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Adsorption and Desorption of Cetyl Pyridinium Ions at a Tungsten-Coated Silicon Wafer Surface

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The use of surfactants to reduce the number of residual particles following chemical–mechanical planarization during integrated circuit manufacturing is relatively new. Recent results using cetyl pyridinium chloride and other cationic surfactant molecules show that surfactants are very effective in reducing the number density of residual polishing particles. The effectiveness of the surfactants is related to their ability to adsorb on the substrate surface. The contact angle and spectroscopic data in this study show that cetyl pyridinium ions can be readily adsorbed or desorbed from a chemical-vapor-deposited tungsten surface by controlling the concentration of other cations in solution. The mechanism for surfactant desorption is likely a competition between the cationic surfactant ions and other cations in solution. © 1998 Academic Press

Key Words: **adsorption; desorption; surfactants; wafer cleaning; particle removal.**

INTRODUCTION

During the past few years, the use of chemical–mechanical planarization or chemical–mechanical polishing (CMP) to globally remove excess dielectric or chemical-vapor-deposited (CVD) material has increased dramatically because of its advantages over other techniques for small circuit architecture as evident from the literature (1–10). However, one major drawback of the CMP process is the high number density of polishing particles that remain on the wafer surface after the initial post-CMP rinse. Reducing the number density of the residual polishing particles is, of course, critical to high wafer yields.

The use of surfactants can reduce the level of particulate contamination on wafer surfaces by several orders of magnitude (11). In many cases the effectiveness of the surfactant in reducing particulate contamination is due to steric forces that prevent the particles from adhering as tightly to the underlying substrate surface, although in some cases there are also electrostatic repulsive forces associated with the adsorbed surfactant (11, 12). However, in order for the surfactant to reduce contamination, the surfactant must adsorb on the surface of the substrate and/or the particle. In some particle removal processes, such as in CMP wafer cleaning, the residual surfactant must also be removed prior to additional processing steps. Thus, understanding surfactant desorption or removal is also important. In this study, the effect of dissolved cations on cetyl pyridinium adsorption and desorption at the CVD-tungsten surface is evaluated.

MATERIALS AND METHODS

This study was designed to simulate the industrial tungsten–CMP process. Tungsten-coated silicon wafers, supplied by Sematech, were scored using a silicon carbide-tipped knife, and broken into 2 × 3 cm blanks. Each wafer blank was manually polished on Rodel (CRIC1000-5) polishing pads in a slurry composed of a 1:1 mixture of Semisperse Fe-10 (Cabot Corporation—which was simulated in some parts of this study using 0.1 *M* $Fe(NO_3)_3$) solution and a 20% alumina slurry that consisted of Sumitomo high-purity alumina in water and the specified quantity of reagent-grade cetyl pyridinium chloride (CPC) (Aldrich) at 26°C (note that the solubility of CPC in Fe-10 solution is lowered significantly below 25°C). The CMC of the CPC was measured to be 0.0001% in 0.1 *M* $Fe(NO_3)_3$. These polishing and solution parameters were selected to represent industrial polishing practice. The average alumina particle size was approximately one micrometer. After polishing for 1 min, each wafer blank was rinsed in deionized/distilled water for approximately 10 s, then the wafer blank was allowed to air-dry for 15 min in a vertical position. Each wafer blank was then analyzed in about 30 locations to determine the number density of residual alumina polishing particles using a television monitor, video camera, and microscope set up.

Contact angle measurements were made goniometrically using 4- to 5-μl droplets of carbon tetrachloride on the wafer surface that was submersed in water that was both deionized and distilled. All measurements were made on 2 × 3 cm wafer blanks immediately following sample preparation. Each data point represents the average of 7–20 contact angle measurements. The contact angle data was obtained to give a qualitative understanding of the surfactant adsorption. The high contact angles indicated high hydrophilicity or low surfactant

