Journal of The Electrochemical Society, **151** (5) G360-G367 (2004)
0013-4651/2004/151(5)/G360/8/$7.00 © The Electrochemical Society, Inc.

Effect of Additives on Copper Outplating onto Silicon Surface from Dilute HF Solutions

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The effects of additives such as acids and surfactants on copper outplating onto silicon surfaces from dilute HF solution were studied. It was found that some additives could significantly reduce copper outplating. Results from potentiommetry, total-reflectance X-ray fluorescence, time-of-flight–secondary ion mass spectroscopy, dynamic light scattering, and electron microscopy suggested that the anionic surfactant had strong interaction with cupric ions in solution, and their complex was adsorbed onto silicon surfaces, causing nonredox-type copper contamination. Dynamic light-scattering results also revealed strong interaction between the anionic surfactant and nickel ions. The roles of surfactants in copper outplating are discussed in this paper.
[DOI: 10.1149/1.1688340]

Manuscript submitted April 24, 2003; revised manuscript received October 18, 2003. Available electronically April 5, 2004.

With semiconductor devices continuously moving to smaller and smaller sizes, it is becoming more critical to keep silicon surfaces contamination free in order to improve device functionality, yield, and reliability. The RCA-based wet chemical clean is still widely used in semiconductor device fabrication processes.[1,2] After SC-1 and SC-2 treatments the silicon surface possesses a chemical oxide layer about 1 nm thick. For pregate clean, the low-quality chemical oxide layer is ideally to be removed before growing a high-quality thermal gate oxide layer. This can be done by dilute HF (DHF) treatment. DHF-based clean is also widely used in other steps in semiconductor processing. However, during DHF cleans particles tend to redeposit onto the silicon surface due to large dispersion interactions between the bare silicon surface and particles,[3] and heavy metal ions such as Cu^{2+} can outplate from DHF baths, leaving pitting and metal particles on silicon surfaces through redox reactions[4]

$$Si + 2Cu^{2+} + 6HF = H_2SiF_6 + 2Cu + 4H^+ \qquad [1]$$

In order to prevent particle redeposition in DHF cleans, surfactants are frequently used to modify electric charges on both silicon and particle surfaces so that a repulsive electrostatic force overcomes attractive dispersion force between the two surfaces.[3,5] Surfactants are also reported to have a different effect on copper outplating from HF solutions onto silicon surfaces. Ohmi *et al.* have shown that copper deposition on silicon wafers from BHF63 solution was decreased if a certain type of hydrocarbon or fluorocarbon surfactant was used.[6] Obeng demonstrated that the addition of anionic perfluorocarbon surfactants to a 5% HF solution reduced silicon surface copper concentration fourfold.[7] Jeon *et al.* reported a tenfold decrease in copper outplating by using surfactant OHS, which is an alkylphenol polyglycidol nonionic surfactant.[8] However, Torcheux *et al.* reported that FC-98, a perfluoroalkylcyclohexylsulfonate clearly increased silicon surface copper contamination.[9]

It has been postulated that the reasons for surfactants to be effective in decreasing copper outplating are (*i*) surfactant films adsorb on and passivate substrate surfaces, and (*ii*) the micelles immobilize cupric ions, which reduces the efficiency of electron transfer kinetics and free cupric ion concentration, and thus the driving force for copper outplating.[7] Nevertheless, the role of surfactants in increasing copper contamination is still unclear.

Because the amount of copper contamination on silicon surface is much less than 1×10^{14} atom/cm^2, the order of magnitude of a monolayer, the characterization of surface copper contamination is usually conducted by employing total-reflectance X-ray fluorescence (TXRF) or inductively coupled plasma mass spectrometry (ICP-MS).[10,11] Recently, Chyan *et al.* reported a novel potentiometric sensor for the detection of trace metallic contaminants in HF solution.[12] They found that metal ions that can oxidize silicon shift the open circuit potential (OCP) of a silicon electrode positively, and the amount of shift is proportional to the logarithm of oxidizing ion concentration in solution. However, the linearity between the OCP shift and the ion concentration has not yet been discussed. Bertagna *et al.* also studied the mechanism of copper outplating on silicon surfaces in DHF solutions by monitoring the OCP change of a silicon electrode as a function of copper contamination time and bulk contamination level.[13]

In this study we combined the potentiometry technique, TXRF, and ICP-MS to determine the effects of different additives on suppressing copper outplating on silicon surfaces in DHF solutions. Surfactant—cupric ion interaction in solutions was studied with light scattering and transmission electron microscopy (TEM). The surfactant effect on reducing copper nucleation on silicon surfaces was studied with scanning electron microscopy (SEM). The absorbed surfactant layer on the silicon surface was verified with an atomic force microscopy (AFM). Based on these results, the surfactant effect on copper outplating in DHF clean was summarized. The mechanism of OCP change of a silicon electrode as a function of surface metal contamination is discussed in the Appendix.

Experimental

Different additives such as HCl, H_2O_2, HNO_3, a cationic surfactant, and an anionic surfactant were selected to study their effects on copper outplating. The cationic surfactant we used is an alkyltetramethylammonium bromide (CTAB), and the anionic surfactant is a sulfur-containing surfactant. They have similar chain structures and molecular weights. Our previous results showed that both of them are effective in preventing particle redeposition during dilute HF cleaning of silicon surfaces.[3]

The potentiometry measurement set up was as follows. A 2 in. (100) n-type silicon wafer with 1-10 Ω cm resistivity (Silicon Quest International) was subjected to SC-1 cleaning, DHF clean, and DI water rinse to remove particles and chemical oxide before being mounted on a custom-made Teflon electrochemical cell. Only the polished side of a wafer was contacted with solution and the back side was contacted to a stainless steel base that had a stainless steel connection to the outside. A thin film of eutectic Ga-In alloy (Alfa Aesar) was employed between the back side of the wafer and the metal base to ensure ohmic contact. A HF-resistant Ag/AgCl reference electrode (Fisher Scientific) was positioned near the wafer. 50 mL 0.5 wt % solutions with/without additives were used in the cell. A 25 W Leica incandescent lamp was employed and the light directly shined onto the wafer. Copper was added by using 1000 ppm atomic absorption spectroscopy (AAS) standard (Fisher Scientific) to different final bulk concentrations in the solutions. Each time the Cu was added, the solution was gently shaken until it appeared well mixed. OCP change with time was recorded using a CHI 660 Electrochemical workstation. After 15 min more Cu was added to the

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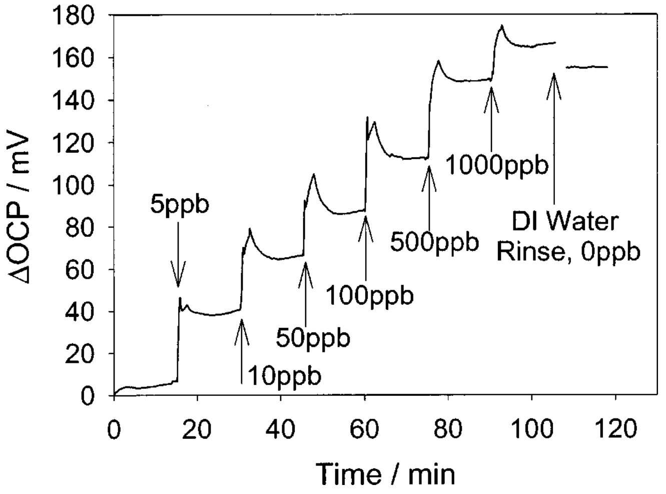

Figure 1. OCP change with copper addition (fresh 0.5% HF is used at the final stage).

