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Copper Thin-Film Dissolution/Precipitation Kinetics in Organic HF Containing Cleaning Solution

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The corrosion behavior of electrochemically deposited copper thin films in deaerated and non-deaerated commercial cleaning solution containing HF has been investigated. Thin-film copper dissolution and reaction kinetics were investigated by monitoring Cu²⁺, employing inductively coupled plasma–mass spectroscopy, and the oxidation states of copper on Si wafer surface, employing X-ray photoelectron spectroscopy. It was determined that the reaction kinetics is first order with respect to both HF and oxygen concentrations. A kinetic scheme involving reduction of oxygen and oxidation of Cu⁰ and Cu¹⁺ is proposed, which is consistent with the experimentally determined reaction kinetic orders and the observed deposition of undesired copper residues on semiconductor wafers during the cleaning process.

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As advanced microprocessors have employed smaller geometric features in the pursuit of low power consumption, increased speed, and high integration density, the traditional interconnect material aluminum^{1,2} has been replaced by copper. Due to its high conductivity, Cu as an interconnect material has been actively explored for many years^{3,4} but its feasibility as a production technology was demonstrated in 1997^{5,6} through a process known as dual damascene (DD). Soon thereafter, the method became the process of record in high volume production of advanced microprocessors.⁷

The introduction of copper in semiconductor devices has brought attention to the phenomenon of thin-film corrosion that must be circumvented for optimal device performance, reliability, and longevity. The presence of copper-rich residues on the wafer surface, after wet clean steps using non-copper compatible chemistry in a semiconductor manufacturing environment, was detected and reported by Mistkawi et al.⁸ These results underscored the need for a better understanding of wet etch clean chemistries for the integration of DD patterning of copper interconnects. In our previous work,⁸ we studied the phenomena of copper corrosion/dissolution during cleaning process, which led to the redeposition/precipitation of undesired copper and copper-rich residues onto the wafer surface, affecting the yield and reliability of devices.^{9–12}

The objective of the study reported herein is to investigate the kinetics of copper thin-film corrosion/dissolution in an aqueous solution containing HF and organic compounds and its relevance to the DD process of copper interconnects. Such solutions are commonly used in the industry for post-plasma-etch cleaning. The kinetics with respect to dissolved oxygen (DO) (O₂^{dis}) and HF concentrations is presented.

Experimental

Substrate.—The experiments were performed using copper on blanket silicon wafers (Cu/Si) substrate. The copper film was uniformly deposited using typical industry electroplating equipment^{5,13} followed by a chemical mechanical planarization step to closely mimic the actual Cu surface during the DD process. The thickness of the Cu film was ~400 nm as determined by a four-point probe method (surface resistivity meter, Guardian Manufacturing Inc., model SRM-232) and cross section scanning electron microscopy.

Surface preparation.—Before proceeding with dissolution experiments, surface treatment with 0.49 wt % HF was carried out to ensure a clean surface. A set of screening experiments to investigate optimal dip time in HF solution for surface cleaning was conducted.

A 1 min HF treatment was appropriate. This pretreatment rendered a clean surface on which the native copper oxide was partially removed to expose a clean elemental copper surface. Longer exposure (~5 min) of the wafer to HF did not alter the X-ray photoelectron spectroscopy (XPS) spectra, which exhibited peaks due to Cu(I) and Cu(0)(8) (Fig. 1 inset) and no peaks due to F (Fig. 1), which were expected in the region of 685–690 eV.¹⁴

Cleaning solution.—The dissolution experiments were performed utilizing a semiconductor cleaning chemical solution (EG3) supplied by Ashland Chemicals, which was composed of 93 wt % ethylene glycol, ~4 wt % ammonium fluoride, 0.033 wt % HF, and ~3 wt % water. The cleaning solution had pH 6.8. All experiments were carried out at room temperature (21 °C).