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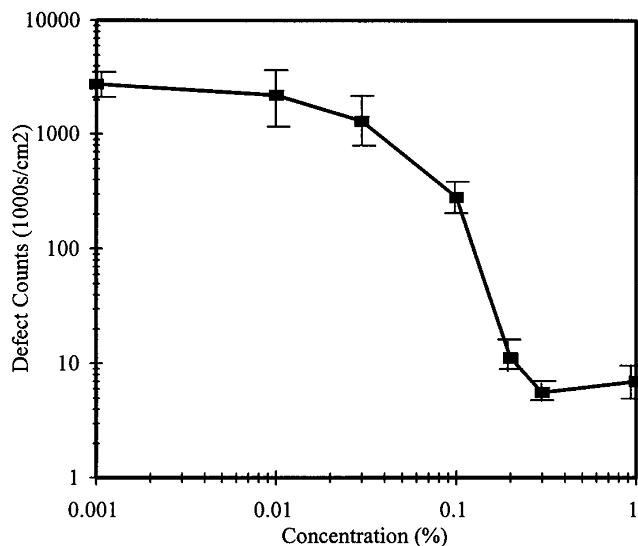

FIG. 1. Comparison of residual alumina particle density versus cetyl pyridinium chloride (CPC) concentration. The error bars represent the standard deviation in the measured values. All experiments were performed at 26 ± 3°C.

adsorption, whereas the low contact angles indicated low hydrophilicity or high surfactant adsorption.

FTIR spectra were obtained using a Bio-Rad FTS-40 spectrometer at a resolution of 4 cm with 4096 scans. The C—H stretching bands at 2925 and 2850 cm^{-1} were used as indicators of the quantity of adsorbed surfactant. Wafer pieces used in FTIR spectroscopy (1.2 × 5.3 cm) were cut using a tungsten-carbide-tipped knife, polished in the presence of alumina particles, then rinsed and lightly scrubbed using soft brushes in deionized/distilled water, then dried. The wafer pieces were then placed in solutions prepared using reagent-grade chemicals for the specified period of time, then rinsed in deionized/distilled water and dried. The wafer pieces were then placed parallel to each other in a multiple reflection cell with a small wafer strip on the top and bottom edges to create a uniform passage for the infrared light. The prepared CVD–tungsten wafer surfaces were oriented to face each other in the FTIR accessory. The tungsten surfaces were set at an angle 55° from the incident beam.

RESULTS AND DISCUSSION

The concentration of surfactant is an important parameter in reducing the number density of alumina particles at the CVD–tungsten surface as shown in Fig. 1. The presence of surfactant in sufficient quantities lowers the final particle density by nearly three orders of magnitude. The data in Fig. 1 clearly show that the surfactant is effective in reducing the residual alumina particle density. The data in Fig. 1 also show that the concentration is critical. Below approximately 0.01%, the surfactant is ineffective and above 0.3% the surfactant does not reduce further the residual alumina particle density at the wafer surface.

Other evidence presented in Fig. 2 shows that there is a relationship between the quantity of adsorbed surfactant (as evidenced by carbon tetrachloride contact angle measurements which decrease with increasing adsorption of surfactant) and the number of residual particles. As the contact angle decreases, which indicates increasing surfactant adsorption, the number density of residual alumina particles decreases. Thus, it appears that surfactant adsorption plays an important role in decreasing the number of particles following the CMP process. Confirmation of the increasing presence of adsorbed surfactant with increasing surfactant concentration is presented using FTIR spectra in Fig. 3, in which the intensity of the hydrocarbon stretching bands is greater at higher CPC concentrations that correlate with high particle removal.

Evaluation of Competitive Adsorption Processes

The concept of competitive adsorption is well known in surface science, where it is established that the equilibrium level of adsorption is determined by both the rate of adsorption and the rate of desorption for each of the species involved. A specific example of this competitive effect can be seen in the adsorption of anionic oleate at the calcium difluoride surface, the rate of which decreases as the concentration of other competitive anions such as hydroxide, fluoride, and carbonate increase (13, 14). Furthermore, it has been shown that the species that had the greatest tendency to adsorb at the fluorite surface also had the greatest inhibitory effect upon the oleate adsorption kinetics (13). In the present study it is believed that the cationic surfactant ions (cetyl pyridinium ions) are competing with ferric ions for tungsten adsorption sites.

