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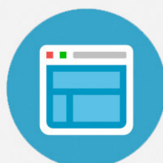

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Electrochemical behavior of copper chemical mechanical polishing in KIO_3 slurry

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The electrochemical behavior of polishing copper with colloidal silica abrasive slurry formulated with KIO_3 oxidizer has been investigated. For planarization of the surface morphology, the control of the surface passivation of Cu is critical during polishing. KIO_3 is not only an oxidizer but also a passivator for copper in an acidic slurry by forming a CuI layer on the surface. With alkaline slurry, Cu_2O is the primary corrosion product on the Cu surface. The copper corrosion rate and removal rate can be decreased dramatically with increasing slurry pH. The low corrosion resistance or high corrosion susceptibility of Cu as determined by electrochemical measurements is the basis for the high removal rates. The copper removal rate is reduced from 4600 to 650 Å/min when the slurry pH is increased from 2 to 5; and the copper removal rate levels off at pH 7 with a steady-state removal rate of 200 Å/min. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1458956]

I. INTRODUCTION

Because of its inherent superior conductivity and also its high resistance to electromigration, copper has begun to replace aluminum and tungsten for high-performance on-chip interconnects. Since the traditional dry etch technique for the definition of Cu wiring is difficult, the metal in-laid damascene process in which the implementation of Cu chemical mechanical polishing (CMP) has developed is the main technology for manufacturing Cu interconnect.

Many challenges still exist in terms of developing a feasible copper CMP process module. A number of slurry chemistries have been developed for bulk copper CMP, e.g., HNO_3 and H_2O_2 as oxidants,[1,2] BTA as an inhibitor,[1,3] NH_4OH as a complexing agent,[4,5] etc. To achieve a slurry formulation that could successfully planarize Cu damascene structure, a requirement has to be met: sufficiently high and uniform Cu removal rate. Chemical agents in the slurry mixture are added to enhance the removal rate of the material being polished and/or to passivate the recess regions. With these systems, the formation of a surface layer during polishing is the key to obtaining good planarization in copper CMP. In an acidic condition, one of the biggest advantages is the high Cu/SiO_2 selectivity due to the fast Cu dissolution rate but poor uniformity. By use of the nonoxygen donor oxidizer (such as HNO_3), in which Cu will follow what is predicted in the Pourbaix diagram, Cu is corroded in acidic but passivated in alkaline media.[6] Nevertheless, the copper polishing process is not successful in acidic slurry because of severe chemical etching at the recessed region during the polishing. The addition of inhibitors, such as BTA, can passivate the exposed copper surface by forming a CuBTA thin film, and then increase the process reliability. The dishing of the copper is reduced,[7] but the removal rate is reduced. By use of oxygen donor oxidizers, such as H_2O_2, IO_3^-, cuprous oxide could be formed even in the acidic water. With an alkaline slurry, a native oxide layer on the copper surface is a result, reducing the etch rate; however poor Cu/SiO_2 selectivity is a drawback.

The mechanism to explain the excellent planarity and high removal rate in metal CMP is based on the cyclical sequence of metal passivation, abrasion of the oxide layer, and ionic dissolution from exposed metal.[8,9] The electrochemical reaction may be expected to play an important role in metal CMP. Hence, understanding the role of the oxidizer in oxide formation and material removal by ionic dissolution of copper will be helpful in improving the Cu CMP process.

In this study, KIO_3 was selected as an oxidizer, capable of not only passivating the copper but also acquiring a high removal rate in the acidic condition. Therefore, electrochemical measurements were used to understand the passivation and etching behavior of copper in the KIO_3 slurry. These results are then compared with the x-ray photoelectron spectroscopy (XPS) results prior to the copper chemical mechanical polishing.