Dissolution experiments.—Dissolution experiments were carried out using 16 cm² (4 × 4 cm) copper/silicon wafer coupons in a 300 mL volume of stirred aerated, deaerated, or non-deaerated cleaning solutions. Deaeration was achieved by bubbling nitrogen, whereas aeration was achieved by bubbling air through the solution. DO concentration measurements were performed using a digital oxygen meter (Traceable DO meter, Control Co., model RS-232) at ~1 cm from the air–water interface.

Aliquots from the cleaning solution containing the copper wafer were collected at approximately the same depth for inductively coupled plasma–mass spectroscopy (ICP-MS) analysis at specific intervals to determine copper concentrations. Experiments were performed in three replicates to ensure reproducibility. ICP-MS measurements were performed using Agilent 7500CS.

Results and Discussion

In a recent paper,⁸ we discussed the electrochemical corrosion process of copper-coated silicon wafers in the cleaning solutions employed in the present work. The corrosion rate depended on the concentration of DO from air (non-deaerated solution); an increase in corrosion rate was observed with an increase in oxygen concentration in the cleaning solution.

To probe further how the oxidizing agents, such as oxygen from the air, can affect the corrosion process, we investigated time-dependent copper concentration, as shown in Fig. 2a. Here, an initial increase in the copper concentration was followed by significantly slower rates of dissolution at later times. This trend is independent of the DO concentration. The concentration of copper at longer times is dependent on the DO concentration (see Fig. 2b). Therefore, we also measured the concentration of oxygen as a function of time and the number of wafers. The objective was to find out if a steady-state (SS) concentration of O₂ (i.e., $d[O_2]/dt = 0$) is reached in the cleaning solution. Figure 3 depicts the DO concentration for clean-

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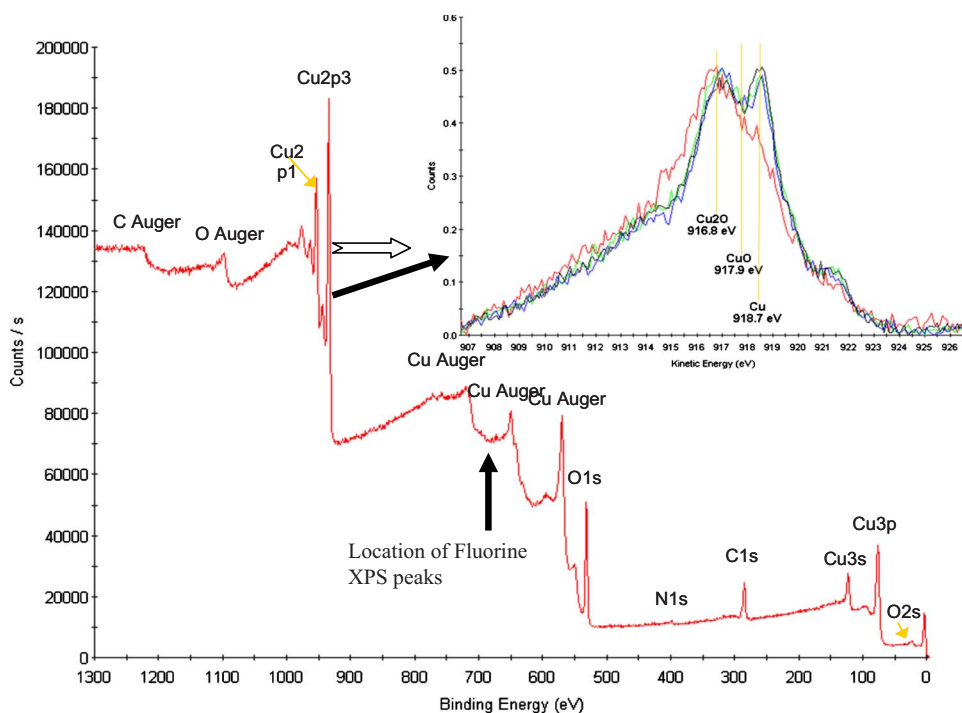