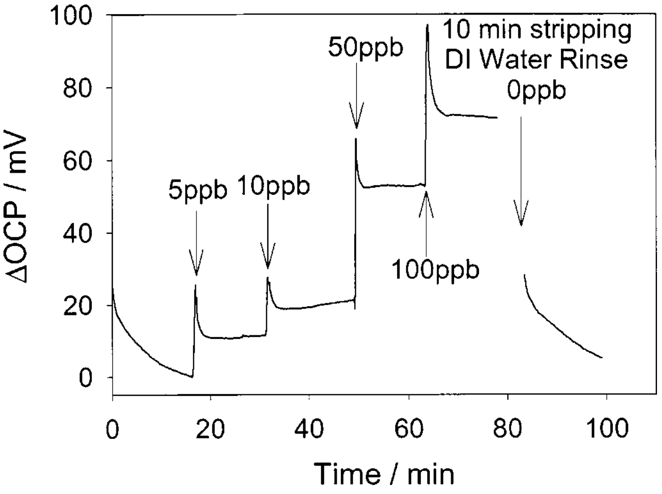

Figure 2. OCP change with copper addition (the surface copper is stripped and fresh 0.5% HF is used at the final stage).

solution and the processes were repeated. To regenerate the silicon wafer electrode, a 5 mL 5% HF + 5% HNO_3 + 5% H_2O_2 (wt) solution was employed to remove surface Cu.

Surface contaminations were examined by TXRF and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Silicon wafer samples were dipped into 0.5% HF + 100 ppb copper baths with/without surfactant for 10 min under illumination. For all the experiments, the surfactant concentrations were 1% (wt). Particle size analyses were carried out in 1% anionic surfactant +500 ppm copper contaminant water solution by dynamic light scattering. TEM analyses on particles in 1% anionic surfactant +500 ppm copper contaminant were also conducted. The TEM sample was prepared by dipping a copper grid covered with an amorphous carbon thin film (Ted Pella) into the solution to capture particles.

Characterization of adsorbed surfactant layers on a silicon surface was done by using a surface force measurement technique with an atomic force microscope (Digital Instruments SPM nanoscope III). The liquid cell and the silicon nitride tips were all from Digital Instruments. The detailed method and experimental setup can be found elsewhere.[3] Solutions for the measurement were prepared with DI water +1% surfactant and the pH values were adjusted with HCl to 1.87-1.90. The solutions contained 0.1% HF in order to prevent oxide formation on the silicon surface.

The surfactant effect on protecting damaged silicon surfaces from copper outplating was also studied. Surface damages were intentionally introduced by scratching the silicon surface with a diamond scribe. Scratched wafer pieces 1 × 1 cm in area were dipped into 0.5% HF + 1 ppm Cu^{2+} solutions with and without surfactant for 10 min under 25 W incandescent light illumination. Then the wafer pieces were DI water rinsed and subject to SEM observation. Secondary electron images and characteristic Cu and Si Kα X-ray images were taken.

Results and Discussion

Potentiometric method to characterize additive efficiency on copper outplating.—Copper ions in a DHF solution cause the change of the OCP between a silicon electrode and a reference electrode.[12] The OCP change of a silicon electrode with copper addition is plotted in Fig. 1. OCP change correlates well with the bulk copper concentration. Each time right after copper is added, the OCP increases suddenly and then gradually changes to a relative stable value after 15 min. With the addition of more copper contaminants, similar change in the OCP value is observed. After a DI water rinse and a fresh 0.5% HF solution without copper contamination is used on the same electrode, the OCP does not go back to its original value, thus suggesting that the OCP response is not caused by copper ions in the solution. This statement is further verified by the results plotted in Fig. 2 in which the stripping solution is used to dissolve the surface copper, and the OCP in fresh 0.5% HF goes back to about the original value. This confirms that the surface copper, not copper in the solution, is responsible for the OCP change.

Figure 3 plots the OCP change as a function of the logarithm of bulk copper concentration. The least-squares regression result shows that the relationship between OCP change and log[Cu/ppb] is linear with $r^2 = 0.99$. Figure 4 summarizes the OCP change *vs.* time on different p-type wafers from the same batch and Fig. 5 shows the same parameter obtained from different n-type wafers from the same batch. It shows that n-type wafers have higher slope than p-type wafers. Norga *et al.* reported that n-type wafers are more susceptible to copper outplating than p-type wafers.[14] Thus, the slope change is qualitatively correlated to the susceptibility of copper outplating. From Fig. 4 and 5 we can see that the slopes of the regression lines are much more repeatable than the absolute OCP values. This is because the OCP of a silicon electrode is also dependent on its surface conditions. It is very difficult to have identical surface conditions on different wafers or on the same wafer in different times (the mechanism of the OCP change of a silicon electrode in a DHF solution is discussed in the Appendix). Nevertheless, the repeatable slope of regression line can provide a qualitative measure of the degree of copper outplating and thus the efficiency of an additive on

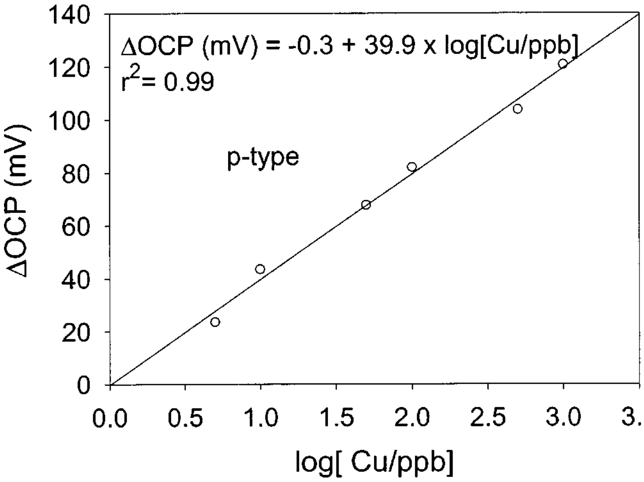

Figure 3. OCP change *vs.* the logarithm of copper bulk concentration.

