the addition of 1 mM to 0.1 M glycine stabilized the zeta potential for alumina particles over a large pH range. Although slurry pH has the largest effect on zeta potential and agglomerate size distribution, sodium dodecyl sulfate (SDS) caused alumina to maintain as a small aggregate size ($\sim$200 nm), while ethylenediaminetetraacetic acid (EDTA) caused alumina to agglomerate ($\sim$1.2–2 μm) over the entire pH range investigated. When the pH was much less than the isoelectric point the particles were positively charged (except for solutions with SDS) and the size distributions were narrow. As the pH neared the IEP, the particle size distributions become broad and even bimodal. In this paper, these agglomerate size distributions are incorporated in the Luo and Dornfeld model through an average abrasive size and standard deviation to obtain MRR trends. For the first time, experimentally measured slurry particle size data has been incorporated into a CMP model instead of using hypothetical particle size distributions. As CMP models are typically specific for each wafer material system, the focus of this work has been on copper CMP.

Results and Discussion

Effect of shear force on effective particle size.— Because slurry particles can agglomerate depending upon solution chemistry,[1] it is important to investigate the maximum aggregate size during the CMP process. The actual nature of the particle distribution during CMP is needed for accurate modeling. Luo and Dornfeld's model assumes that the abrasive particles in the slurry have a normal size distribution.[1] Due to slurry chemistry and the polydispersed nature of the abrasive particles, this may not necessarily be the case. Additionally, during CMP, particles can experience a shear rate in the range of 10^4 to 10^6 s^{-1} which may cause aggregates to break up.[11]

The agglomerate size distributions that were used in Luo and Dornfeld's model to predict MRR to be discussed were necessarily measured under quiescent conditions.[1] To understand the agglomerate size distribution under CMP conditions, an analysis was done on the forces acting on the particles during CMP.[1] For the particle aggregates (flocs) to break up, other external forces experienced, namely the shear force, must exceed the binding force between the particles. To estimate the maximum aggregate size, the limiting collision efficiency, which is the fraction of collisions that lead to permanent attachment, was calculated.[1] The approach used to calculate limiting collision efficiency considered van der Waals attraction, neglects double layer repulsion, and assumes one particle size. The limiting collision efficiency as a function of applied shear and particle size was calculated for primary particle sizes of 100–500 nm.[1] In the shear rate range relevant to CMP, the limiting collision efficiency ranges from 0.1 to 0.37. This means that for most typical ranges of particle size and shear rate in CMP, particles do not aggregate. The small fraction that does agglomerate will be limited by a maximum floc size.[12]

Table I. Maximum floc effective diameter for particles under shear.

	Maximum floc effective diameter (nm) for shear rate (s^{-1})		
Particle diameter (nm)	10^4	10^5	10^6
100	940	300	94
200	1300	440	130
300	1600	520	160
400	1900	600	190
500	2100	670	210

Torres et al. balanced the van der Waals force between two particles with the hydrodynamic force acting to separate two aggregates resulting in the following expression that gives the maximum aggregate diameter D_{max} as a function of applied shear rate and particle size[13]

$$D_{max} = \left(\frac{aA}{18\pi\mu G\delta^2} \right)^{1/2} \qquad [8]$$

where A is the Hamaker constant (J), G is the shear rate (s^{-1}), μ is the viscosity (Pa-s), a is the particle radius (nm), and δ is the separation of the particles in the primary minimum potential energy (nm). For typical linear velocities of 5–20 cm/s and approximate distance between a particle and pad of 10–100 nm for CMP, shear rates of 10^6 to 5×10^8 s^{-1} were calculated.[1] Assuming $A = 10^{-20}$ J, $\mu = 10^{-3}$ Pa-s, and $\delta = 1$ nm as approximate values for alumina in an aqueous suspension,[12] the maximum aggregate diameter was calculated as a function of particle diameter and shear rate as shown in Table I. If the shear rate is 10^6 s^{-1} or greater, all aggregates will totally break up for particle diameters of 100–500 nm (as $D_{max} < 2a$). As shown in Table I, for lower shear rates of 10^5 and 10^4 s^{-1} particles may aggregate with floc diameters from approximately 300 nm to 2 μm.