Figure 1. (Color online) Survey XPS spectra from a clean copper-coated wafer surface, lacking fluorine peaks in 685–690 eV region. The region where oxidation states of copper can be identified (yellow vertical lines) is shown in the inset. It shows XPS spectra from wafers treated with different cleaning solutions: Control (red), aqueous HF (blue), and organic cleaning solution (green).

ing solutions. The results show that within 50 min, a timescale comparable to the initial surge in copper dissolution shown in Fig. 2, the corresponding oxygen concentration in the cleaning solution decreases and reaches an SS. When two more wafers were immersed in the same solution at $t = 8700$ min, a further decline in O_2 concentration occurred on a similar timescale, reaching a new lower SS of oxygen concentration (≈ 1.5 ppm). Therefore, the corrosion process involves oxygen participation, as is further demonstrated.

The essential component of the cleaning solution is HF. It can attack exposed oxide surfaces of copper and silicon, thereby functioning as a cleaning agent, provided the duration of cleaning is precisely controlled. Thermodynamically, the free energy of formation for Cu^{2+} from Cu^0 or Cu^+ is negative. However, in our earlier

electrochemical studies, H_2O_2 treated copper surface forms a CuO film that confers a degree of passivity to the copper film, whereas aerated and non-deaerated solutions generally corrode at an appreciable rate.⁸

A simple electrochemical model of the dissolution process is proposed in Fig. 4. It depicts a reduction of oxygen coupled with oxidation of Cu^0 that can lead to the formation of Cu^{2+} species (through disproportionation) in the cleaning solution. Given that the

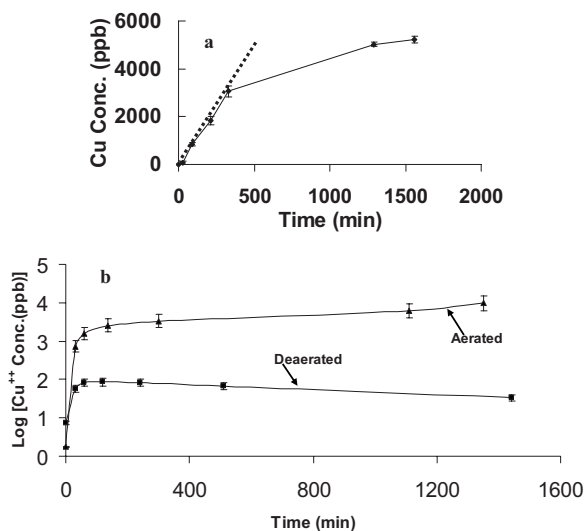


Figure 2. (a) Cu dissolution in non-deaerated samples. The dashed lines indicate the initial copper dissolution rate. (b) A log of copper concentration in ppb vs time for aerated and deaerated cleaning solutions is shown. The O_2^{dis} concentrations were 8.9, 4.5, and 0.6 mg/L in the aerated, non-deaerated, and deaerated solutions, respectively.

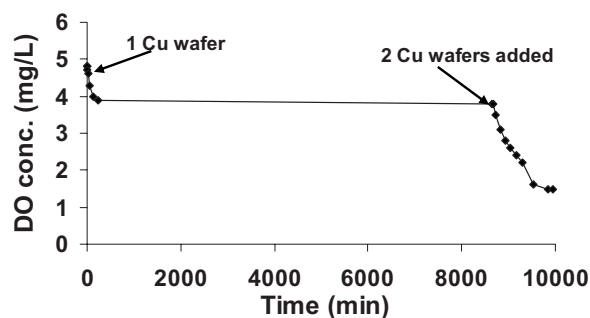


Figure 3. Temporal evolution of oxygen concentration in the cleaning solution as a function of time and Cu surface area are shown.