With competition between ferric and CPC ions for tungsten surface sites, it is expected that the concentrations of these

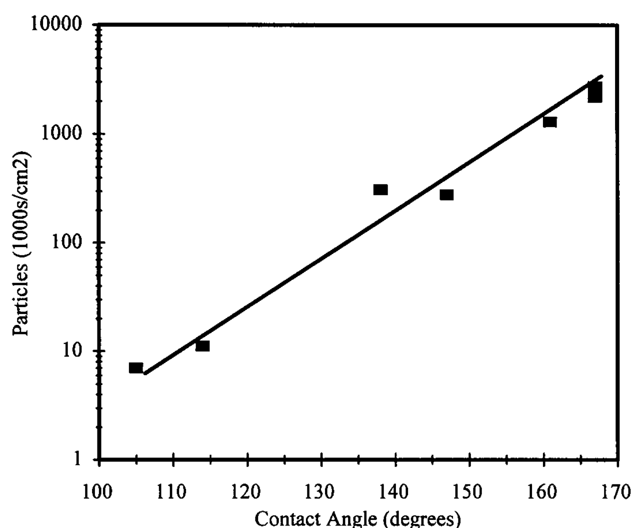

FIG. 2. The relationship between carbon tetrachloride contact angle, which is related to surfactant adsorption, and residual particle density. Each data point represents the average of 7 to 30 individual particle density and contact angle measurements.

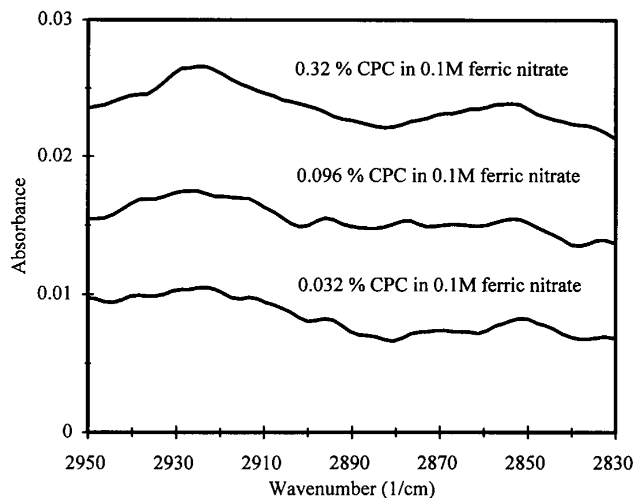

FIG. 3. Multiple reflection FTIR spectra of CVD–tungsten surface after 1-min exposure to specified solution during polishing and subsequent rinsing with purified water. The absorption bands at 2925 and 2850 cm^{-1} are the asymmetric and symmetric C—H stretching bands, respectively.

species will influence the adsorption of surfactant as well as the associated cleaning effectiveness. As expected, the data in Fig. 4 show that as the concentration of ferric iron in the CMP solution increases, the effectiveness of the surfactant, which remains at a constant concentration level in this comparison, decreases. This relationship between the concentration of similarly charged ionic species and the ability of the surfactant to reduce the number density of residual particles, which is related to surfactant adsorption, suggests competitive adsorption.

The likely process of competitive adsorption between ferric and CPC ions can be viewed schematically in Fig. 5. As shown in Fig. 5, the surface of the tungsten is negatively charged

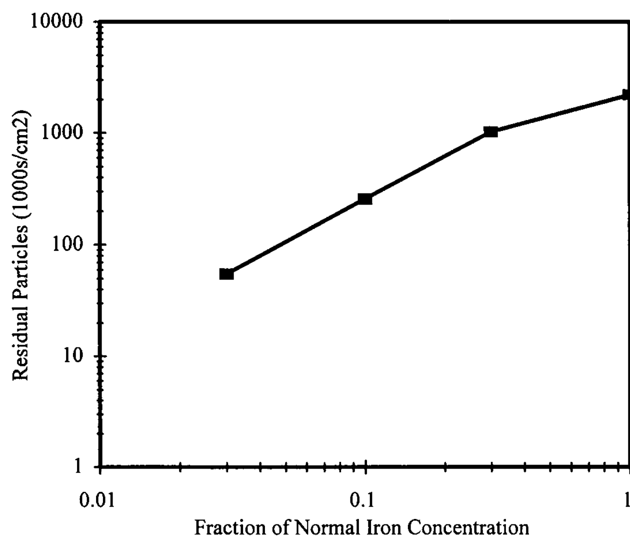

FIG. 4. Comparison of residual alumina particle density and the fraction of normal iron concentration (1:1 water:Fe-10 solution) in the CMP slurry with 0.1% surfactant present in each test.