From these calculations it is concluded that Luo and Dornfeld's assumption that typical abrasive particles of 100–500 nm diam are generally not agglomerated during the CMP process is valid as long as the shear rate is above 10^6 s^{-1}. However, if particles experience a shear of 10^6 s^{-1} or less aggregate formation and its effect on the effective particle size distribution must be taken into consideration, as shown in Table I.

The average agglomerate size and standard deviations obtained from our measurements were used in the Luo and Dornfeld model. All MRR predictions that are presented were for a shear rate of 10^3 s^{-1} where agglomeration effects would have to be taken into consideration. For a shear rate of 10^6 s^{-1} or larger, the model would predict the same MRR for the entire range of pH investigated, be-

Table II. Comparison of experimental and predicted MRR for reported aggregate size data for alumina slurries with various organic acids.[14]

Organic acid	Zeta potential (mV)	Mean particle diameter (nm)	Particle size standard deviation (nm)	Experimental MRR (nm/min)	Predicted MRR (nm/min)
Citric acid	−27	110	3	357	100
Oxalic acid	−14	600	25	453	130
Succinic acid	−8	2100	350	69	1

cause all agglomerates would completely break up and the effects of changes in particle size distribution with different slurry chemistries do not need to be considered.

Comparison of experimental and model material removal rates.— Our experimental particle size distribution data as a function of slurry chemistry were used in the Luo and Dornfeld model to predict MRR.[1] Because Luo and Dornfeld's model assumes a normal particle size distribution, the average abrasive size and standard deviation from our experimental particle size measurements were used in the model to predict MRR. These predictions are compared to experimental copper polishing data from the literature. Luo and Dornfeld's model for MRR predictions requires abrasive size, abrasive size standard deviation, down pressure, and wafer velocity. Although there are many studies of copper CMP, only two were found that have published copper CMP experimental removal rates with these parameters by Hong et al.[14] and Seal and co-workers.[15] Typical Cu CMP values were assumed when other necessary MRR parameter values for the model were not stated and these will be reported for each set of data.

Hong et al. studied the effects of slurry additives on the etch rate of copper and on the MRR during copper CMP with alumina slurries.[14] The focus of their investigation was the effects of three different organic acids, citric ($C_6H_8O_7$), oxalic ($C_2H_2O_4$), and succinic ($C_4H_6O_4$) acid, as oxidizing agents buffered to pH 6. The slurry contained 1 wt % of an organic acid as well as 3 wt % alumina (primary alumina abrasive diameter of 50 nm), 10 vol % H_2O_2, and NH_4OH to buffer to pH 6. Hong et al.'s experimental removal rates were compared to model predictions by using the reported particle size distributions as listed in Table II, carrier and platen velocity of 30 rpm, abrasive concentration of 3 wt %, and down pressure of 6.5 psi. A wafer hardness of 7.9 GPa was used in the model as assumed by Luo and Dornfeld.[3] Because pad hardness was not reported in the Hong paper, the pad hardness of a commonly used Cu CMP pad, namely the IC60 pad, was used (100 MPa).