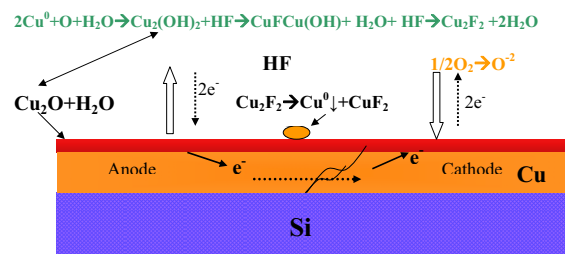
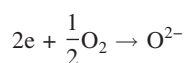


Figure 4. (Color online) A simple electrochemical model of the dissolution process showing the reduction of oxygen coupled with oxidation of Cu^0 that leads to the formation of Cu^{2+} species in the cleaning solution.

cleaning solution contains 3–4% water and ppb level concentration of copper species in the cleaning solution, we expect the formation of mainly ionic species, although we cannot rule out the possibility of forming neutral ion pairs at higher concentrations. More specifically, we write the redox reactions involved in the dissolution of copper from a wafer substrate:

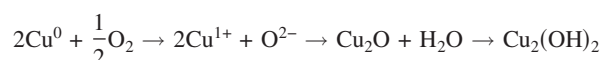
Reduction reaction



Oxidation reaction



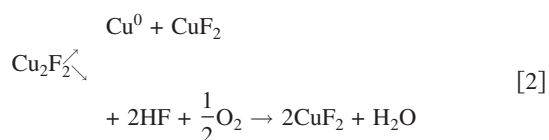
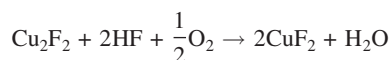
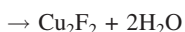
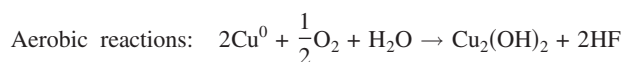
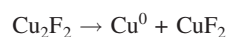
Net reaction



[1]

Given that our XPS data always show the presence of Cu^{1+} species (Fig. 1 and Ref. 8), oxidation of $Cu^0 \rightarrow Cu^{1+}$ through the formation of hydrated cuprous oxide might be a route toward the copper dissolution process. Copper hydroxide may exist in the form of an ion pair. Our XPS data of the copper surface could not be collected during the active cleaning procedure, thus making it difficult to ascertain chemical species present during the cleaning. Likewise, the electrospayed ICP-MS evaluation of the copper concentration only reports the concentration of positively charged copper species. Our working hypothesis here is that the final copper species remaining in the cleaning solution is Cu^{2+} , created by the oxidation of Cu^+ or Cu^0 . The most likely anion interacting with Cu^{2+} species is fluoride ion. Here, we estimate the solubility of the cupric ions in the cleaning solution by noting that the aqueous solubility of CuF_2 at room temperature is 750 ppm.¹⁵ As the cleaning solution contains protic solvent ethylene glycol (93%), 3% water, and 4% NH_4F (which reduces the solubility of CuF_2 through common ion effect), the observed 2–10 ppm copper concentration in the long time limit is consistent with the aqueous solubility data. However, the solubility of Cu(I) species such as Cu_2F_2 ¹⁶ (CuF) or $Cu_2(OH)_2$ ($CuOH$) is likely to be far lower (perhaps in the sub-ppb level) following the general trend in copper halide/hydroxide solubility.^{17,18} We consider below the thermodynamic and kinetic aspects for the observed dissolution of copper into the cleaning solution.

