

# The Mechanism of Low pH Silica Based Oxide Slurries

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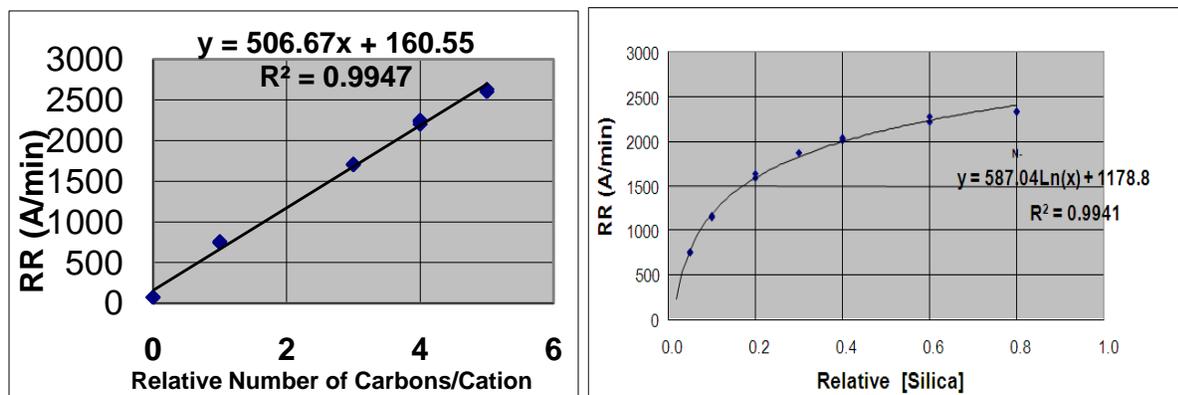
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**Abstract** The mechanism of oxide polishing at low pH in the presence of an organic cation is discussed. The role of the cation is thought to involve increasing the nucleophilicity of the silanolate active site on the particle surface by lowering the hydration state. Additionally, the activation energy of the reaction may be lowered by charge attraction between the particle and wafer surface and by increased hydrophobic interactions.

**Introduction** The use of high pH oxide slurries such as Semi-Sperse® SS25 to polish various forms of silicon dioxide wafers at high rates has been prevalent for many years. However, typically such an approach uses fumed silica at silica concentrations exceeding 10%. Much lower removal rates are obtained with colloidal silica at similar concentrations. For instance, fumed silica yields a removal rate of 2700 Å/min on TEOS while colloidal silica has a removal rate of 410 Å/min at pH 12. At a pH less than 7, the removal rate for colloidal silica is a mere 90 Å/min. However, the addition of cationic rate additives can increase the TEOS removal rate to 3000 Å/min at the same CMP process and at less than half the solids of fumed silica based slurries while maintaining low defectivity (DCN/DCO < 50 at 225 nm). This represents a removal rate of over 30 times that of colloidal silica without the rate additives. The mechanism of the rate acceleration is believed to involve increased silanolate nucleophilicity in the presence of the organic cation and the inversion of the negative charge on the particle surface yielding a coulombic attraction between the particle and the wafer, thus lowering the activation energy and dramatically increasing the removal rate. This mechanism is supported by zeta potential titrations on the particle and streaming potential measurements on the charge on the wafer surface.

**Experimental** 4" and 8" diameter, TEOS, BPSG, thermal oxide, silicon nitride and silicon wafers were polished on a IPEC Planar 472, a Logitech IC M51 or a Mirra 3400 at various down forces, table speeds and slurry flow rates. Removal rates were determined by ellipsometry on a Filmetrics F50 or a KLA-Tencor UV-1050. pH was measured with an Accumet Ap61 meter. Formulations were prepared by mixing colloidal silica under high shear with the appropriate chemical additives. Defectivity (DCO and DCN) were measured via a KLA-Tencor SP1 TBI. Zeta potential was measured on a Dispersion Technologies DT-1200. Particle sizes were determined by a Malvern Zetasizer 3000HS<sub>A</sub> in a 1 mM NaCl buffer solution. Streaming potential was measured on an Anton Paar EKS100.