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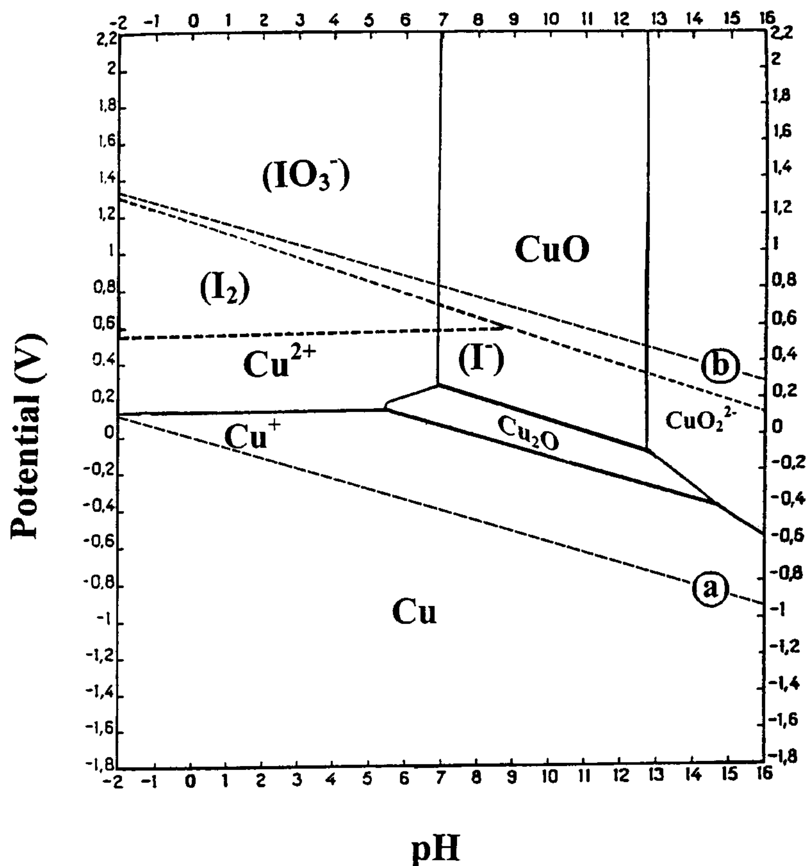

FIG. 1. $E-p$Hs diagram for the Cu–I_2–H_2O system; line a and b representing the lower and the upper limit of the water stability, respectively (activity of soluble iodine species = 0.1, activity of dissolved copper species = 10^{-6}).

II. EXPERIMENT

The electrochemical apparatus using a traditional three-electrode configuration for *in situ* CMP measurements has been shown in a previous publication.[10] Briefly, this apparatus consisted of a rotor where a working electrode was attached. A Pt mesh net and a saturated calomel electrode were used as counter and reference electrodes, respectively. All electrodes were connected to both the EG&G lock-in amplifier model 5301 and potentiostat model 273 and were immersed in the slurry with a polishing pad (Rodel Politex Regular E) located at the bottom. The working electrode was made of a copper (99.99%) cylinder embedded in epoxy resin with only one side of the embedded cylindrical specimen (1 cm^2) exposed to the slurry.

For dc polarization measurements, the scan rate was 1 mV/s. As for electrochemical impedance spectroscopy (EIS) measurements, the amplitude of the perturbation was ± 10 mV, and the frequency was varied from 0.01 Hz to 100 kHz at 6 steps/decade. In all experiments, the specimen was polished with a rotational speed of 100 rpm and a downward pressure of 4 psi. The slurry used in the experiments contained 0.1 M KIO_3, as the main oxidant, and colloidal silica abrasives (50–80 nm) of 3 wt % with slurry's pH value adjusted from 10 to 2 by adding oxalic acid.

III. RESULTS AND DISCUSSION

A. Pourbaix diagram

In order to understand the electrochemical behavior of copper during the copper CMP in a 0.1 M KIO_3 base slurry, thermodynamic data related to copper species were collected and analyzed through the construction of the $E-p$H diagram for a Cu–IO_3^-–H_2O system at 25 °C.[6] These data are plotted in Fig. 1. In constructing this diagram, the activity of soluble iodine species was assumed to be 0.1 and the activity of dissolved copper species was assumed to be 10^{-6}. The solid lines and dashed lines represent the copper and iodine $E-p$H diagram, respectively. It can be seen in Fig. 1 that Cu_2O/CuO is stable at pH 7–12. When $p\text{H}<7$ with a potential above +0.1 V, Cu^{2+} is the most stable phase. At pH 2–7, Cu is likely to be oxidized to Cu^{2+}; and IO_3^- to be reduced to I_2 or to I^-.

The reaction mechanism of KIO_3 oxidizer is as follows:

$$I^- + 3H_2O = IO_3^- + 6H^+ + 6e,$$

$$E^0 = 1.085 \text{ V}. \quad (1)$$

Based on the Nernst equation, it is obvious that the reduction potential of KIO_3 decreases significantly with increasing pH values, thus decreasing the driving force for the oxidation of Cu. Hence, with acid media, it is reasonable to speculate that copper and iodide ions form a soluble complex CuI_2^- by the following mechanism:

$$Cu = Cu^+ + e^-, \qquad E^0 = 0.337 \text{ V}, \quad (2)$$

$$Cu + I^- = CuI + e^-, \quad E^0 = 0.101 \text{ V}, \quad (3)$$

$$CuI + I^- = CuI_2^-. \quad (4)$$

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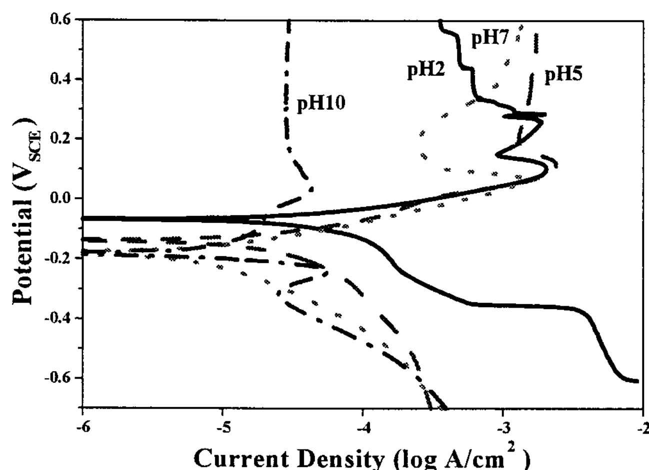

