Using surfactants in iron-based CMP slurries to minimize residual particles

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During recent years, the use of chemical-mechanical planarization (CMP) to remove excess coating material from wafer surfaces has increased dramatically, as has the literature on CMP research.[1-13] Basically, the CMP process involves polishing wafers using a slurry that combines a chemical component, which oxidizes the substrate surface, with a mechanical component that abrades the oxidized substrate, resulting in a very flat surface. The major drawback of the process is that a large number of particles may remain on the wafer

Testing indicates that cationic surfactants with a high tendency to aggregate and adsorb on immersed substrates can reduce post-CMP contamination on the wafer surface.

because of the enormous number of ultrafine (<2-μm) particles present in the slurry. Such residual particles often cause short-circuiting in the final integrated circuits, thereby decreasing product yield. Reducing the number of post-CMP particles on the wafer surface is, therefore, a critical concern of the semiconductor industry.

Particle removal from substrate surfaces is dependent upon the adhesion forces between the particles and the surface, with van der Waals and electrostatic forces often being the most dominant. Van der Waals force, which is nearly always attractive, is a function of the particle; surface, and separation medium properties and of the separation distance between the particle and the surface. Electrostatic force, however, is a function of the particle and surface charges or potentials, the ionic strength of the separation medium, and the separation distance. (In most literature on adhesion, the separation distance for particles adhering to surfaces is assumed to be 4 Å.[14,15]) Under certain conditions, adhesion can also be dependent on hydration, capillary, or steric forces, or other factors. Small particles, particularly those smaller than about 10 μm, are more difficult to remove than larger ones because attractive forces are typically dependent on the particle radius, whereas removal forces are usually dependent on the radius squared. Thus, as particle size decreases, the decay in the removal force is much more rapid than the decay in the attraction force. The presence of surfactant molecules that adsorb on either the particles or the substrate surface can help
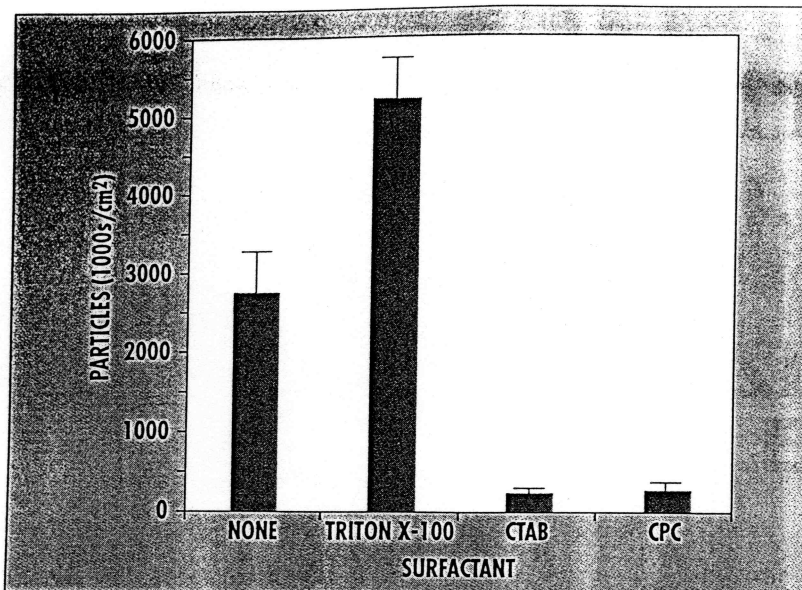
Figure 1: Comparison of residual particle counts following CMP with and without various surfactants present in the iron-based alumina slurry at a 0.18 ± 0.02% concentration level. The standard deviations in the measurements are indicated by error bars.

reduce the attractive force, allowing even small particles to be removed using typical rinsing processes.

Ionic surfactant molecules have been used in a number of industrial applications for many years to alter particle adhesion forces by reducing, neutralizing, or reversing surface charges. Examples include surfactants for removing soil during clothes cleaning and agglomerating particles during separation processes. However, the use of surfactants in wafer cleaning has only recently been evaluated,[10] and the use of

various types of surfactants in CMP processing has been found to present difficulties. The highly acidic conditions commonly encountered in CMP solutions, combined with the natural tendency for the charge on the tungsten wafer surface to be negative under most acidic conditions, make cationic surfactants the most appropriate choice for surface charge modification that leads to reduced particle adhesion forces. However, it should be noted that anionic surfactants can also be effective in reducing particle adhesion to various surfaces when the solution chemistry is less acidic and the surface charge is positive. The objective of the study reported in this article was to evaluate the use of various surfactants to reduce the level of ultrafine particles following CMP processing and to better understand the mechanism of surfactant-enhanced particle removal.