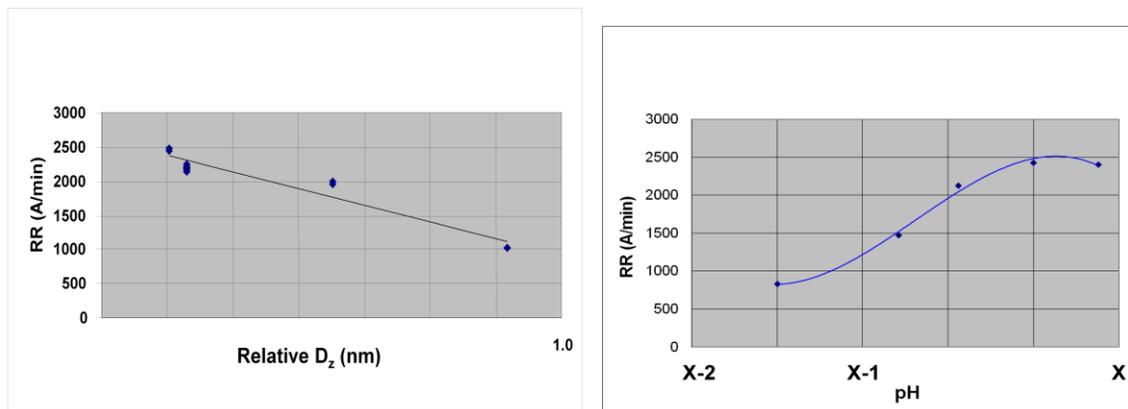
**Discussion** A number of organic cations were studied in an attempt to increase the removal rate of colloidal silica at pH's lower than 7. We have found that primary, secondary and tertiary amines and quaternary ammonium along with phosphonium salts can be used as rate accelerants. In addition, the removal rate is related to the cation hydrophobicity. Figure I displays the relationship between the thermal oxide removal rate and the chain length of the alkyl groups on the cation at a constant silica concentration and pH. The role of cation hydrophobicity will be discussed below.



**Figure I (left).** The effect of alkyl side group chain length on the thermal oxide removal rate.

**Figure II (right).** The effect of the silica concentration (normalized) on the thermal oxide removal rate in the presence of an organic cation.

Although it is not surprising that the removal rate is affected by the silica concentration (Figure II), the observation that the removal rate logarithmically increases with silica concentration suggests a first order chemical reaction where the silica is directly involved in the rate determining step. Although a rate increase with silica concentration would be likely in a purely mechanical polishing as modeled by Preston,<sup>1</sup> one would expect a linear increase in removal rate if the particles were simply mechanically plowing away the surface. Chemical softening followed by mechanical removal, such as the mechanism proposed by Kaufman,<sup>2</sup> is contraindicated by the fact that we see no appreciable static etch rate and have very low removal rates without particles (8 A/min). Additionally, very low hydroxide concentrations are present at pH's <7 compared to high pH CMP slurries and thus the hydrolysis of silyl ethers by soluble species such as hydroxide are expected to be minimal given the high rates of removal and fast kinetics during CMP. Another observation is that the removal rate increases with decreasing particle size as measured by dynamic light scattering (Figure III). While morphology and particle size distribution can also play a role, this relationship suggests that the reaction rate is proportional to the available surface area and that an interfacial reaction between the silica and oxide wafer surfaces may be occurring. Cook proposed an interfacial reaction in the case of ceria polishing silica glass surfaces.<sup>3</sup>



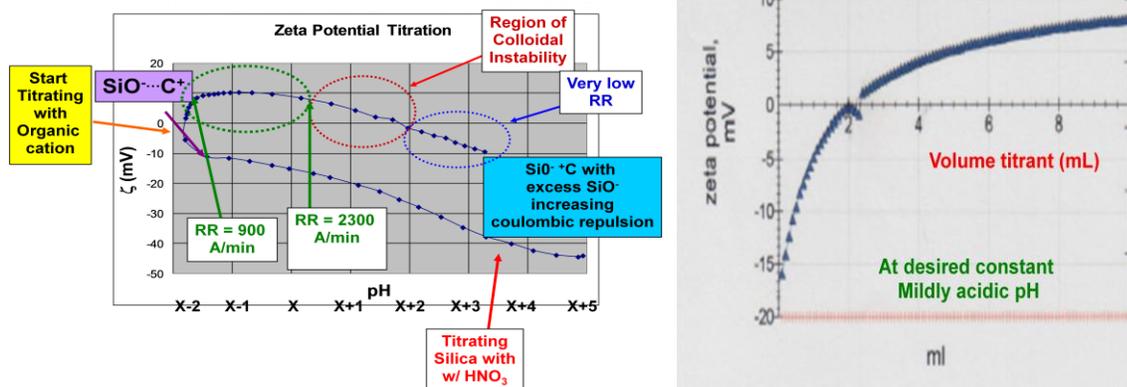
**Figure III (left).** The effect of particle size on the thermal oxide removal rate in the presence on an organic cation. **Figure IV(right).** The effect of pH on the thermal oxide removal rate in the presence on an organic cation.