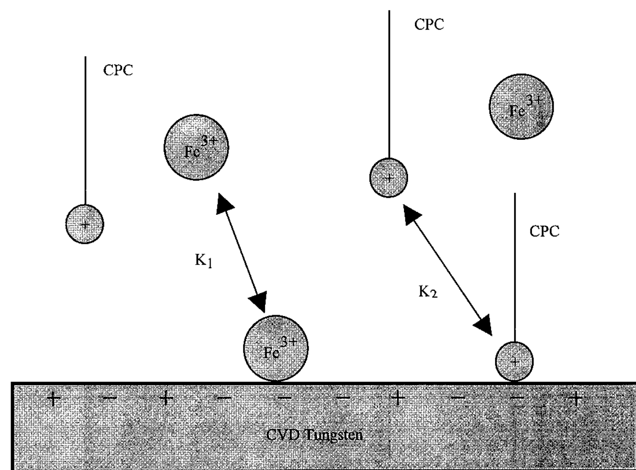

FIG. 5. Schematic diagram illustrating competitive adsorption at the tungsten surface.

under all but extreme acidic conditions (15). Mathematically, the competitive adsorption process can be represented by two reactions, shown as Eqs. [1] and [2], that compete with each other for tungsten, *W*, surface sites following methods applied in gas adsorption (16). The adsorption of charged species is the expected outcome based upon traditional adsorption theory (17, 18). The reactions [1] and [2] can also be written in terms of equilibrium constants K_1 and K_2 as shown in Eqs. [3] and [4].

$$W + Fe \leftrightarrow W \cdot Fe \quad [1]$$

$$W + S \leftrightarrow W \cdot S \quad [2]$$

$$K_1 = \frac{[W \cdot Fe]}{[W][Fe]} \quad [3]$$

$$K_2 = \frac{[W \cdot S]}{[W][S]} \quad [4]$$

By simultaneously solving Eqs. [3] and [4] together with a surface site balance, it can be shown that

$$[W \cdot S] = \frac{K_2[S]W_{\text{tot}}}{1 + K_1[Fe] + K_2[S]}. \quad [5]$$

Eq. [5] shows that if competitive adsorption follows the above mathematical description, the concentration of adsorbed surfactant will depend upon the ratio of the surfactant and iron concentrations as well as the equilibrium constants. For the extreme case when K_2 is small and K_1 is relatively large, the adsorbed surfactant concentration should be linearly related to the ratio of the surfactant concentration to the competitive ion concentration (i.e., $[W \cdot S] \propto [S]/[Fe]$).

Experiments using different concentrations of iron and sur-

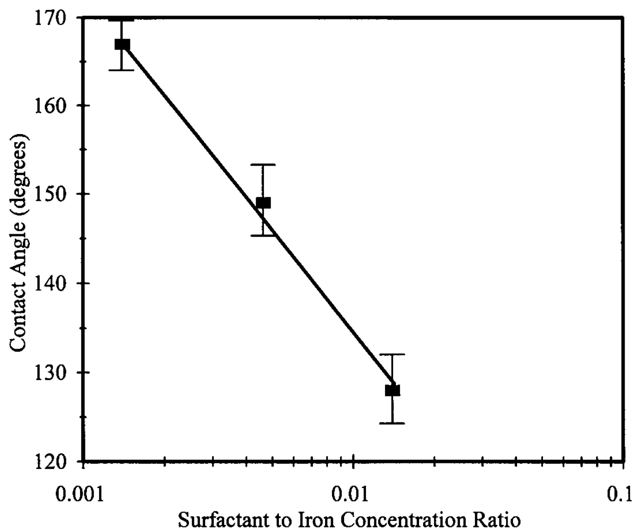

FIG. 6. Comparison of carbon tetrachloride contact angle and the surfactant to iron molar concentration ratio.

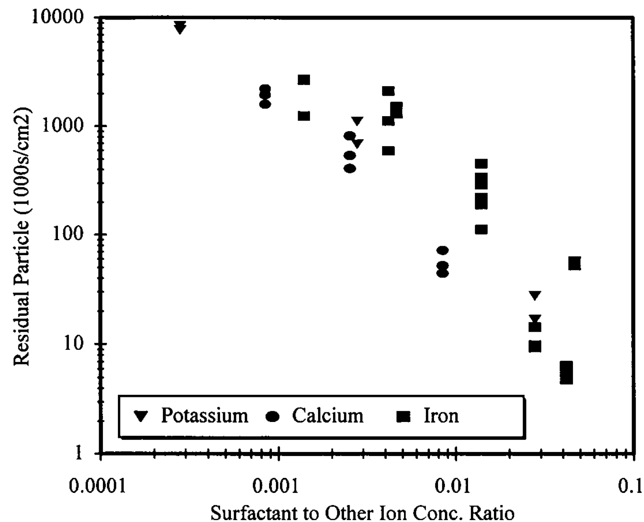

FIG. 8. Comparison of residual particle density and the surfactant to other ion molar concentration ratio.