Experimental Procedures

Two cationic surfactants—cetyl pyridinium chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB)—and the nonionic surfactant Triton X-100 were evaluated in this study. The industrial tungsten CMP process was simulated using CVD-tungsten-coated silicon wafers supplied by Sematech, which were scored using a silicon carbide–tipped knife and broken into 2 × 3-cm blanks. The wafer blanks were manually polished on Model CRIC1000-5 polishing pads (Rodel, Phoenix) in a slurry composed of a 1:1 mixture of Semi-Sperse FE-10 solution and a 20% alumina solution consisting of Sumitomo high-purity alumina in water and various specified quantities of the respective test surfactants. The temperature was maintained at 26°–27°C to avoid the Krafft point of CPC in 0.1-M ferric nitrate that occurs at 25°C. The average alumina particle diameter was about 1 μm. After it had been polished for 1 minute, each wafer blank was rinsed in deionized/distilled water for approximately 10 seconds, then allowed to air dry for 15 minutes in a vertical position. About 30 locations on each blank were then examined using a television monitor/video camera/microscope setup, and the number of residual particles was tallied. Unless otherwise noted, contact angle measurements were made goniometrically using carbon tetrachloride droplets approximately 2 mm in diameter on the CVD-tungsten surface, which was submersed in water that was both deionized and distilled.
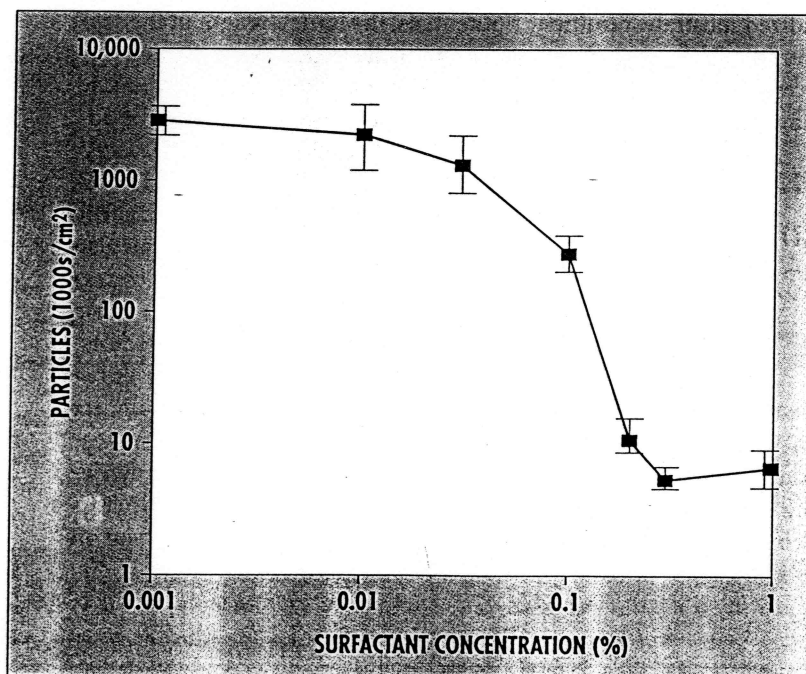

Figure 2: Residual particle levels as a function of CPC concentration in the slurry. Standard deviations are indicated by error bars.

Results

In the initial tests, the three surfactants were added to the slurry at a 0.18% concentration
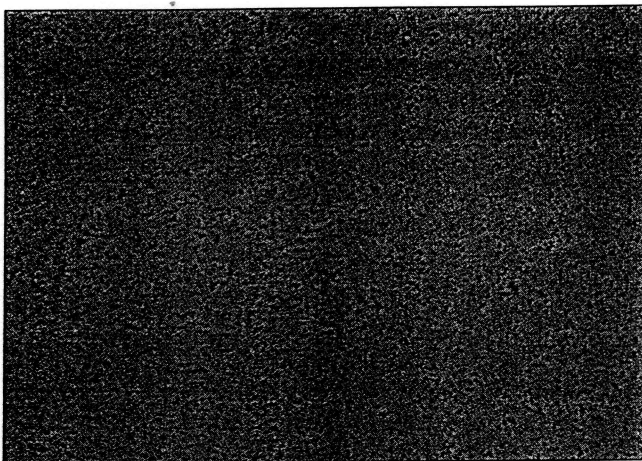
Figure 3: Typical micrograph of residual alumina particles (after rinsing/drying) on a tungsten-coated wafer blank surface when no surfactant was present in the polishing slurry (100×).