Thermodynamically, the following stoichiometrically balanced reaction steps are energetically feasible



The first step accounts for the fact that the copper surface has a native thin film of cuprous oxide. The second step suggests a disproportionation of Cu(I) salts by analogy with other copper(I) halides in protic solvents,¹⁷ although it has never been firmly established in Cu_2F_2 . Disproportionation is consistent with our observed copper-rich residues on the dielectric surfaces, although it does not

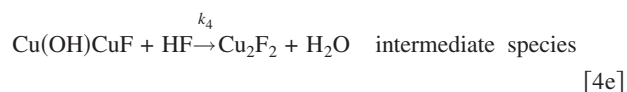
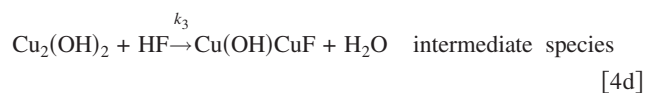
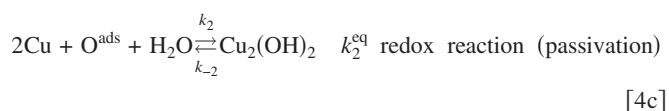
prove its occurrence.⁸ In this reaction scheme, we emphasize the role of O_2 in the corrosion process to account for the DO-dependent copper dissolution presented in Fig. 2 and 3 through the formation of $Cu_2(OH)_2$ and its reaction with HF. The rationale for this step is as follows. Given that K_{sp} for the cuprous hydroxide species coexisting with cuprous oxide and water is about 10^{-14} and, hence, at the most, a sub-ppb level concentration of copper can be contributed by it to the cleaning solution at equilibrium (i.e., long time limit). The contribution of cupric hydroxide, should it form, would be even lower because its K_{sp} is about 10^{-19} or lower.¹⁸ The solubility data for Cu_2F_2 ¹⁹ (or CuF) are not available,¹⁷ but by extrapolating the solubility trends for other copper halides,¹⁷ we expect an even lower contribution of copper in the cleaning process from cuprous fluoride. Therefore, by default, the reaction of HF with Cu^0 or Cu^{1+} species must be invoked (as discussed above and later) to account for the observed high copper concentrations (8–10 ppm), at a slightly acidic (6.8) pH of the cleaning solution.

To develop a molecular mechanism for the kinetics of copper dissolution, we focus on the short-time behavior. This is directly relevant for semiconductor processing, as typically wafers are expected to be cleaned in less than 5 min. To study the kinetics in this time region, we employed the method of initial rates, where $d[Cu^{2+}]/dt$ ^d was determined by drawing a tangent to the copper concentration vs the t curve in the limit $t \rightarrow 0$ (see Fig. 2a). Under these conditions a general rate equation for the appearance of $[Cu^{2+}]$ (assuming that ultimately it is the most soluble and chemically stable) species in the cleaning solution can be written as

$$\frac{d[Cu^{2+}]}{dt} = k[O_2^{dis}]^n[HF]^m \quad [3]$$

Here, n and m are the reaction orders with respect to DO (O_2^{dis}) and HF concentration, respectively. Figure 5a shows the copper dissolution rate as a function of the O_2^{dis} concentration in a fixed HF concentration (note dissolution rates are in ppb/min, whereas the concentration of HF is in the high 100 s of ppm range). Similarly for fixed oxygen concentration (<10 ppm range) in well-stirred cleaning solutions, the dissolution rate was determined as a function of HF concentration (Fig. 5b). The slopes of the best fitted lines yielded values for $n \approx m \approx 1.0 \pm 0.1$. Also, plots of $\ln(O_2 - O_2^{SS})$ (where O_2^{SS} denotes the SS concentration of O_2^{dis}) vs time were linear (not shown), implying a first-order kinetic rate process for the decrease in the dissolved O_2 concentration for the data presented in Fig. 3.

A plausible set of elementary kinetic reactions are presented below



^d Here the copper concentration is the concentration as determined by ICP-MS.