FIG. 2. Potentiodynamic polarization curves of copper in 0.1 M KIO_3 slurry with various pHs.

B. Electrochemical measurements

The successful CMP slurry formulation will include reagents to increase the solubility of the copper in the slurry and to prevent dissolution of the copper in the recess regions on the surface. Figure 2 presents the potentiodynamic polarization curves for copper at different pHs in slurry containing 0.1 M KIO_3 oxidizer. The nature of the passivation layer influences the magnitude of the corrosion current density of copper. The anodic current density decreased with increasing slurry pH, suggesting a lower dissolution rate of Cu at a high slurry pH. Many researches have show that the slurry pH has a strong influence on the removal rate of copper.[11,12] For pH 2–7, with the anodic polarization curves in the range from 0.1 to 0.3 V, a kink is observed, implying a distinct transition from an active state to a passive state. Under HNO_3 based slurry,[1,13] there is no active–passive transition but a passivation in KIO_3 slurry will be observed even at pH 2. The high etch rate results in a high removal rate in the recess regions, which is undesirable in the CMP process. At pH 10, an abrupt change on the anodic curve, where the critical current density for passivation is almost 100 times lower than the acidic environments, shows an excellent passivation behavior. As shown in Fig. 1, copper–oxides are not thermodynamically stable in acid solutions and an oxide layer formed at lower pH solutions, which is less protective than that formed at higher pH solutions. According to reactions (1)–(4), it is suggested that the passivation layer on the Cu surface is a CuI layer at $p\mathrm{H}<7$ slurries. Examination of the $E-p$H diagram allows the speculation that the Cu_2O/CuO on the copper surface at $p\mathrm{H}>7$ slurries is dense and stable and is formed according to the following electrochemical reactions:

$$2Cu+H_2O=Cu_2O+2H^++2e,$$

$$E^0=0.471-0.0591p\mathrm{H}, \qquad (5)$$

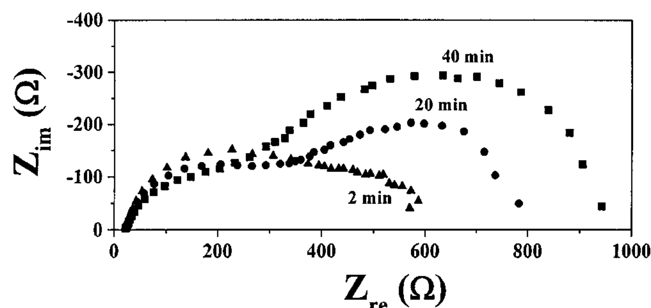

FIG. 3. Nyquist plots of copper in 0.1 M KIO_3 slurry with pH 2 after 2, 20, and 40 min immersion.

$$Cu+H_2O=CuO+2H^++2e,$$

$$E^0=0.471-0.0591p\mathrm{H}. \qquad (6)$$

EIS measurements were performed on copper in KIO_3 slurries at pH 2 after various immersion times. This Nyquist plot is composed of real Z_{re} and imaginary Z_{im} impedance magnitudes for each frequency. The diffusion of either I^- toward the surface or the Cu^+ toward the bulk solution became more difficult as the immersion time increased as shown in Fig. 3. This can be due to formation of a protective surface layer. Hence, the impedance increases with increasing immersion time corresponding to the growth of an oxide layer (in thickness).

Figure 4 presents the Nyquist plots for copper in slurries with various pHs. The left upper corner is the expansion plot of copper in KIO_3 slurry at pH 2. It is seen that the impedance or corrosion resistance increases with the increase of slurry pH. It is known that the corrosion rate is related to the slurry pH and consequently one can expect that the removal rate is inversely proportional to the slurry pH, i.e., the higher the removal rate, the lower the slurry pH.