Figure 4: Typical micrograph of residual alumina particles (after rinsing/drying) on a tungsten-coated wafer blank surface when 0.1% CPC was present in the polishing slurry (100×).
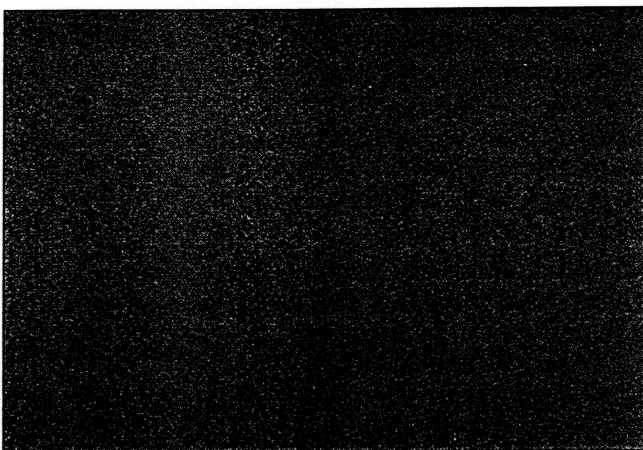
Figure 5: Typical micrograph of residual alumina particles (after rinsing/drying) on a tungsten-coated wafer blank surface when 0.3% CPC was present in the polishing slurry (100×).

level to compare their effectiveness in reducing the level of residual particles on the wafer surface following the CMP process. As presented in Figure 1, the results from these tests show that with both of the cationic surfactants, CPC and CTAB, particle levels were much lower than when no surfactant was present in the slurry. The addition of CPC decreased the particle level by 90% relative to the control test, while the presence of CTAB led to a 91% reduction in the particle level. In contrast, when the nonionic surfactant, Triton X-100, was present, the number of residual particles was actually higher than in the control test. The ineffectiveness of this surfactant is probably due to its lack of charge, which reduces its ability to adsorb on the tungsten surface and form a stable film.

With the cationic surfactants, particle levels were much lower than when no surfactant was present in the slurry.

Effect of Surfactant Concentration. Additional tests were run to determine whether the surfactants' concentration in the polishing slurry affected the number of residual particles present after rinsing. The results for CPC are presented in graph format in Figure 2, and corresponding micrographs of the wafer blanks are shown in Figures 3–5. These figures clearly indicate that surfactant concentration strongly influences particle levels: the number of particles decreases sharply as the surfactant concentration increases. Thus, a relatively high concentration of surfactant is necessary to minimize residual particles following CMP processing. As seen in Figure 2, approximately 0.01% CPC was needed before any appreciable benefit was observed. However, the effect of concentration appeared to peak at 0.3% CPC. At this concentration, the residual particle level was only 5600 ± 800 particles/cm², which is near the lower limit of reasonable detection (1000 particles/cm²) for the microscopic evaluation technique used in the study. At concentrations above 0.3% CPC, the level of defects did not change significantly.

Effect of Surfactant Adsorption. As discussed above, the mechanism for reducing the number of residual particles is related to surfactant concentration. Measurements of the surface contact angle at various concentrations, shown in Figure 6, indicate that the change in surfactant concentration leads to a change in surfactant adsorption. As the surfactant concentration increases, the contact angle, which is indicative of surface hydrophilicity (when using carbon tetrachloride droplets), decreases. This decrease in the contact angle is attributable to the adsorption of surfactant at the wafer surface. As shown in Figure 7, additional measurements taken using
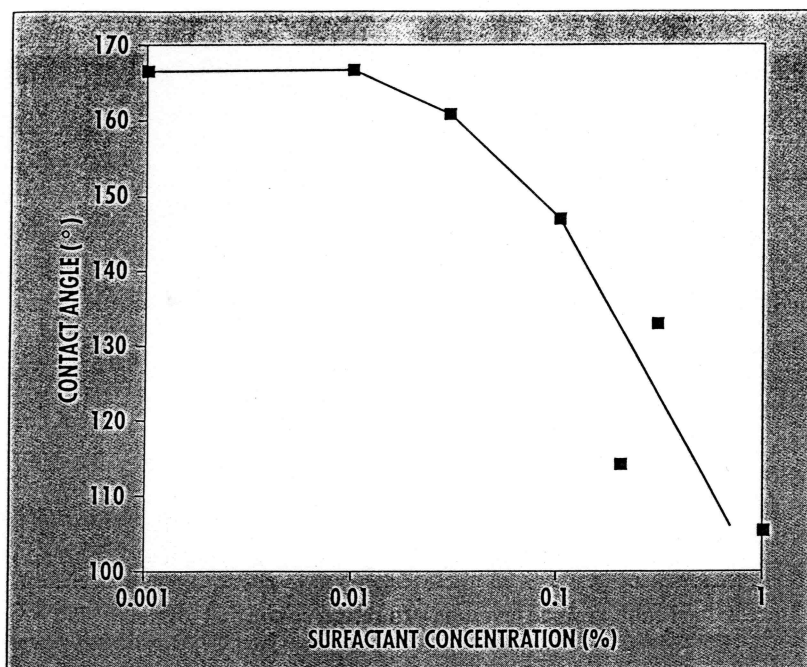
Figure 6: Surface contact angle as a function of surfactant concentration.