Hong et al. found that the removal rate of copper was strongly dependent on the type of organic acid used as shown in Table II.[14] Table II also lists the reported zeta potential and mean particle diameter for the alumina slurries with the different organic acids. The standard deviation for the alumina slurries was not reported and hence standard deviation values typical for alumina for the given size and zeta potential range were used as observed in our previous work.[1] The highest experimental removal rate was 453 nm/min for the oxalic acid-containing slurry and the lowest was 69 nm/min for the succinic acid-containing slurry. The model predicted a similar trend as that seen with experimental polishing results of Hong et al., but under-predicted the removal rate. The experimental removal rate increased approximately 26% from 357 nm/min for oxalic acid to 453 nm/min for citric acid. The model predictions also saw a similar increase of 30% from 100 nm/min for oxalic acid to 130 nm/min for citric acid. Both the experimental and model predicted removal rates were significantly lower for the slurry containing succinic acid. The differences in predicted and experimental removal rates could be due to the assumed hardness parameters for the copper wafer and the pad in the model. As the hardness values of copper and copper oxides are not readily available and dependent on the various methods of measurement, the model assumed a hardness of 7.6 GPa for the wafer surface.[3] However, because oxidation occurs with the presence of typical oxidizing agents like H_2O_2, either CuO or Cu could be the actual wafer material being polished, thus causing the difference between the predicted and experimental removal rates. As reported by Doyle and Asku,[16] different copper oxides and complexes can form at a given pH and potential depending on the chemistry of the slurry. Therefore, the surface hardness parameter in the model can affect the MRR value predicted. Studies of the formation of copper oxides in the presence of these organic acids must be performed so that the appropriate surface hardness value can be used in the model. Also, MRR is inversely proportional to pad hardness in the Luo and Dornfeld model.

The reported etch rate seemed independent of the type of organic acid used and was in the range of 33 to 43 nm/min.[14] Hong et al. observed that the slurry containing citric acid was the most stable suspension and the least agglomerated.[14] Of the three slurries, the one containing citric acid had the highest reported absolute zeta potential value (27 mV) resulting in it being the most dispersed.

In the second study, Seal et al. investigated the etch rate and removal rate during copper CMP with an alumina slurry in the presence of glycine and varying concentrations of hydrogen peroxide as the oxidizer.[15] A Rodel alumina slurry containing 28% alumina with a mean particle diameter of 170 nm was used for the experimental polishing of 9 mm diam copper disks using a Buehler Polimet pad. The wafer velocity was 30 rpm. Slurries without additives and containing 0.1 M glycine and varying concentrations of H_2O_2 up to 10 wt % at pH 4 were used.

The experimental etch rate was small (under 10 nm/min) and remained constant with H_2O_2 concentration ranging from 1 to 10 wt %.[15] Seal et al. concluded that the highest removal rate for copper occurs when the solution contains 3.6 wt % H_2O_2 and 0.1 M glycine and this enhanced polish rate is due to the Cu^{2+}-glycine complexation reaction. They also concluded that in the absence of glycine, the removal rate of copper decreases with increasing H_2O_2 concentration due to the formation of a less soluble copper oxide film. It is stated that the removal of copper is achieved as a result of mechanical abrasion and that the role of the chemical etchant is only to dissolve the abraded copper particles rather than to etch the material directly from the surface. They report that further increasing the concentration of H_2O_2 beyond 3.6 wt % with 0.1 M glycine decreased the polishing rate of copper due to dynamic repassivation.

Seal et al. found that in the absence of glycine, the removal rate decreased continuously as the H_2O_2 concentration was increased up to 12.7 wt %. They theorized that this decrease is due to the formation of a surface oxide layer on the copper substrate with the chemical action of hydrogen peroxide.[15] However, with the addition of 3.6 wt % of H_2O_2 the removal rate reached its maximum and then decreased as the peroxide concentration was further increased. Wang et al. also observed this enhanced polishing rate with the addition of H_2O_2.[17]

Asku and Doyle have studied the electrochemical behavior of glycine in aqueous solutions.[16] They reported that glycine can exist in aqueous solutions in three different ionic forms, namely cation $^+H_3NCH_2COOH$, zwitterion $^+H_3NCH_2COO^-$, and anion $H_3NCH_2COO^-$.[16] Asku and Doyle suggested that the presence of zwitterions would predominate over the other two ionic species for a