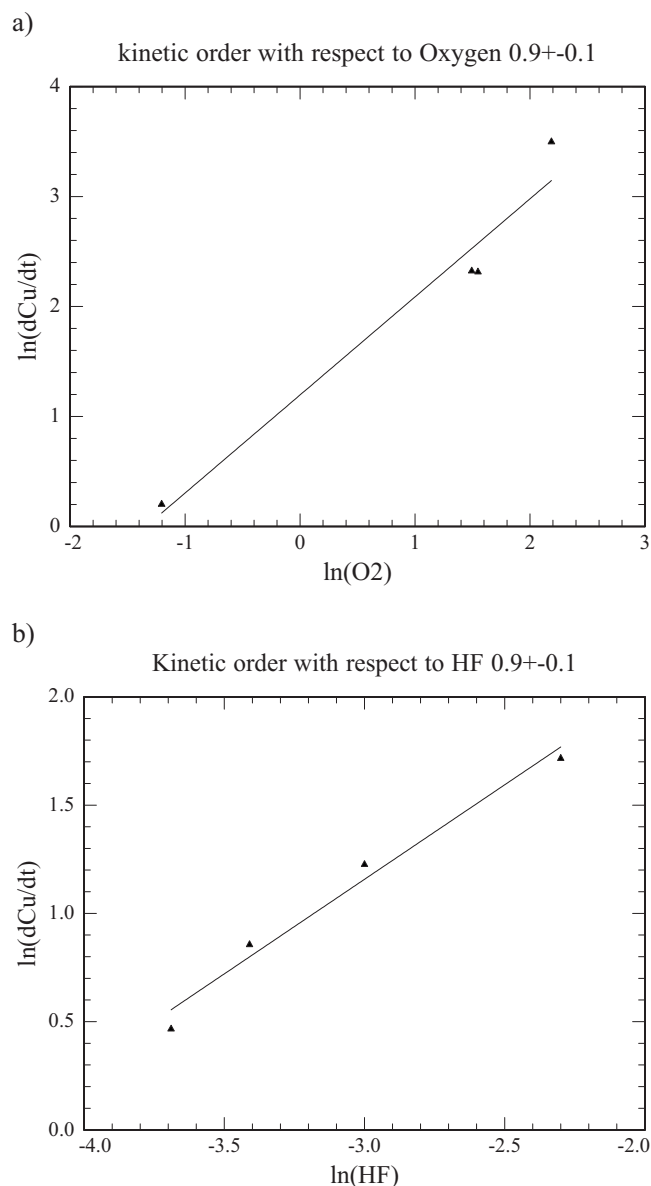


Figure 5. An ln–ln plot of initial copper dissolution rate vs (a) DO and (b) HF concentration allows determination of kinetic orders. The copper dissolution rate is in ppb/min, whereas the concentration units for DO and HF are in mg/L and percentage concentration, respectively.



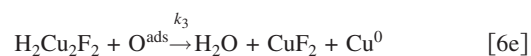
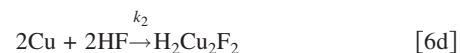
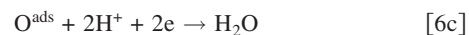
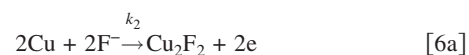
The corresponding kinetic analysis is detailed in the Appendix, along with the rationale for selecting these elementary reaction steps and the intermediates. The main simplification we make here is that all the Cu^{1+} species as well as atomic oxygen are subjected to the SS approximation. In this limit, a simple rate expression for copper dissolution may be given as

$$\frac{d[\text{Cu}^{2+}]}{dt} = k_3[\text{Cu}_2(\text{OH})_2][\text{HF}] = \frac{2k_0^{\text{eq}}k_1k_2^{\text{eq}}k_3[\text{O}_2^{\text{dis}}][\text{HF}]}{(k_2 - k_{-2}k_2^{\text{eq}})} \quad [5]$$