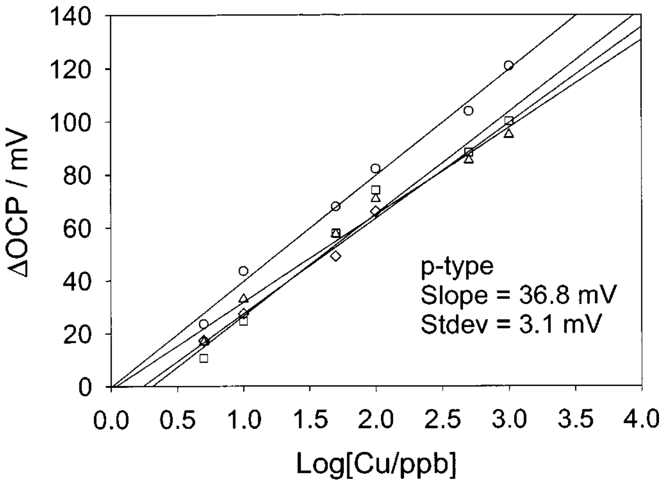

Figure 4. p-Type wafer OCP change *vs.* the logarithm of copper bulk concentration (different wafers from the same batch). The slope is repeatable but the absolute OCP values are not repeatable. Each type of symbol represents data from the same run of experiment.

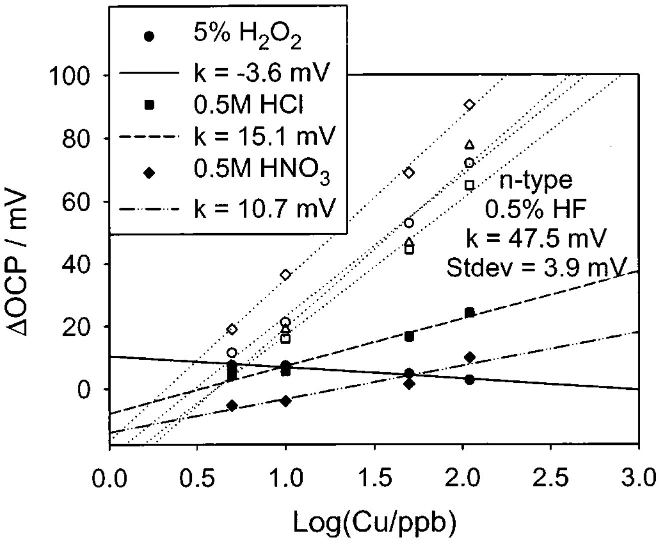

Figure 6. Effects of H_2O_2, HCl, and HNO_3 on copper outplating (5% H_2O_2, 0.5 M HCl, and 0.5 M HNO_3 in 0.5% HF, respectively). Plots of 0.5% HF only are also graphed. These additives clearly decrease the slopes, indicating decreased copper outplating. Each type of symbol represents data from the same run of experiment.

copper outplating. We used three additives, H_2O_2, HCl, and HNO_3, to further examine this correlation, whose effects on minimizing copper outplating are well documented.[15-18] The effects of additives are shown in Fig. 6. When 5% H_2O_2, 0.5 M HCl, or 0.5 M HNO_3 is added the slope is much smaller than that obtained in the reference sample. Therefore the slope of OCP change can be used to characterize the surfactant effect on copper outplating in dilute HF solutions.

Surfactant effect on copper outplating from dilute HF solution on the silicon surfaces.—In this study, we combined the potentiometric method and direct measurement methods (TXRF and TOF-MS) to characterize copper outplating onto silicon surfaces. The plots of OCP change with bulk copper concentration with and without the cationic surfactant are shown in Fig. 7a. The open symbols represent the case without surfactant, the solid symbols represent the case with surfactant, and each type of symbol represents data from the same run of experiment. At low copper contamination level (<50 ppb), the slope is remarkably smaller when surfactant is present (13.4 mV with surfactant *vs.* 47.5 mV without surfactant); at high copper contamination level (>50 ppb), the slopes with and without surfactant are about the same (44.5 mV with surfactant *vs.* 47.5 mV without surfactant). This suggests that the cationic surfactant can reduce copper outplating effectively at low copper contamination level. The TXRF surface copper concentration results in Fig. 7b indicate that the surfactant indeed decreases copper outplating. At 100 ppb bulk contamination level as in TXRF experiments, the surfactant starts losing its capability to reduce copper outplating suggested by Fig. 7a. Nevertheless, the overall surface copper contamination is still lowered. It could be understood by drawing a regression line passing only the first four points of the same experimental run with surfactant, *i.e.*, the points corresponding to the bulk concentration up to 100 ppb. The slope of this line is lower than that of the control sample.

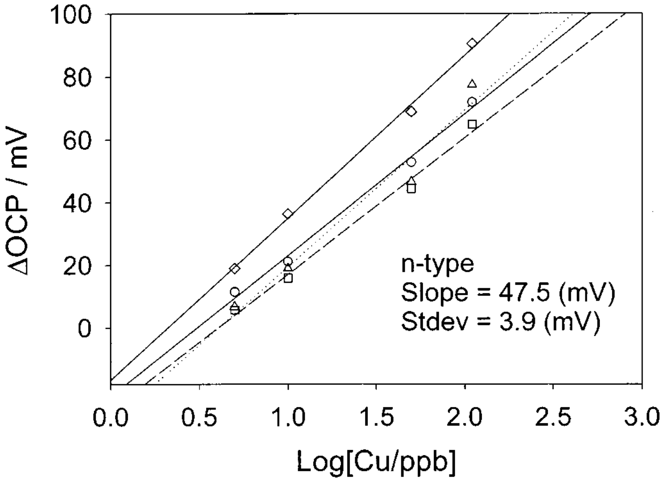

Figure 5. n-Type wafer OCP change *vs.* the logarithm of copper bulk concentration (different wafers from the same batch). The slope is repeatable but the absolute OCP values are not. Each type of symbol represents data from the same run of experiment.