ditional surfactant leads to the formation of dissolved spherical aggregates (i.e., micelles) at concentrations above the critical micelle concentration (CMC). Thus it can be said that surfactants that decrease surface tension at low concentrations or have low CMCs have a high tendency toward aggregation and are therefore more likely to adsorb on an immersed solid surface.

The effect of surfactant concentration on surface tension at the air/water interface for CTAB and CPC is shown in Figure 9. These data indicate that CPC reduces surface tension at lower concentrations than CTAB does; thus CPC is more likely to adsorb at those concentrations. However, because the concentrations of CPC and CTAB used in the study were much higher than the CMCs of the compounds, it is difficult to observe this difference in aggregation tendencies in the particle data.

As the hydrocarbon chain of a surfactant molecule lengthens, it is more likely to aggregate at interfaces because of its increased hydrophobic nature. (Hydrophobic surfactant molecules combine readily with other surfactant molecules as interfacial or solution aggregates in order to reduce their contact with water.) This effect is easily observed in Table I for alkyl trimethyl ammonium bromide; the compounds' CMC decreases rapidly as chain length grows, indicating that the aggregation tendency increases with longer chain lengths. In terms of using surfactants in order to enhance particle removal — which is dependent upon surfactant aggregation/adsorption at the surface — those surfactants with long

Fourier transform infrared (FTIR) spectroscopy revealed that the presence of hydrocarbon on the tungsten surface increases as the surfactant concentration increases. This is indicated in the figure by the increasing absorbance values in the hydrogen-carbon stretching bands at 2925 and 2850 cm^{-1}.

The relationship between surfactant adsorption as evidenced by contact angle measurements and the number of residual particles is very distinct, as shown in Figure 8. As the contact angle increases, which indicates that the quantity of adsorbed surfactant is decreasing, the number of residual particles increases. Stated another way, an increase in surfactant adsorption clearly leads to a reduction in the number of residual particles.

Effects of Surfactant Properties. The ability of a surfactant to adsorb on an interface is closely linked to the solution chemistry, the surfactant charge, and the tendency for the surfactant to aggregate as micelles in solution (or hemimicelles at the surface). Solution chemistry is important because anionic surfactants are ineffective in very acidic solutions, where they react with the abundant hydrogen ions. Solution chemistry can also affect surfactant solubility. The importance of surfactant charge is readily apparent from the data presented earlier in this article: the nonionic surfactant being evaluated did not improve particle removal because of its lack of charge. The importance of surfactant aggregation is best illustrated by describing the tendency of surfactant molecules to assemble at the air/water interface as a function of surfactant concentration. Aggregation at the interface causes a decrease in the surface tension, until the aggregation is complete and the presence of ad-
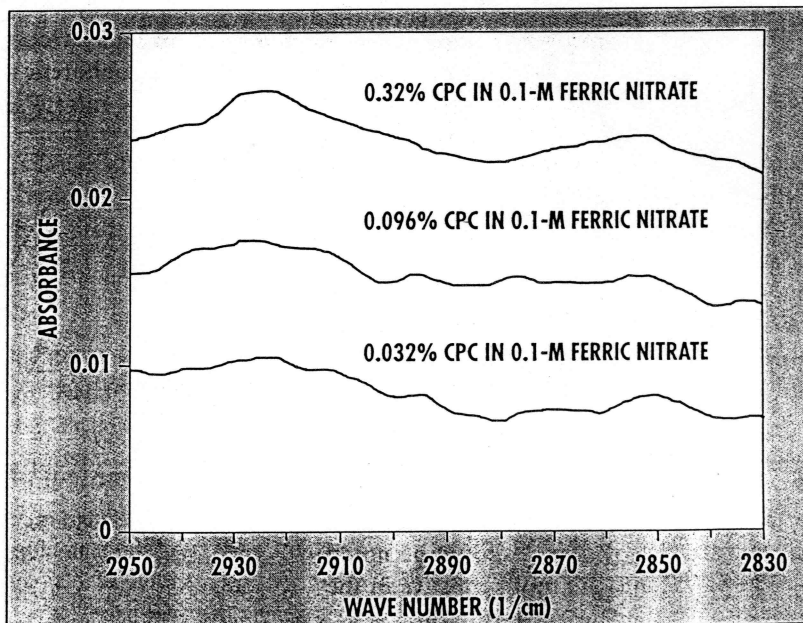