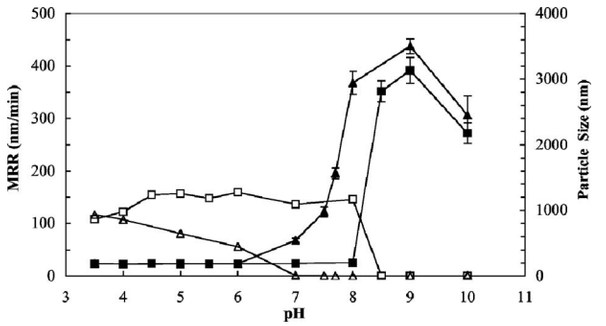


Figure 1. MRR predictions (open symbols) and effective agglomerate size (closed symbols) for alumina without additives (squares) and with 0.1 M glycine (triangles) (error bars indicate standard deviation of agglomerate size data).

slurry pH of 4.[16] Therefore, in this case, the complexation reaction of zwitterions with copper ions forms highly soluble complexes like $Cu(H_2NCH_2COO)^+$, $Cu(H_3NCH_2COO)^{2+}$, $Cu(H_2NCH_2COO)_2$, and $Cu(H_2NCH_2COO)_2^-$.[16] Therefore, Seal et al. concluded that the formation of these Cu–glycine complexes attributed to an increased removal rate of copper.[15]

We measured zeta potential and particle size distribution of an EKC Tech alumina (average particle diameter of 120 nm) slurry with concentrations of glycine and similar range of hydrogen peroxide as used by Seal et al.[1,2] This particle size distribution data were used in the Luo and Dornfeld model to obtain removal rate predictions and these results were compared to the experimental copper removal rates of Seal et al.[15] The following parameters were assumed for the model: pad hardness of 100 MPa, platen and carrier velocity of 100 rpm, and down pressure of 1 psi.

Figures 1 and 2 show the measured average particle size for EKC Tech alumina slurry with varying concentrations of glycine and hydrogen peroxide as a function of pH and the model predictions for material removal rate. The MRR predicted at pH 4 is compared to Seal et al.'s extrapolated experimental results in Table III. The model predicted a significantly higher removal rate at a similar concentration of H_2O_2 (2 wt %) and 0.1 M glycine as that reported by Seal et al.[15] A 30% increase in the maximum predicted removal rate is observed by increasing the peroxide concentration from 0.1 to 2 wt %. Seal et al. reported a very large increase in MRR (150%) when the H_2O_2 concentration was increased from 1.4 to 3.6 wt %. For all model predictions, it is observed that once the particles become micrometer size ($pH > 7$) the removal rate drops and becomes negligible. This trend of an increase in removal rate of copper with an increase in H_2O_2 concentration was also observed by both Kim et al.[18] and Hirabayashi et al.[19]

Table III. Comparison of experimental[15] and maximum predicted MRR for varying concentrations of H_2O_2 and glycine.

Figure	H_2O_2 (wt %)	Glycine (M)	Experimental MRR (nm/min)	Predicted MRR at pH 4 (nm/min)
1	0	0	N/A	120
1	0	0.1	16	110
2	0.1	0.1	17	170
2	2	0.1	207	220

Although there is no MRR data available for more complicated CMP slurry chemistries, the model was used to predict MRR for EKC Tech alumina slurries that contained common additives as would be used during Cu CMP. Specifically, the model was used for an EKC Tech alumina slurry containing 0.01 wt % BTA, 10^{-3} M SDS, 0.1 wt % H_2O_2, 10^{-3} M KNO_3, and either 0.1 M glycine or 0.01 M EDTA. The predicted material removal rates were much smaller (10 nm/min or smaller) than the previous predictions for MRR for EKC Tech alumina slurry with only peroxide and glycine as shown in Fig. 3. This is due to the overall larger particle size for both sets of measurements. Both show consistently low removal rates (~1 nm/min) over the given pH range with the highest removal rate occurring at pH 3.5 (10 nm/min) for the slurry containing 0.1 M glycine. Although this is the highest predicted removal rate, it is still low for copper CMP and is higher than the other predicted removal rates, as for this particle size (~500 nm) the model is sensitive to small changes in standard deviation.[1].