The effect of the selected anionic surfactant on copper outplating is shown in Fig. 8. The OCP change *vs.* log[Cu] plots in Fig. 8a indicate that the surfactant is also effective in decreasing copper outplating, because it gives significantly smaller slopes (7.8 mV with surfactant *vs.* 50.0 mV without surfactant). However, TXRF results in Fig. 8b show only about twofold decreases in copper outplating, contradicting our prediction. In order to investigate the copper outplating mechanism with the presence of this surfactant, surface copper change with dipping time was measured. The bulk copper concentration was still 100 ppb. The results are given in Fig. 9. The most important observation in this experiment is that the surface copper concentrations do not change with dipping time when the surfactant is present, implying that the surface copper may not be due to redox reaction but some kind of adsorption-type reaction. In the solution some free cupric ions associate with surfactant molecules on the anionic group, and the charges are neutralized. Thus, surfactants lose their hydrophilicity, and they have more tendency to adsorb onto hydrophobic bare silicon surfaces. Furthermore, the final rinse by DI water cannot remove adsorbed surfactant-copper complexes totally from silicon surfaces. Therefore, copper surface contamination is high. The OCP method responds only to metallic copper (see Appendix). That is why the OCP method suggests low copper contamination while TXRF results show high copper contamination.

In order to support our hypothesis on copper-surfactant association, we increased the copper concentration to 500 ppm in a 0.5% HF + 1% anionic surfactant solution, and the solution was

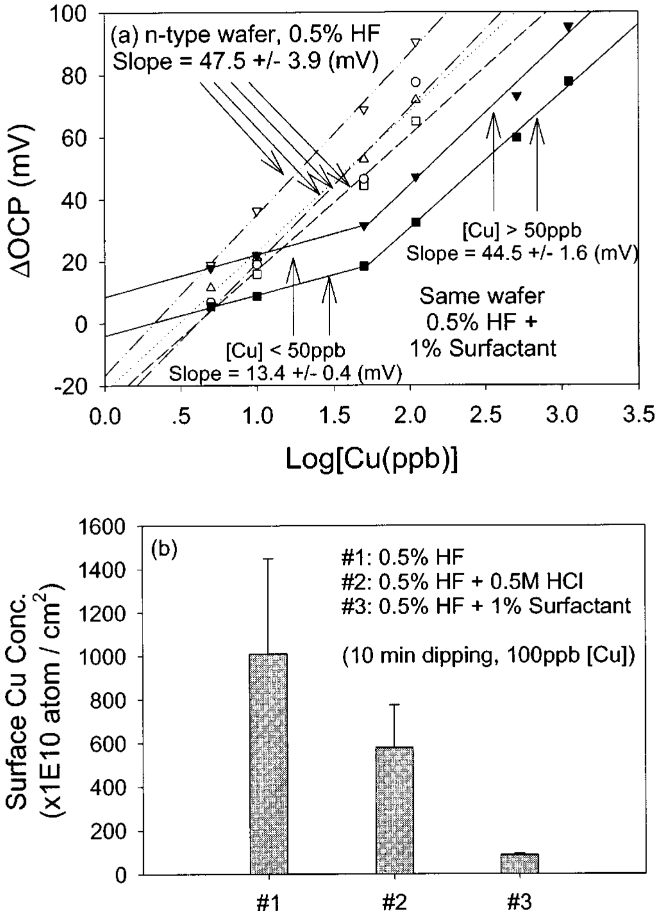

Figure 7. Effect of the selected cationic surfactant on copper outplating from DHF solution onto silicon surfaces. (a) Plots of OCP change *vs.* log[Cu]. The cationic surfactant decreases the slope. (▽,○,△,□) The case without surfactant; (▼,■) the case with surfactant. Each type of symbol represents data from the same run of experiment. (b) TXRF results of surface copper concentration after 10 min dipping into 100 ppb copper-contaminated DHF solution. The cationic surfactant decreases surface copper contamination.

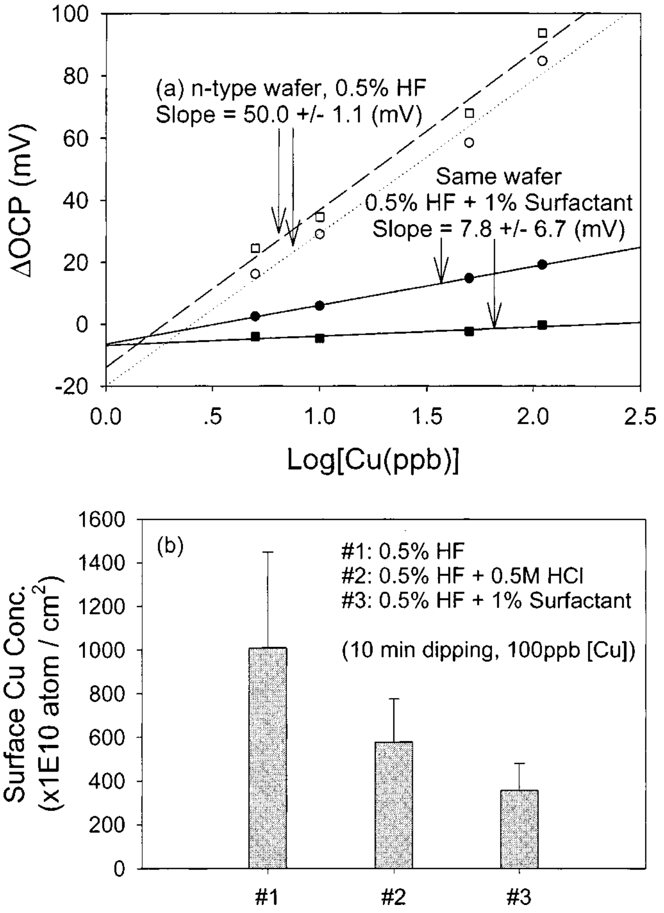

Figure 8. The effect of the selected anionic surfactant on copper outplating from DHF solution onto silicon surfaces. (a) The plots of OCP change *vs.* log[Cu]. The anionic surfactant also decreases the slope significantly. (□,○) The case without surfactant; (■,●) the case with surfactant. Each type of symbol represents data from the same run of experiment. (b) TXRF results of surface copper concentration after 10 min dipping into 100 ppb copper-contaminated DHF solution. The surfactant decreases copper outplating only about twofold.

subject to dynamic light-scattering particle size analysis. The results are graphed in Fig. 10. They show that after the addition of cupric ions to achieve bulk concentration of 500 ppm, the measured particle distribution clearly shifted to larger sizes compared with the case without copper contaminants. Those particles were subjected to TEM analysis. The bright-field TEM in Fig. 11 shows that the precipitation formed an oily film with localized droplets on amorphous thin carbon film of copper grid. The selected area diffraction (SAD) was done both on the oily film and the droplets. The SAD pattern indicates that they are amorphous.