Figure 7: Multiple reflection FTIR spectra of CVD-tungsten-coated wafer blank surface after 1-minute exposure to specified polishing slurry and subsequent rinsing with purified water. The absorption bands at 2925 and 2850 cm^{-1} are the asymmetric and symmetric carbon-hydrogen stretching bands, respectively.[16]

hydrocarbon chains should be more effective than those with short ones. The data shown in Figures 10 and 11 confirm this prediction. The differences in concentration necessary for the

Surfactants with long hydrocarbon chains should be more effective than those with short ones.

surfactant molecules with chains of various lengths to achieve a given level of particle removal are similar to the differences in CMCs shown in Table I. Unfortunately, the solubilities of the cetyl (C-16) and myristyl (C-14) trimethyl ammonium bromide compounds limited the study to

Figure 8: Residual particle levels as a function of contact angle.[16]

Number of Carbon Atoms	CMC (mol/L)
8	1.4×10^{-1}
10	6.8×10^{-2}
12	1.6×10^{-2}
14	3.6×10^{-3}
16	9.2×10^{-4}

Table I: Effect of hydrocarbon chain length on the CMC of alkyl trimethyl ammonium bromide compounds at 25°C in water.[17]

the values shown in Figure 11. It is believed that if CTAB were more soluble, its effectiveness in particle removal would have been similar to that of CPC.

Effect of Using Surfactant in the Rinse Solution. The results discussed above show that the adsorption of surfactant molecules present in a CMP slurry can reduce the number of residual particles at the wafer surface. Additional testing revealed that a reduction in surface particles can also be achieved by adding CPC to the rinse solution rather than to the CMP slurry. These results are shown in Figure 12. As with the use of surfactant in the slurry, particle removal depended on the surfactant concentration. However, it should be noted that the surfactants are more effective in the CMP slurry than in the rinse solution.

Discussion

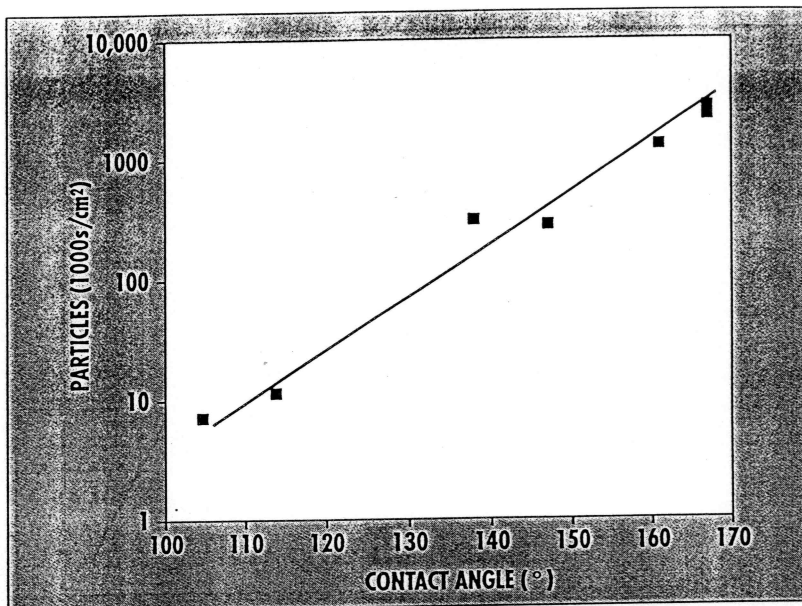Clearly, surfactant adsorption at the tungsten wafer surface can play a key role in reduc-