The effect of pH on the oxide removal rate was also studied for the colloidal silica/organic cation system. The removal rate increases with pH (Figure IV). Since the pKa of the silanols on the surface of the silica is 7, the silanolate anion concentration increases as the pH increases. This suggests that the active site may be silanolate groups which can nucleophilically attack silyl ethers on the oxide wafer surface. The nucleophilic attack of silanolate active sites on silicon has been proposed as the mechanism for high pH silicon polishing.<sup>4</sup> Evidence for that hypothesis included a direct relationship between the charge and therefore the silanolate active site concentration and the removal rate as well as evidence for transesterification of silicate by-products to the particle surface by dynamic light scattering.

The mechanism of oxide polishing is believed to be an SN<sub>2</sub> nucleophilic attack of silanolate groups on the silica particle surface on the silyl ethers present on the wafer and vice-versa. Removal may be achieved by transesterification of silicate onto the particle surface. Solvent effects in SN<sub>2</sub> reactions are well known in that increased polarity reduces the rate of an anionic attack on a neutral electrophile.<sup>6</sup> Landini<sup>7</sup> studied the role of quaternary ammonium and phosphonium ions and found higher rates for nucleophilic reactions with increased alkyl chain length. Maia<sup>8</sup> proposed that the increase in anion nucleophilicity with cation hydrophobicity is due to decreasing the number of hydrogen bonded water molecules that diffuse the charge and found that tetrahexyl ammonium cations were sufficiently hydrophobic to completely exclude the hydrogen bonding of water to fluoride and increase its rate of nucleophilic attack on certain electrophiles in water by 10<sup>7</sup>. Thus, it is highly likely that the primary role of the organic cation is to increase the nucleophilicity of the silanolate by hydrophobic exclusion of anion-centered, hydrogen bonded water thereby increasing the reaction rates.

Zeta potential titrations were utilized in an effort to gain a mechanistic understanding of the rate increases with pH in the presence of an organic cation. As received, the silica particles

have a zeta potential of -44 mV (Figure V). When titrated with nitric acid, the zeta potential decreases as the silanols are protonated.<sup>5</sup>



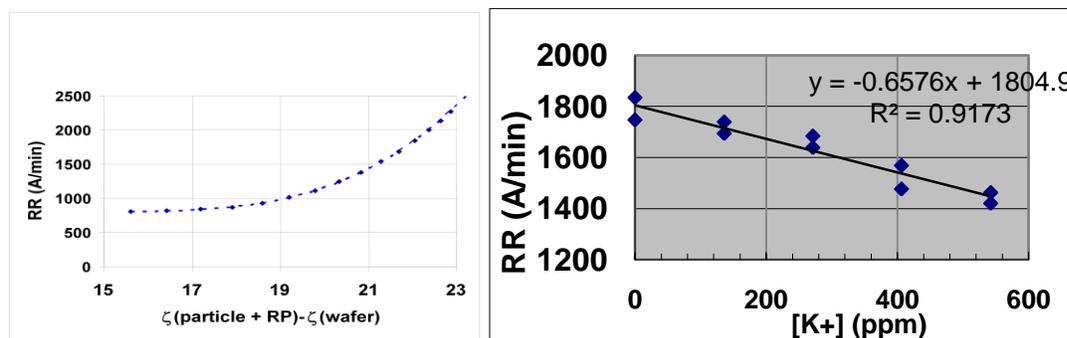
**Figure V (left).** Titration of silica with nitric acid followed by an organic hydroxide.

**Figure VI (right).** Titration of silica an organic cation at pH X.

When the zeta potential was 2 pH units below the target pH, the organic cation with a hydroxide counterion was used as a basic titrant to slowly raise the pH to and above the target pH (X and >X, respectively). The charge rapidly increased to +10 mV and is relatively constant until the target pH was reached where the maximum removal rate occurs (Figure IV). This indicates that a molecule of organic cation is adsorbing to the silica particle surface to neutralize each silanolate moiety as it forms via the deprotonation of a silanol. Above the target pH, cations are no longer adsorbing perhaps due to steric crowding. The charge on the surface starts to decrease as more silanols are deprotonated with increasing pH until the system becomes unstable due to insufficient charge on the particle surface to keep the particles electrostatically separated by charge repulsion. The silica particles and silicon dioxide wafer become negatively charged at high pH's resulting in very low removal rates above pH 7 (<200 A/min) probably due to charge.