If copper is indeed precipitated onto silicon surfaces with surfactants, then the silicon surfaces should have high sulfur contamination as well, because the anionic surfactant we studied contains sulfur. Unfortunately, TXRF did not detect a sulfur signal at this contamination level. In order to prove our hypothesis, another anionic surfactant with two sulfur-containing groups was briefly studied on its effect on copper outplating by OCP monitoring and TOF-SIMS surface analysis. Because this surfactant has two sulfur atoms on one molecule, it is expected to give a higher sulfur signal even if the adsorption amount is about the same as the previous surfactant. OCP change with bulk copper concentration plots in Fig. 12a suggest it is effective in reducing copper contamination. However, the TOF-SIMS results in Fig. 12b reveal increased copper contamination. This time the sulfur signal was clearly observed to be higher than the control sample. These results are in agreement with

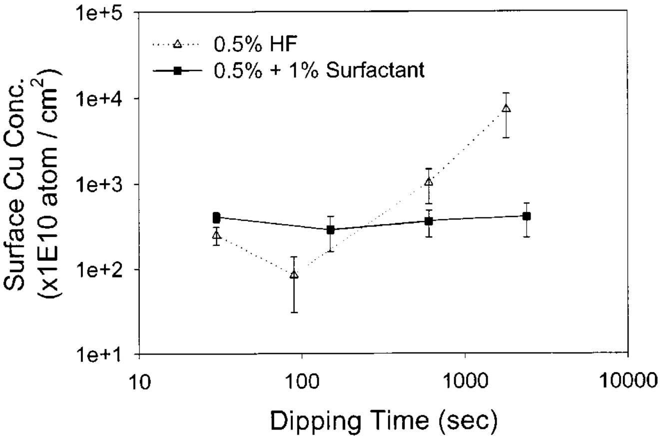

Figure 9. TXRF results of surface copper concentrations as a function of dipping time. The copper contamination with the presence of the anionic surfactant does not change with time. The solution is 0.5% HF + 100 ppb copper with/without surfactant.

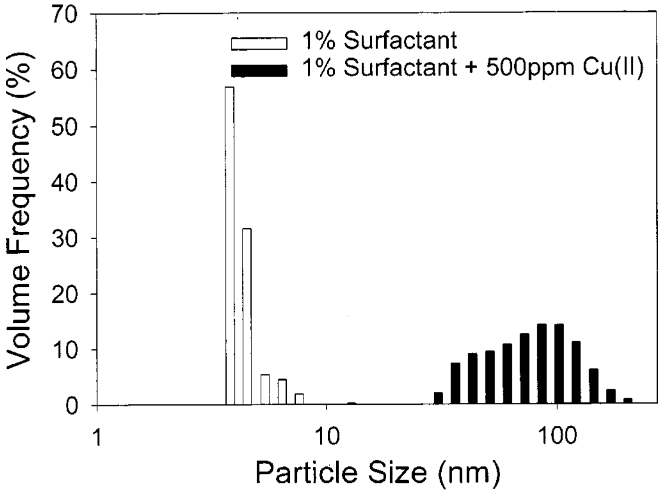

Figure 10. Particle size distributions in 0.5% HF + 500 ppm copper with/without the anionic surfactant. Addition of the surfactant clearly shifts particle size distribution.

our hypothesis. Our experiment also explained the observation by Torcheux*et al.*, who reported that a perfluoroalkylcyclohexylsulfonate clearly increased silicon surface copper contamination.[9]

Generally speaking, in DHF clean only noble metals are concerned for metal contamination, because the mechanism for metal outplating from HF solution is redox reaction. However, if anionic surfactant is used, the adsorption mechanism should also be considered. In this mechanism, not only cupric ions but also other metal ions are possible to form precipitation with the surfactant and are adsorbed onto silicon wafer surfaces. Therefore, we also briefly studied the interactions between the selected surfactant and Fe^{3+} and Ni^{2+}. Figure 13a and b shows the dynamic light scattering results on 1% surfactant +500 ppm Fe^{3+} and Ni^{2+}, respectively, illustrating that Fe^{3+} does not form precipitation with the surfactant, while Ni^{2+} indeed forms precipitation with this surfactant. Therefore, it is also possible to increase nickel contamination if this surfactant is used in DHF clean.

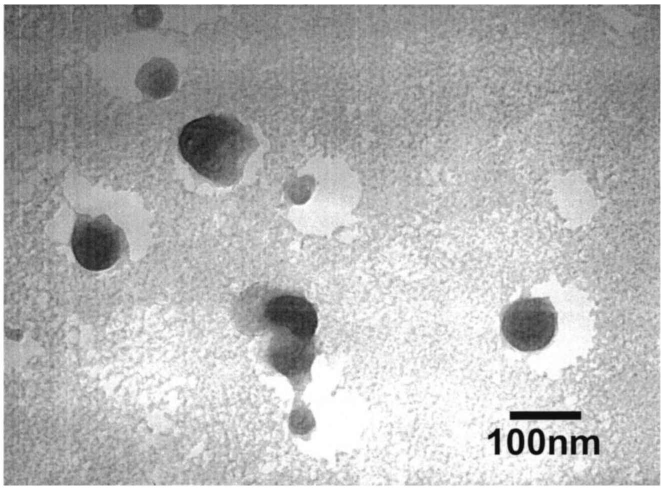

Figure 11. TEM bright-field image of surfactant-copper particles, amorphous in nature (SAD pattern is not shown).

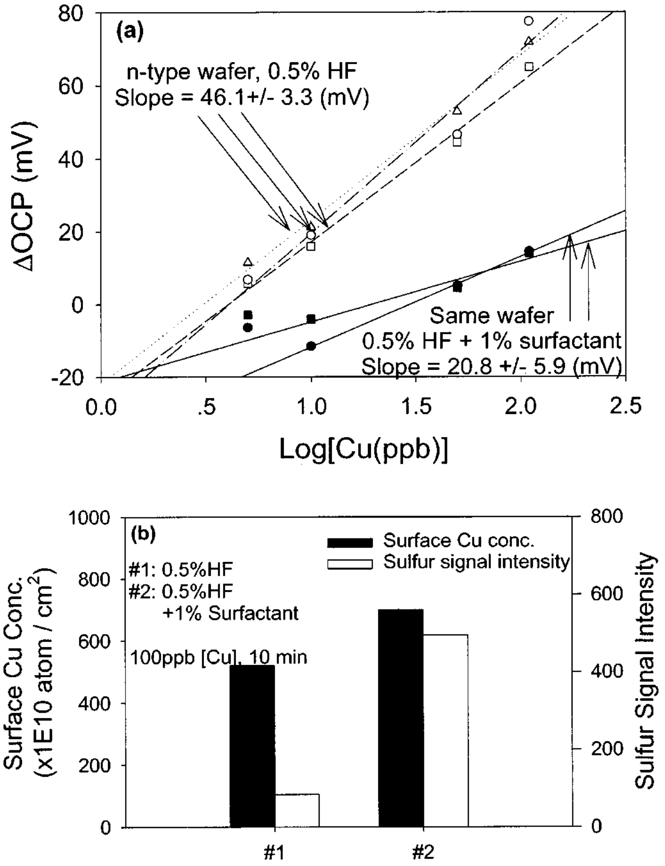

Figure 12. The effect of an anionic surfactant with two sulfur groups on copper outplating. (a) Plots of OCP change *vs.* log[Cu], also providing a smaller slope. (b) TOF-SIMS surface analysis results. Copper contamination and sulfur contamination are higher.