ing the number of residual particles following polishing in CMP slurries. The adsorption of surfactant molecules may affect van der Waals, steric, electrostatic, and hydration forces. Van der Waals forces are attractive rather than repulsive (except in extremely rare cases) and would not tend to be affected significantly by adsorbed surfactant molecules. However, the molecules' presence may significantly affect the separation distance over which these forces operate by preventing close direct contact between the wafer surface and the slurry particles. Because van der Waals forces are very sensitive to separation distance, the presence of surfactant may significantly alter these forces by changing the effective separation distance through steric intervention. Electrophoretic measurements of a tungsten surface in 0.1-M ferric nitrate solutions have shown that the tungsten surface
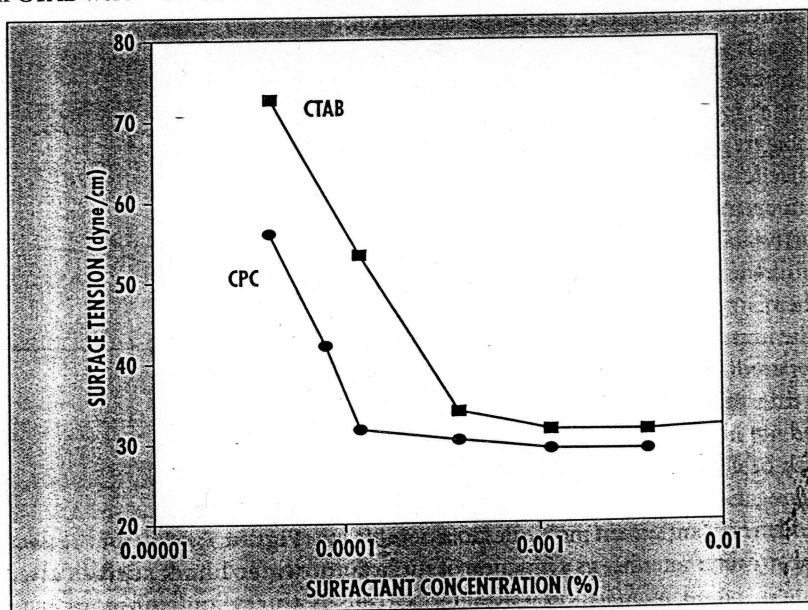

Figure 9: Surface tension as a function of surfactant concentration for CTAB and CPC.

holds a positive charge, as does the surface of alumina particles; thus, even without surfactant present, there is a natural electrostatic repulsive force between the particles and the surface. However, because of the high ionic strength of the ferric nitrate solution, this electrostatic repulsion is extremely short range and is overshadowed in magnitude by the van der Waals attractive force. It is believed, therefore, that the effect of surfactant adsorption on electrostatic forces is negligible. The effects of hydration forces in this system are not known, although generally such forces contribute to the attractive rather than the repulsive forces and would not be likely to facilitate particle removal. Thus, the only likely mechanism for surfactants to enhance particle removal is through steric intervention or steric forces that extend the separation distance between the surfaces and limit the accompanying van der Waals forces.

Surfactants are already being used in CMP processes to lower the surface tension of the slurry, thereby reducing the force and related material stresses that result when the wafers are removed from the polishing surface. The substitution of cationic surfactants such as CPC for those currently used could reduce particle adhesion as well as surface tension. However, it should be noted that CPC's chloride counter ion should be replaced with a nitrate counter ion to minimize corrosion of stainless-steel components. During this study, extensive testing in nitrate media has shown that cetyl pyridinium ions are not limited with respect to solubility or effectiveness in 0.3-M nitrate solutions at 26°–27°C. Other testing was conducted using contact angle measurements and FTIR spectroscopy.[16] These studies indicated that adsorbed cetyl pyridinium ions are easily removed from CVD-tungsten surfaces using ammonium hydroxide, potassium hydroxide, and other compounds, provided that the surfactant concentration is at the low levels that would likely be encountered in rinsing operations. Ammonium hydroxide is commonly used during rinsing/scrubbing operations; thus residual surfactant removal could be accomplished using current industry practices.
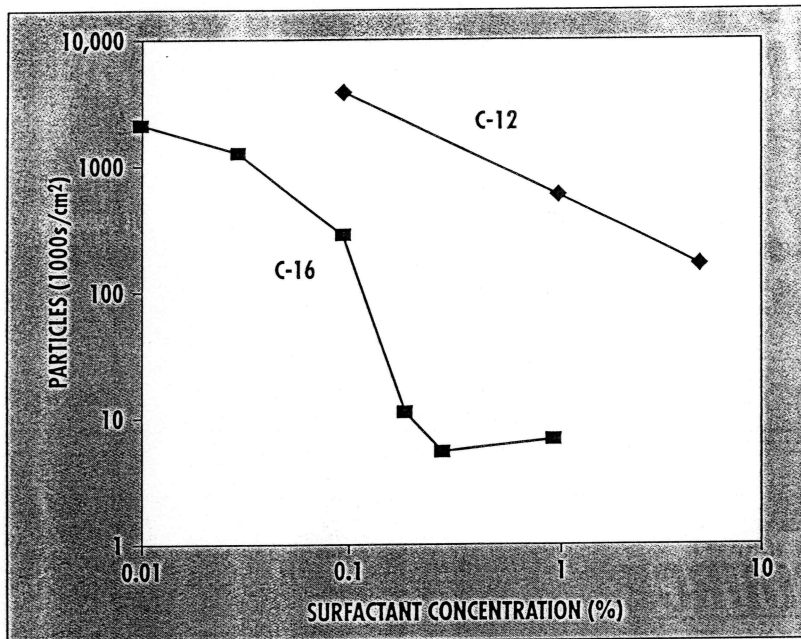