In a second experiment, the cation was used as the titrant at a fixed target pH (X), (Figure VI). The silanolates on the silica particles were neutralized by the adsorption of organic cations. The zeta potential then increased 8 mV with increasing organic cation concentration. This indicates the formation of a double layer of organic cations. At low pH, the charge on the particle is positive due to the presence of the organic cation double layer while the wafer surface is negative. The concentration of the adsorbed cation determined by titration is in good agreement with that measured by HPLC. This suggests that charge attraction may play a role increasing the removal rate by decreasing the activation barrier of the interfacial reaction. Babu was the first to study the role of charge attraction in CMP.<sup>9</sup> The kinetic energy of the process may be transferred to the particle to facilitate overcoming the activation barrier of the interfacial chemical reaction.<sup>10</sup> At high pH, both the particle and wafer surface are negatively charged and therefore charge repulsion may dramatically reduce the removal rate. Figure VI shows the that

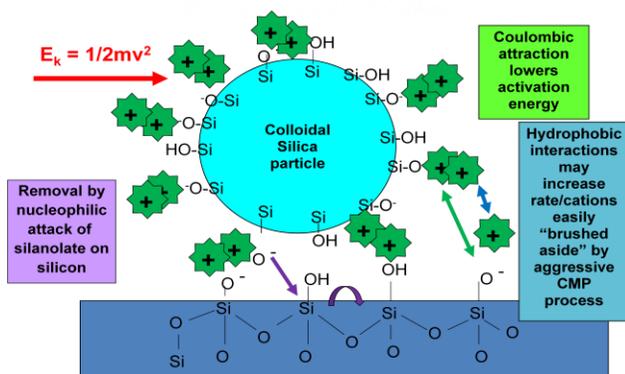
the removal rate increases as the difference in zeta potential between the particle with adsorbed organic cation and the oxide surface charge determined by streaming potential increases. Since the charge on the wafer is negative and the charge on the particle with the adsorbed cation double layer is positive, the difference increases as the pH increases. Although the cation can also adsorb to the wafer surface, the cations presumably cannot diffuse into the active area between the particle/wafer surface and may be easily brushed aside. At minimum, the cations may shield the negative charges that are present on both the wafer and particle surface to reduce charge repulsion. This may account for the very low rates of removal for colloidal silica without organic cations. If charge attraction is playing a role in decreasing the activation energy, then increasing the ionic strength should shield the charges and decrease the removal rate.<sup>11</sup> Figure VII shows that the rate decreases as the [KNO<sub>3</sub>] increases supplying additional support for the involvement of charge attraction in the removal mechanism. Hydrophobic interactions between the cation alkyl groups on the particle and wafer may also lower the activation barrier and therefore increase the removal rate. Such hydrophobic interactions could also lead to increased coupling of the cation-coated particle to the hydrophobic pad surface (water contact angle 130°).



**Figure VI (left).** A plot of the removal rate vs. the particle with absorbed cation minus the wafer surface charge. **Figure VII (right).** The effect of potassium nitrate concentration on the removal rate.

**Conclusions** The proposed mechanism of the oxide rate enhancement by organic cations at low pH can be summarized as follows and is displayed in figure VIII.

1. Removal may occur by nucleophilic attack of silanolate on the particle and wafer surface on silyl ethers followed by transesterification onto the particle surface.
2. The organic cation is likely to increase silanolate nucleophilicity by decreasing the number of silanolate-centered hydrogen bonded water molecules.
3. Charge attraction and/or shielding of charge repulsion may lower the activation barrier of the proposed SN<sub>2</sub> transesterification reaction.
4. Alkyl group interactions may decrease the activation barrier and improve coupling of the particles to the pad surface enabling more efficient transfer of kinetic energy.



**Figure VIII..** The proposed mechanism of oxide rate enhancement with organic cations.

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1. Preston F. J. Soc. Glass; Technol. 11 214-256 (1927).
2. Kaufman, F. B etal. *J. Electrochem. Soc.* **1991**, 138(11), 3460.
3. Cook, L. J. Non-Crst. Solids 120, 152. (1984).
4. White, M. L.; et al; *Mater. Res. Soc. Symp. Proc.* **991**, 0991-C07-02 (2007).
5. Iler, R. *The Chemistry of Silica*; Wiley and Sons, 1979.
6. March, J, *Advanced Organic Chemistry*, 3<sup>rd</sup> Ed. Wiley and Sons (1985).
7. Landini, et al. *J. Am. Chem. Soc.* 100(9), p2796 (1978)
8. Maia, A. *Pure and Appl. Chem.* V67(5), p.697 (1995)
9. Babu, et al-*Electrochem. Solid-Sate Lett.* V7, 12, pp.G316-318
10. White, et al. *Materials Science Forum* (Volumes 600 - 603). Volume 600, p837 (2009)
11. Choi, W. etal *J. Electrochem Soc.* **151(3)** G185-189 (2004)