factant were performed to confirm the importance of the surfactant to iron concentration ratio on surfactant adsorption. The results of these tests are shown in Fig. 6. These results show that the carbon tetrachloride/surface contact angle, which is indicative of surface hydrophilicity, decreases as the surfactant to iron concentration ratio increases. This shows that the level of adsorption is a strong function of the surfactant to iron concentration ratio as expected from Eq. [5]. Because the surfactant adsorption is critical in reducing the adhesion force between the alumina particles and the tungsten surface, it is expected that the final number density of adhering particles will correlate with the surfactant to iron concentration ratio, which is indeed the case as shown in Fig. 7.

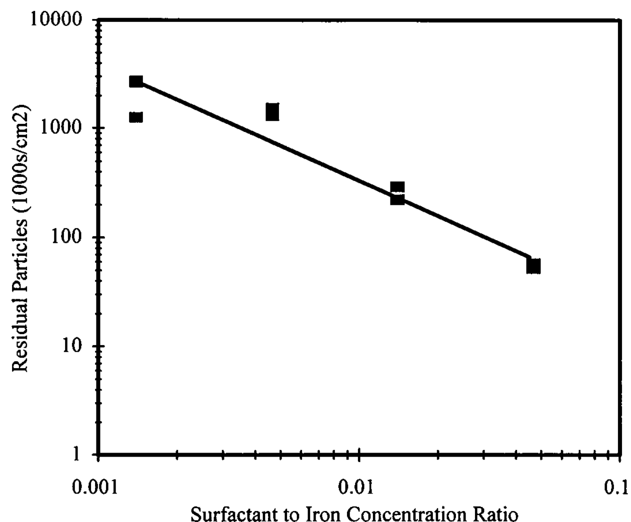

FIG. 7. Comparison of residual particle density to the surfactant to iron molar concentration ratio.

The data presented in Figs. 6 and 7, as well as their qualitative agreement with Eq. [5], strongly suggest that there is competitive adsorption between cationic surfactant molecules and other cations present in solution. These data also show that the surfactant to iron concentration ratio is important to both surfactant adsorption and the corresponding decrease in particle adhesion.

The concept of competitive adsorption was extended to other cationic species to further evaluate the effect. Tungsten-coated wafer polishing experiments were also performed in calcium and potassium nitrate solutions to evaluate the effect of different cations—specifically those with a different charge. The results from these experiments are shown in Fig. 8 as a function of residual particle density and the surfactant to other ion concentration ratio. These results show that the number density of residual particles decreases as the concentration ratio increases. This general trend appears to be independent of the cations present, although the effectiveness of a given cation will be dependent upon its ability to adsorb on the surface.

Surfactant Desorption

All of the data presented thus far show that other cations influence surfactant adsorption and that surfactant adsorption is an important parameter in decreasing the particle adhesion. However, in many particle removal processes, such as post-CMP rinsing, the adsorbed surfactant must be removed before further processing can be performed. Using the principle of competitive adsorption, it would be expected that a very low surfactant to competitive ion ratio during the rinsing process could result in the desorption of the adsorbed surfactant molecules. This concept of desorption was tested by first coating CVD–tungsten surfaces with cationic surfactant molecules (CPC) in a solution containing

no additional salts. These coated samples were then rinsed in water to remove the surfactant solution and placed in small beakers containing various salts for 5 min. Common acidic and basic salts were selected for comparative purposes. After soaking in the salt solutions, the samples were rinsed in water and then resubmerged in water for carbon tetrachloride contact angle measurements. The experimental results are presented in Fig. 9. The results show that the initial contact angle after coating and soaking in water (i.e., the control sample with salt present) had a carbon tetrachloride/surface contact angle of 118°, indicating a very hydrophobic surface with a high concentration of adsorbed surfactant. On the other hand, the sample that was soaked in ferric nitrate solution had a contact angle of 158°, thus showing substantial removal of surfactant molecules from the tungsten-coated surface. The other cations also contribute to the removal of surfactant as indicated by the increase in contact angles relative to the control sample. The results also show that potassium hydroxide is more effective in surfactant removal than potassium nitrate, suggesting that the role of the anion may also be important—perhaps due to complexation with the removed cationic surfactant in the case of hydroxide anions. The effectiveness of the hydroxide salts is also encouraging from an industrial application viewpoint because hydroxides such as ammonium hydroxide are already in use in wafer cleaning following the CMP process.