Figure 10: Effect of chain length and surfactant concentration on particle removal for alkyl pyridinium chloride compounds with 12 and 16 carbon atoms in the alkyl chain, respectively.
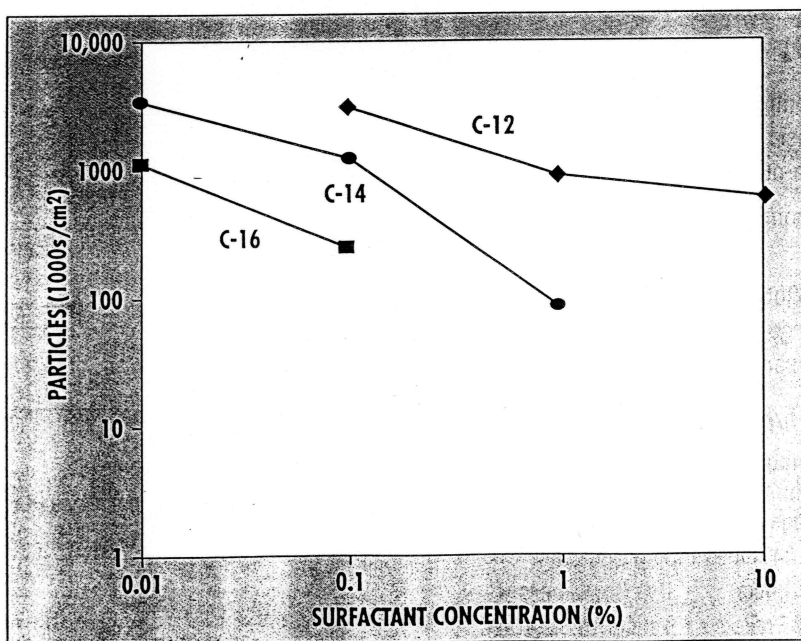

Figure 11: Effect of chain length and surfactant concentration on particle removal for alkyl trimethyl ammonium bromide compounds with 12, 14, and 16 carbon atoms in the alkyl chain, respectively.

Conclusion

Comparative testing revealed that the use of cationic surfactants in CMP slurries can reduce the number of residual alumina particles on processed CVD-tungsten wafer surfaces by nearly three orders of magnitude compared with control samples. The surfactants' effectiveness was found to be closely related to their tendency to aggregate in solution or on substrates, and surfactant adsorption was shown to be the dominant factor in reducing particulate contamination. It is believed that the role of the adsorbed surfactant is to present a steric barrier to particle adhesion.
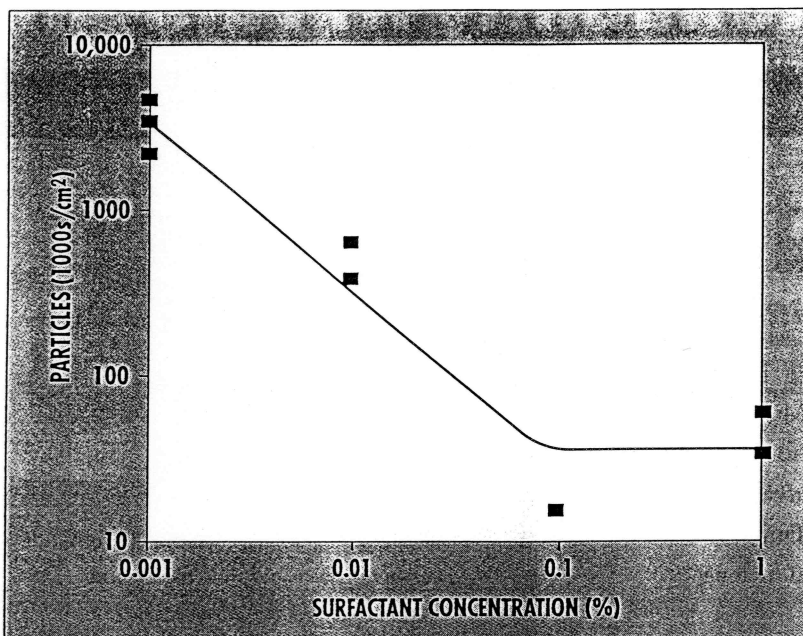
Acknowledgments