In this analysis, the kinetic rate of adsorbed O_2 dissociation as well as the rate of $\text{Cu}_2(\text{OH})_2$ ¹⁸ formation provide plausible rate-determining steps. The expression in Eq. 5 is consistent with the observed rate law, although we have not detected the postulated intermediates such as Cu_2F_2 ¹⁹ or $\text{Cu}(\text{OH})\text{CuF}$ in our experimental work. If the SS approximation is valid, their concentrations are ex-

pected to be too low. In view of these considerations, we have not further modeled the detailed kinetics that could include the second oxidation step involving oxygen for the Cu^+ species (see Eq. 2 above) as it would entail postulating additional intermediates (e.g., $\text{H}_2\text{Cu}_2\text{F}_4$), etc. Nonetheless, if the branching ratio of Cu_2F_2 favors disproportionation, then the kinetic analysis presented above becomes applicable as the molecular level mechanistic model of copper corrosion and deposition of undesired copper-rich residues on the dielectric surfaces in the HF containing cleaning solution.

Finally, we compare our findings with an early study of copper electrolyte interface in aqueous medium by Chan et al.²⁰ In this classic work, surface oxide formation was detected in basic/neutral pH conditions, whereas in strongly acidic conditions, the formation Cu-X (where X is an anion) species was observed.²¹⁻²⁴ Chan et al. observed that even in weakly acidic conditions adsorbed oxygen species, as opposed to oxide formation, were observable in their surface enhanced Raman studies. It is this observation that led us to postulate steps 4a and 4b. However, near the neutral pH, these authors suggest both formation of oxide as well as halides of Cu^{1+} . In this scenario, copper oxidation is facilitated by halides. The following sequences can be suggested for anodic dissolution of copper by fluoride ions based on their work



In this scheme, copper oxidation is initiated by F^- and the compensating oxygen reduction involving protons is postulated. This mechanism does not lead to a first-order kinetics with respect to HF^- or F^- (note Eq. 6d). Also, Eq. 6a depends on fluoride ion concentration, which is in excess in the cleaning solution (4% NH_4F) so that the dissolution rate would be controlled by the adsorbed oxygen concentration and $[\text{H}^+]$ (Eq. 6c) is raised to power 2 (i.e., the order with respect to HF concentration would be 2; see Eq. 6d). Given that our cleaning solution exhibits a pH that is nearly neutral (pH 6.8), the formation of $\text{Cu}_2(\text{OH})_2$ (i.e., Eq. 4c) is expected to dominate the dissolution kinetics. This is also consistent with the weak passivation observed in potentiodynamic studies.⁸

A more detailed verification of these models would require systematic studies that involve variation in pH of the cleaning solution to observe differing kinetic exponents n and m consistent with reaction sequences presented in Eq. 6. Such studies are beyond the scope of the present investigation, which focuses on copper surface dissolution using the commercial cleaning solution.

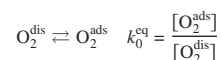
Conclusions

A simple kinetic model is proposed for the copper dissolution during wet chemical cleaning process. It predicts experimentally observed first-order kinetics with respect to DO and HF, the two key ingredients involved in corrosion of copper. If DO is eliminated, the rate of copper corrosion can be suppressed.

Intel Corporation assisted in meeting the publication costs of this article.

Appendix

Potential elementary reactions



$$\text{O}_2^{\text{ads}} \xrightarrow{k_1} 2 \text{O}^{\text{ads}} \quad \frac{d[\text{O}^{\text{ads}}]}{dt} = 2k_1[\text{O}_2^{\text{ads}}] + k_2[\text{Cu}_2(\text{OH})_2] - k_2[\text{O}^{\text{ads}}] = 0$$