Spectroscopic confirmation of surfactant desorption or removal from tungsten surfaces in the presence of ammonium and potassium hydroxide solutions is presented in Fig. 10. The spectra in Fig. 10 show that after adsorption of cetyl pyridinium ions, the assymetric and symmetric C—H absorbance is high due to cetyl pyridinium ion adsorption. However, after treating the surfactant coated CVD–tungsten surface with ammonium and hydroxyl ions, the assymetric and symmetric C—H absorbances are nearly eliminated. These spectral results corroborate the previous results from contact angle measurements, and they indicate that adsorbed cetyl pyridinium ions can effectively be displaced in the presence of other cations when the concentration of the other cations is sufficient.

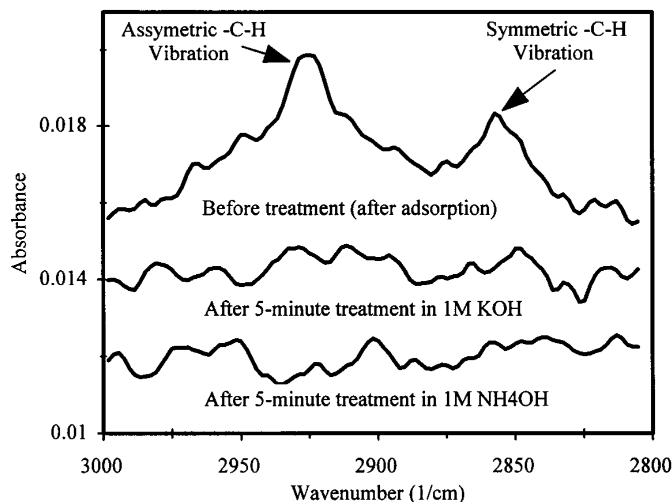

FIG. 10. FTIR spectra of surfactant-coated tungsten surfaces before and after exposure to the specified salt solutions.

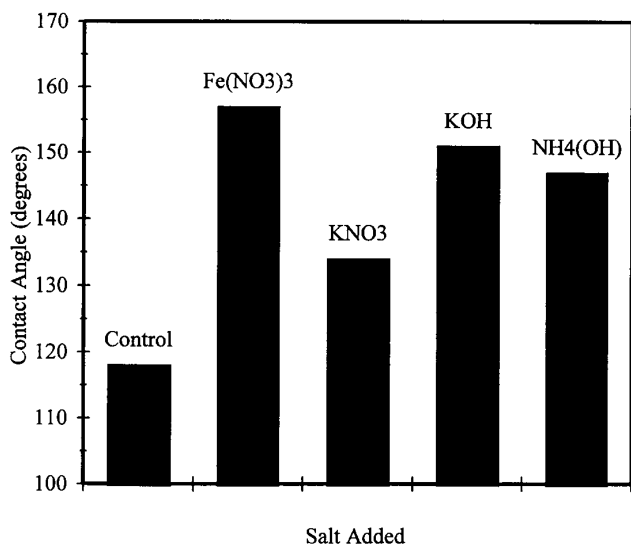

FIG. 9. Effect of various salts on the contact angle. In each test tungsten-coated wafer blanks were polished in a surfactant/alumina suspension, then rinsed in water and soaked for 5 min in the specified 0.1 *M* salt solutions. The samples were then rinsed thoroughly and the carbon tetrachloride contact angles were measured in water. The control test consisted of soaking in water rather than salt solution.

SUMMARY

The data in this study indicate that competitive adsorption processes are important in surfactant adsorption and desorption at CVD–tungsten-coated silicon wafer surfaces. As the cationic surfactant to other cation concentration ratio increases, the adsorption of surfactant molecules increases, leading to decreased particle adhesion at the wafer surface. As the ratio decreases, fewer cationic surfactant molecules absorb on the wafer surface. After adsorption of cetyl pyridinium ions has occurred, desorption can be accomplished by reducing the surfactant to other cation concentration ratio. Thus, the degree of adsorption or desorption or cetyl pyridinium ions can be controlled by controlling the molar ratio of cetyl pyridinium chloride to other cations.

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