Figure 12: Residual particle levels as a function of concentration of surfactant in the post-CMP rinse solution.

during this study) for sending polishing supplies and CVD-tungsten-coated silicon wafers as well as for providing useful information.

References

1. Fury MA, "Emerging Developments in CMP for Semiconductor Planarization," *Solid State Technology*, 38(4):47–54, 1995.
2. Osburn CM, Berger HR, Donovan RP, et al., "The Effects of Contamination on Semiconductor Yield," *The Journal of Environmental Sciences*, 31(2):45–57, 1988.
3. Bowling RA, O'Brien SC, Loewenstein LM, et al., "MMST Wafer Cleaning," *Solid State Technology*, 37(1):61–65, 1994.
4. Kaufman FB, Thompson DB, Broadie RE, et al., "Chemical-Mechanical Polishing for Fabricating Patterned W Metal Features as Chip Interconnects," *Journal of the Electrochemical Society*, 138:3460–3464, 1991.
5. Hayashi Y, Sakurai M, Nakajima T, et al., "Ammonium-Salt-Added Silica Slurry for the Chemical Mechanical Polishing of the Interlayer Dielectric Film Planarization in ULSIs," *Japanese Journal of Applied Physics*, 34(2b):1037–1042, 1995.
6. Itano M, Kern FW, Miyashita M, et al., "Particle Removal for Silicon Wafer Surface in Wet Cleaning Process," *IEEE Transactions on Semiconductor Manufacturing*, 6(3):258–267, 1993.
7. Ali I, Roy SR, Shinn GB, et al., "Investigating the Effect of Secondary Platen Pressure on Post–Chemical Mechanical Planarization Cleaning," *Microcontamination*, 12(10):45–50, 1994.
8. Meyers TL, Fury MA, and Krusell WC, "Post-Tungsten CMP Cleaning: Issues and Solutions," *Solid State Technology*, 38(10):59–64, 1995.
9. Fletcher P, "Chemical Mechanical Polishing Will Smash High-Density IC-Performance Roadblock," *Electronic Design*, November 2, pp 32–34, 1992.
10. Itano M, Kezuka T, Ishii M, et al., "Minimization of Particle Contamination during Wet Processing of Si Wafers," *Journal of the Electrochemical Society*, 142:971–976, 1995.
11. Patrick WJ, Guthrie WL, Standley CL, et al., "Application of Chemical Mechanical Polishing to the Fabrication of VLSI Circuit Interconnections," *Journal of the Electrochemical Society*, 138:1778–1784, 1991.
12. Martinez MA, "Chemical-Mechanical Polishing: Route to Global Planarization," *Solid State Technology*, 37(5):26–31, 1994.
13. Kolenkow R, and Nagahara R, "Chemical-Mechanical Wafer Polishing and Planarization in Batch Systems," *Solid State Technology*, 35(6):112–114, 1992.
14. Israelachvili JN, *Intermolecular and Surface Forces*, 2nd ed, New York, Academic Press, 1992.
15. Bowling RA, "A Theoretical Review of Particle Adhesion," in *Particle Adhesion*, vol 2, Mittal KL (ed), New York, Plenum Press, pp 129–142, 1988.
16. Free ML, and Shad DO, "Adsorption and Desorption of Cetyl Pyridinium Ions at a Tungsten-Coated Silicon Wafer Surface," submitted for publication in *Journal of Colloid and Interface Science*, 1997.
17. Rosen MJ, *Surfactants and Interfacial Phenomena*, 2nd ed, Wiley, New York, 1989.

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