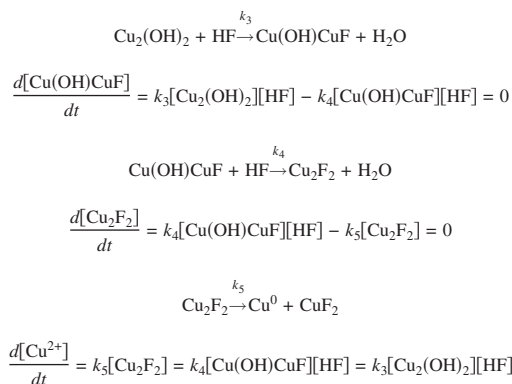
$$2\text{Cu} + \text{O}^{\text{ads}} + \text{H}_2\text{O} \xrightleftharpoons[k_{-2}]{k_2} \text{Cu}_2(\text{OH})_2 \quad k_2^{\text{eq}} = \frac{[\text{Cu}_2(\text{OH})_2]}{[\text{O}^{\text{ads}}]} = \frac{k_2[\text{Cu}_2(\text{OH})_2]}{2k_1[\text{O}_2^{\text{ads}}] + k_{-2}[\text{Cu}_2(\text{OH})_2]}$$

$$= \frac{k_2[\text{Cu}_2(\text{OH})_2]}{2k_1k_0^{\text{eq}}[\text{O}_2^{\text{dis}}] + k_{-2}[\text{Cu}_2(\text{OH})_2]}$$

$$\therefore [\text{Cu}_2(\text{OH})_2] = \frac{2k_1k_0^{\text{eq}}[\text{O}_2^{\text{dis}}]}{\left(\frac{k_2}{k_2^{\text{eq}}} - k_{-2}\right)} = k'[\text{O}_2^{\text{dis}}]$$

Noting that the order with respect to oxygen concentration is unity, we postulate two reaction steps for the generation of atomic oxygen on the surface as opposed to a one-step reversible dissociative adsorption of dissolved $[\text{O}_2]$. The one-step model predicts a kinetic order of $\frac{1}{2}$ with respect to DO, inconsistent with the experimentally observed value. Furthermore, we assume that the concentration of the dissociatively adsorbed atomic O is in the SS, and quasi-equilibria are established rapidly for the first and third reactions. If the reaction of the adsorbed oxygen with copper is made irreversible as opposed to reversible, then under the conditions of SS approximation for the intermediates $[\text{Cu}_2(\text{OH})_2]$, $[\text{CuOHCuF}]$, and $[\text{Cu}_2\text{F}_2]$ the initial Cu^{2+} dissolution rate in the cleaning solution becomes independent of HF concentration, whereas experimentally we noted a first-order dependence with respect to HF concentration.

Intuitively, one expects $\text{Cu}_2(\text{OH})_2$ concentration in the solution to be very small, way below the ppb level Cu^{2+} concentration observed during the initial stages of reaction. Unfortunately, such a sub-ppb level concentration makes the detection of this species, as well as other intermediates described below, difficult in practice, so the sequence of reactions outlined above should be treated as a plausible but not confirmatory sequence of elementary reactions. The reaction steps given below consider the generation of Cu^{2+} species in solution through the attack of HF on $\text{Cu}_2(\text{OH})_2$



Again, the choice of two stepwise reactions is presented rather than a single termolecular reaction involving two HF molecules reacting with $\text{Cu}_2(\text{OH})_2$ to yield Cu_2F_2 directly. This choice was made to rationalize the observed first-order dependence of copper dissolution rate with respect to HF concentration. The above cascade of reactions assumes the formation of $\text{Cu}(\text{OH})\text{CuF}$ and Cu_2F_2 species. Experimentally, we have no

evidence for the formation of either species. We make the SS approximation for these latter species by assuming their high reactivity that could lead to their very low concentrations. Substituting for the $[\text{Cu}_2(\text{OH})_2]$ concentration

$$\frac{d[\text{Cu}^{2+}]}{dt} = k_3[\text{Cu}_2(\text{OH})_2][\text{HF}] = \frac{2k_1k_3k_0^{\text{eq}}[\text{O}_2^{\text{dis}}][\text{HF}]}{\left(\frac{k_2}{k_2^{\text{eq}}} - k_{-2}\right)} = \frac{2k_0^{\text{eq}}k_1k_2^{\text{eq}}k_3[\text{O}_2^{\text{dis}}][\text{HF}]}{(k_2 - k_{-2}k_2^{\text{eq}})}$$

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