Additionally, the average effective particle size was measured[1,2] and removal rate predictions predicted for a Cabot silica slurry. The particle size remained constant in the range of 168–173 nm. The standard deviation for each measurement also remained very constant in the range of 2–4 nm. The resulting model material removal rate predictions were nearly consistent at 35–39 nm/min. The lowest MRR occurred at pH 10 (24 nm/min), due to the model's sensitivity to particle size standard deviation for this particle size range. At pH 10 the mean particle size was 171 nm and the standard deviation was 4 nm. If a standard deviation of 3 nm was used instead in the model, the MRR would have been 35 nm/min, similar to the other predicted removal rates.

Conclusions

Instead of using hypothetical particle size data as done previously by others, we have used experimentally measured slurry particle size data with Luo and Dornfeld's model to predict the trends of material removal rate and then compared the predictions to experimental polishing rates from the literature. For slurries containing various concentrations of H_2O_2 and glycine, the model predicted the highest MRR for a solution with 2 wt % H_2O_2 and 0.1 M glycine,

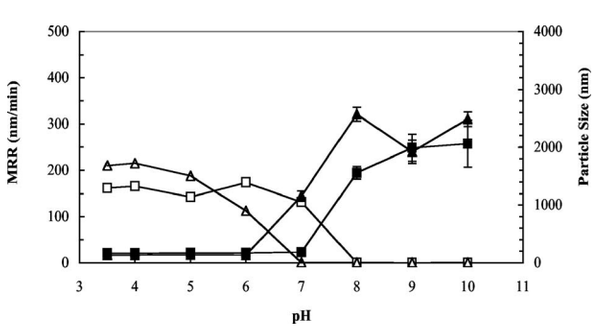


Figure 2. MRR predictions (open symbols) and effective agglomerate size (closed symbols) for alumina with 0.1 M glycine and 0.1 wt % H_2O_2 (squares) and with 0.1 M glycine and 2 wt % H_2O_2 (triangles) (error bars indicate standard deviation of agglomerate size data).

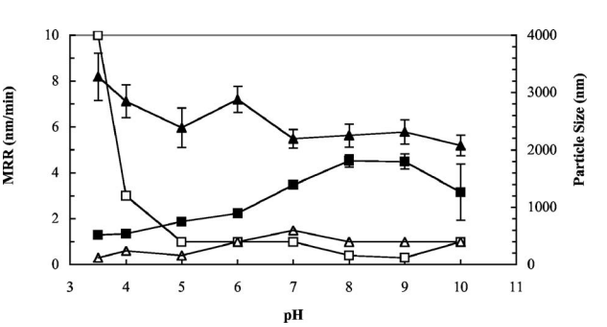


Figure 3. MRR predictions (open symbols) and effective agglomerate size (closed symbols) for EKC Tech alumina slurry with 0.01 wt % BTA, 10^{-3} M SDS, 0.1 wt % H_2O_2, 10^{-3} M KNO_3, and either 0.1 M glycine (squares) or 0.01 M EDTA (triangles).

which are similar to that observed in the literature that yielded high experimental polishing rates. The lowest predicted MRR were obtained for the solutions that contained a combination of all the slurry additives investigated. This could be due to the lack of dissolved copper or copper particles in the solution that would be present during the CMP process, which is the subject of further investigations.[20]

It was shown that the model is sensitive to small variations in standard deviation for particles that are 500 nm in diameter or smaller. In general, the model underpredicted the material removal rates. This could be due to the surface hardness parameter not being linked with slurry chemistry. Different copper oxides can form at a given pH and potential depending on the slurry chemistry and currently the model only assumes that H_2O_2 is the oxidizing agent and that CuO is the oxide forming. The passivation rate is a function of slurry chemistry and this model parameter is currently not linked with CMP chemistry. The lower MRR from the model could also be due to a lack of accurate pad hardness values, which can have a large influence because pad hardness is inversely proportional to material removal rate. Further investigations compare our own experimental copper CMP removal rates with model predictions using various slurry chemistries.[21]

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