Preferential surface copper nucleation and the effect of surfactant on elimination of such preferential nucleation.—We reported that for a silicon surface with both an amorphous region and a crystalline region, copper was preferentially deposited on the amorphous region[19] due to preferential nucleation in the amorphous region because of higher dangling bond density. We also reported that the preferential deposition of Cu onto a silicon surface could be induced by employing an AFM scratch on the surface.[20] Here we studied the effect of surfactant on preferential nucleation of copper on a silicon surface by intentionally introducing surface scratches on the samples with a diamond scribe and then performing copper contamination experiments. Figure 14 is the result with no surfactant present in the contaminating solution. It shows that copper only outplates on the scratch-damaged region. The X-ray mapping (Fig. 14b, Cu Kα mapping; Fig. 14c, Si Kα mapping) verified that the deposited particles are copper. Amazingly, some surfactants can eliminate the structural-defect-enhanced copper outplating. We added 1% CTAB into the copper outplating solution and dipped a silicon sample with intentional scratches on its surface into this solution for 10 min under the same conditions as the control sample (Fig. 14). The micrographs of this sample are presented in Fig. 15. The SEM image (Fig. 15a) shows that the scratches are intact and even the sharp features are preserved, which are most prone to copper outplating. The Cu Kα map (Fig. 15b) and Si Kα map show that the copper contamination level is lower than electron-dispersive spectroscopy detection limits; the random white dots in Fig. 15b are due to noise.

Summary on surfactant effects on copper outplating during DHF cleans.—According to the results presented and those published previously, the roles a surfactant plays in copper contamination during DHF cleans can be summarized as follows:

1. Surfactants form a protecting layer on silicon surfaces. The adsorbed surfactant molecular layer on silicon hinders electron transfer between a silicon surface and a cupric ion. Because the

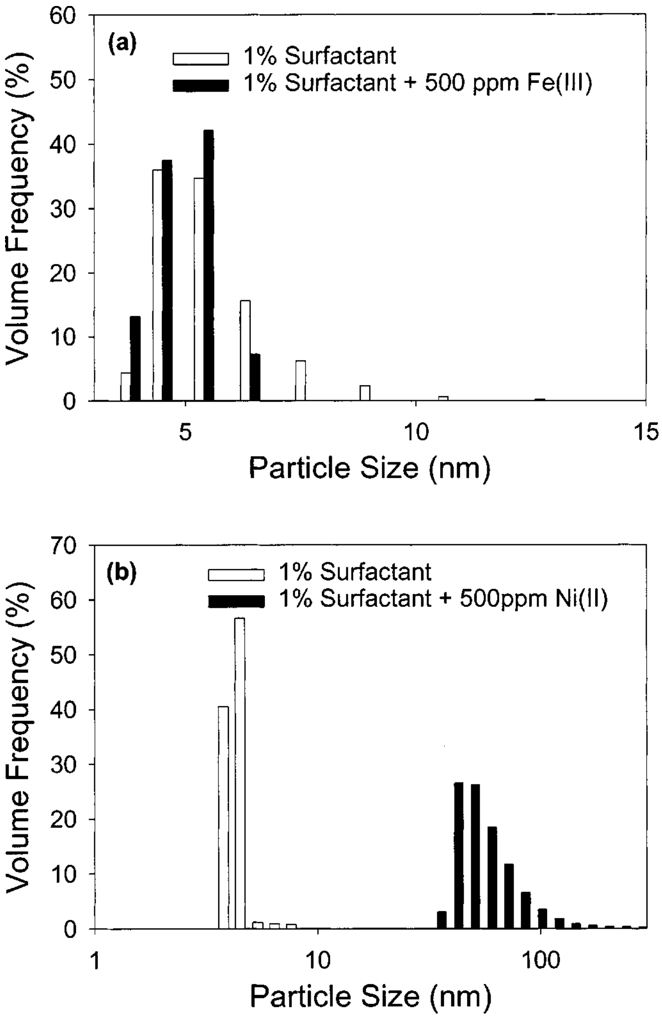

Figure 13. Particle size distributions in 0.5% HF + 500 ppm metal ions with/without surfactant: (a) Fe(III) and (b) Ni(II) ions. Ni(II) also forms particles with this surfactant.

copper reduction on a silicon surface is no longer diffusion controlled (Fig. 9), it is deduced that the rate-limiting step is electron transfer. Direct observance of the lack of preferential nucleation (Fig. 15) also supports this conclusion. The evidences of surfactant layer formation on the silicon surface are the zeta-potential changes[3] and the results from direct force measurement. Figure 16 is a plot of interaction force between a silicon nitride AFM tip and a silicon surface in a 0.1% HF + 1% CTAB solution as a function of separation distance. The pH of the solution was adjusted with HCl to about 2. The force is normalized by the effective tip radius, *R*. The force curve in Fig. 16 is discontinuous at about 2.2 nm separation, indicating a surface film structure. This film is broken by the continuous movement of the tip toward the silicon surface.

2. Surfactants interact with cupric ions. Surfactants, especially anionic surfactants, may have strong interaction with cupric ions. Our light-scattering experimental results can serve as evidence (Fig. 10). Surfactants have two effects on copper outplating. One is surfactants decrease free cupric ion concentration, resulting in decreased driving force for copper outplating (Fig. 8). The other is the surfactant-cupric ion complex may be adsorbed onto silicon surfaces. If this complex cannot be rinsed totally by following DI water rinse, then the copper contamination increases (Fig. 12).

The roles of surfactants in copper outplating are not isolated. Hence, we observed different effects of surfactants on copper outplating. The contamination mechanism via adsorption suggests that if surfactants are used in DHF cleans, which is proposed to minimize particle redeposition, it is critical to study its effect on metal contamination and also other metals with low reducing potentials.

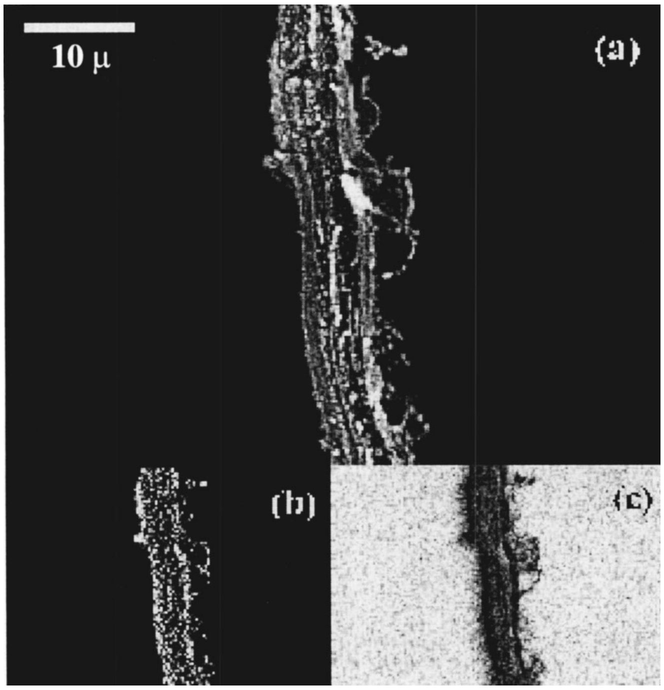

Figure 14. Micrographs of a scratched silicon surface after copper contamination in a 0.5% HF solution: (a) SEM image, (b) Cu Kα X-ray image, and (c) Si Kα X-ray image. Copper deposits only in the scratch-damaged region.

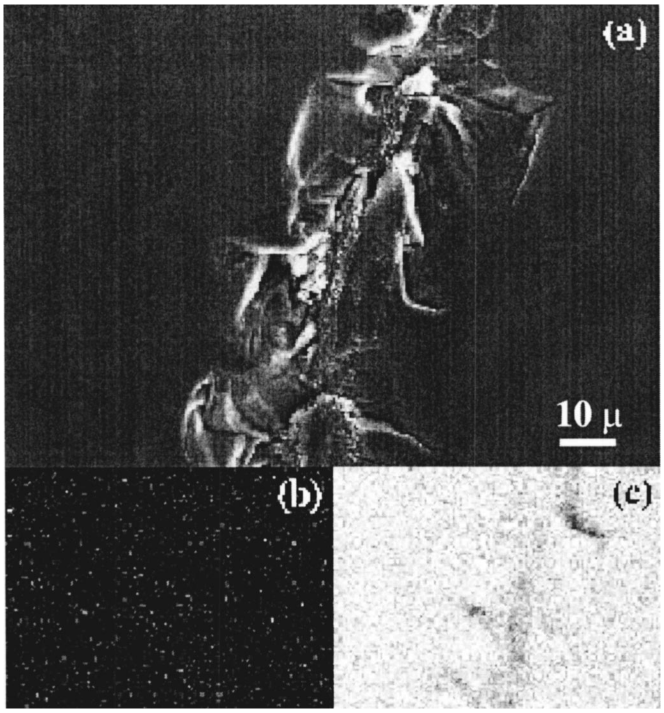

Figure 15. Micrographs of a scratched silicon surface after copper contamination in a 0.5% HF solution with the presence of 1% CTAB: (a) SEM image, (b) Cu Kα X-ray image (white dots due to noise), and (c) Si Kα X-ray image. No copper was observed even in the scratch-damaged region.

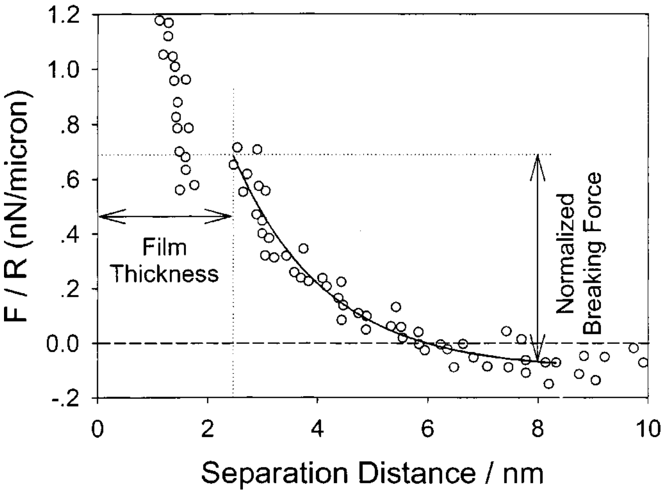

Figure 16. Plot of interaction force as a function of separation distance between a silicon nitride tip and a silicon surface in a pH ~2 solution with 1% CTAB. The force is normalized by effective tip radius, *R*. Discontinuity at about 2.2 nm suggests the presence of a surfactant film structure.

Conclusions

Additive effects on copper outplating onto silicon surfaces during DHF cleaning were studied. We verified through different experimentation that additives such as HCl, H_2O_2, and HNO_3 are effective in reducing copper outplating during DHF cleans. We reported that CTAB is effective in reducing copper outplating onto silicon surfaces during DHF cleans. Anionic surfactants may increase metal outplating, not only copper but also other metals such as nickel, by forming complexes with metal ions and subsequent adsorption onto silicon surfaces. Combining OCP monitoring, surface metal analysis, and microscopy study, one can differentiate different mechanisms of copper outplating. Experimental data suggest (*i*) that the adsorbed surfactant layer on a silicon surface can retard electron transfer between a silicon surface and a cupric ion, and that (*ii*) the surfactant molecules in bulk solution can interact with metal ions and can both decrease metal outplating driving force and increase the tendency of physical adsorption of metal ion—surfactant complexes.

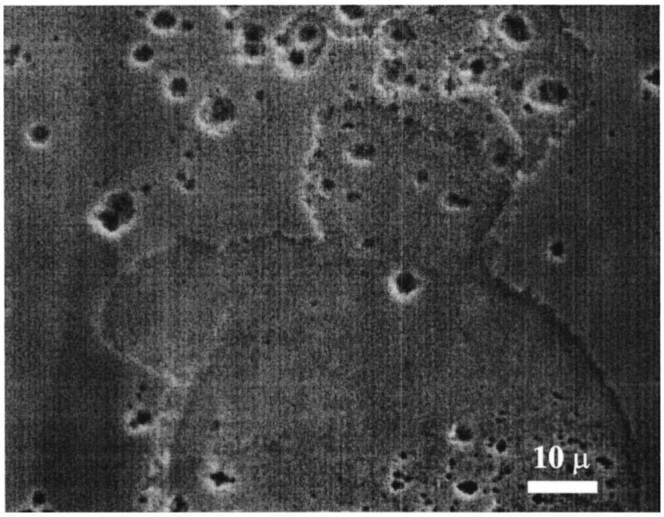

Figure 17. SEM micrograph of a copper-contaminated silicon surface dipped into 0.5% HF + 10 ppm Cu^{2+} for 30 min under illumination. The copper particles were then stripped by a stripping solution. Note the clear bubble marks due to hydrogen evolution. Bubbles were observed with the naked eye during copper outplating.

Acknowledgments

We acknowledge Ashland Chemical Company, who funded this project. We also give special thanks to Rita Vos at IMEC and Christopher Hobbs at Motorola for their generous help on TXRF and TOF-SIMS measurements.

The University of Florida assisted in meeting the publication costs of this article.

Appendix

Mechanism of silicon electrode OCP change as a function of bulk metal contamination level in DHF solutions

The mechanism of silicon electrode OCP change as a function of bulk cupric ion concentration can be understood by considering catalyzed mixed potential theory. In our system if there are no copper ions, the silicon is oxidized and the proton is reduced, as described by following equations

$$\mathrm{Si} - 4e + 6\mathrm{HF} = \mathrm{H_2SiF_6} + 4\mathrm{H^+} \quad (\text{Oxidation}) \qquad [\text{A-1}]$$

$$2\mathrm{H^+} + 2e = \mathrm{H_2} \quad (\text{Reduction}) \qquad [\text{A-2}]$$

Therefore, the overall reaction on a silicon electrode at OCP is the summation of these two half reactions

$$\mathrm{Si} + 6\mathrm{HF} = \mathrm{H_2SiF_6} + 2\mathrm{H_2} \quad (\text{Total reaction}) \qquad [\text{A-3}]$$

The partial anodic current density, I_A, of Reaction A-1 can be described by

$$I_A = n_A F a_{\mathrm{Si}} k_{0,A} \exp\left(\frac{\alpha_A n_A F}{RT} E\right) \qquad [\text{A-4}]$$

where n is the number of electron transfer, F is the Faraday constant, a_{Si} is the chemical activity of silicon which can be taken as one, α_A is the anodic transfer coefficient, R is the ideal gas constant, T is the absolute temperature, E is the electrical potential, and k_0 is the rate constant for electron transfer at the equilibrium potential. The subscript A denotes the anodic reaction, Reaction A-1.

For the reduction half reaction, if copper contaminants are present, then we also need to consider the reduction of Cu^{2+} as well as the reduction of H^+. However, results in Fig. 1 and 2 suggest that the OCP shifts are due to the surface copper, not the bulk copper in the solution. Therefore, the effect of copper on OCP shift does not result from copper ion reduction itself. The mechanism can be understood by considering catalyzed hydrogen evolution (Reaction A-2) with the presence of copper metal. When copper is outplated onto a silicon surface, the copper particles act as cathodes on which protons are reduced to hydrogen. Then the total cathode current density is the sum of the cathode current densities from the copper particles and the bare silicon. Therefore, for the cathodic current density we should write

$$-I_C = F a_{\mathrm{H^+}}(1 - \theta) k_{0,C} \exp\left(-\frac{\alpha_C F}{RT} E\right) + F a_{\mathrm{H^+}} \theta k_{0,C}^{\mathrm{Cu}} \exp\left(-\frac{\alpha_C^{\mathrm{Cu}} F}{RT} E\right) \qquad [\text{A-5}]$$

where $a_{\mathrm{H^+}}$ is the chemical activity of protons, the subscript C denotes the cathodic reaction (Eq. A-2), and θ is the coverage of copper particles, and the superscript Cu denotes the cathode reaction on copper particles. In Eq. A-5, the number of electron transfer for hydrogen evolution is taken to be one.

Although the copper coverage is small, the reaction rate is much faster than that without copper. Figure 17 shows an SEM micrograph of a silicon surface contaminated with 10 ppm Cu^{2+} in 0.5% HF solutions for 30 min under illumination. The surface copper contamination was removed by using a stripping solution. The figure shows the formation of pits due to silicon dissolution. More importantly, one observes clear bubble markers due to hydrogen evolution. In fact, we have observed in our experiments that bubbles were formed on the silicon surface when the silicon was dipped into HF solution with high concentration of copper contaminants for a long time. If clean HF solution was used no bubbles were observed, suggesting that the galvanic corrosion of silicon is much faster than HF etching. Hence, we can neglect the contribution of cathodic current from the area not covered by copper in Eq. A-5. Furthermore, we assume that the surface coverage is linearly proportional to copper surface concentration, *i.e.*,

$$\theta = k_1[\mathrm{Cu}]_{\mathrm{surf}} \qquad [\text{A-6}]$$

where k_1 is a constant. Then Eq. A-5 can be simplified to

$$-I_C = F a_{\mathrm{H^+}} k_1 \Big[\mathrm{Cu}\Big]_{\mathrm{surf}} k_{0,C}^{\mathrm{Cu}} \exp\left(-\frac{\alpha_C^{\mathrm{Cu}} F}{RT} E\right) \qquad [\text{A-7}]$$

Equating Eq. A-4 and A-7, we obtain

$$\mathrm{OCP} = \frac{RT}{F(n_A\alpha_A + \alpha_C^{Cu})}\ln\left(\frac{k_1 k_{0,C}^{Cu}}{n_A k_{0,A}}\right) + \frac{RT}{F(n_A\alpha_A + \alpha_C^{Cu})}(\ln a_{H^+} + \ln[\mathrm{Cu}]_{surf}) \quad [\text{A-8}]$$

The correlation between bulk copper concentration and silicon surface concentration after HF dipping has been extensively studied.[9,14,17,18,21-24] However, the results are characterized with large within-run and between-run variations during surface copper measurements. Nevertheless, on a linear scale the plot of surface *vs.* bulk concentration at relatively narrow range seems parabolic,[9,14,21] and on a log-log scale the plot is quite linear.[18,21-24] Therefore, the relation between bulk copper concentration and surface copper concentration can be described as

$$[\mathrm{Cu}]_{surf} = k_2[\mathrm{Cu}]_{bulk}^{k_3} \quad [\text{A-9}]$$

Thus

$$\ln[\mathrm{Cu}]_{surf} = \ln k_2 + k_3 \ln[\mathrm{Cu}]_{bulk} \quad [\text{A-10}]$$

where k_2 and k_3 are constants which characterize the outplating of copper. Combining Eq. A-8 and A-10, we finally obtain

$$\mathrm{OCP} = \text{const.} + k \log[\mathrm{Cu}]_{bulk} \quad [\text{A-11}]$$

where k is a constant. Thus, OCP *vs.* log[Cu] gives a straight line.

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