According to Carpio *et al.*,[1] in a dissolution-dominated process such as the one taking place between copper and HNO_3, mechanical abrasion does not enhance the chemical corrosion rate. On the contrary, it may reduce the corrosion rate due to the transport limitations. However, the impedance of copper at pH 2 with abrasion is smaller than that without abrasion as can be seen from the impedance spectra shown in Fig. 5. The remarkable impedance decrease can be due to the removal of the surface oxide layer. Thus, during the abrasion, the corrosion rate is increased. The conclusion by Carpio *et al.* from dc polarization curve measurements was a result of mass transport limitations, which is consequently questionable. However, under the practical CMP process, diffusion of species is not a problem. The solution resistance R_S increased while the copper was under abrasion because the pathway between the specimen and the polishing pad for the fluid flow became smaller. At the same time, dc polarization measurements cannot eliminate the effect of solution resistance on the polarization of the electrode. Therefore, one may underestimate the corrosion rate determined by dc polarization curves. Planarity of the surface results from upper regions on the copper being polished at a higher rate than the removal rate for recess regions. The corrosion rate increases

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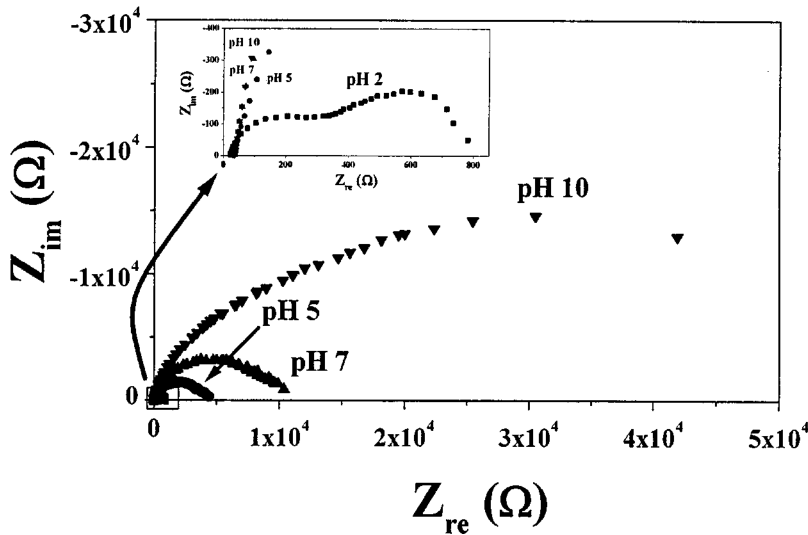

FIG. 4. Nyquist plots of copper in 0.1 M KIO_3 slurry with various pHs after 40 min immersion.

as a result of abrasion; therefore we would expect that during the polishing the passivated recess regions with low corrosion rate conduced to a more planar topography.

C. Surface analysis

As described earlier, the formation of oxide plays an important role in CMP. Figures 6(a) and 6(b) shows the results of XPS spectra of the copper sample after 40 min immersion with varying pH. It is not possible to distinguish Cu^0 from Cu^+ on the basis of binding energy, since there is no detectable shift in the Cu $2p_{3/2}$ photoelectron peak between these two chemical states of the copper within experimental uncertainties. Hence, it is only practicable to compare I $3d$ and O $1s$ spectra. In Fig. 6(a), iodine peak shifts from its I^0 (619.9 eV) position to 619.0 eV.[14,15] As the slurry pH increases to 7, the iodine peak totally disappears. Numerous studies reported that the O $1s$ photoelectron peak appears at a binding energy of 530.5 eV in Cu_2O (at 529.7 eV in CuO).[16,17] Roberts *et al.*[18] assigned the XPS peak at 532.2 eV to the chemisorbed oxygen on copper oxides. As shown in Fig. 6(b), the O $1s$ photoelectron peak can be deconvoluted into two peaks, a major peak at 532.6 eV and a minor peak at 530.4 eV. The O $1s$ peak intensity becomes stronger as slurry pH increases. This strongly suggests that the Cu_2O layer is formed uniformly on the copper surface. From these results, we infer that the CuI (619.0 eV) layer was formed on the copper surface in the slurries of pH 2 and pH 5. As the slurry pH increases to 7, Cu_2O is thermodynamically stable in alkaline solution. The results obtained from the XPS analysis further supported the suggestion that Cu had passivation in KIO_3 slurry even in acidic conditions.

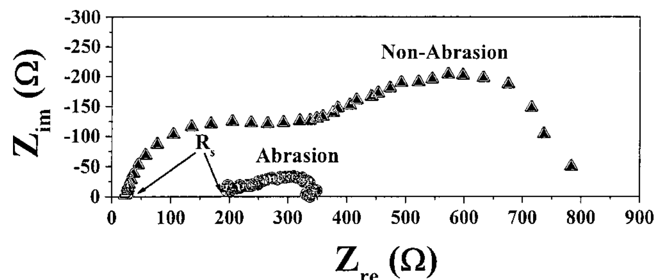

FIG. 5. Nyquist plots for copper in 0.1 M KIO_3 slurry of pH 2 with and without abrasion.

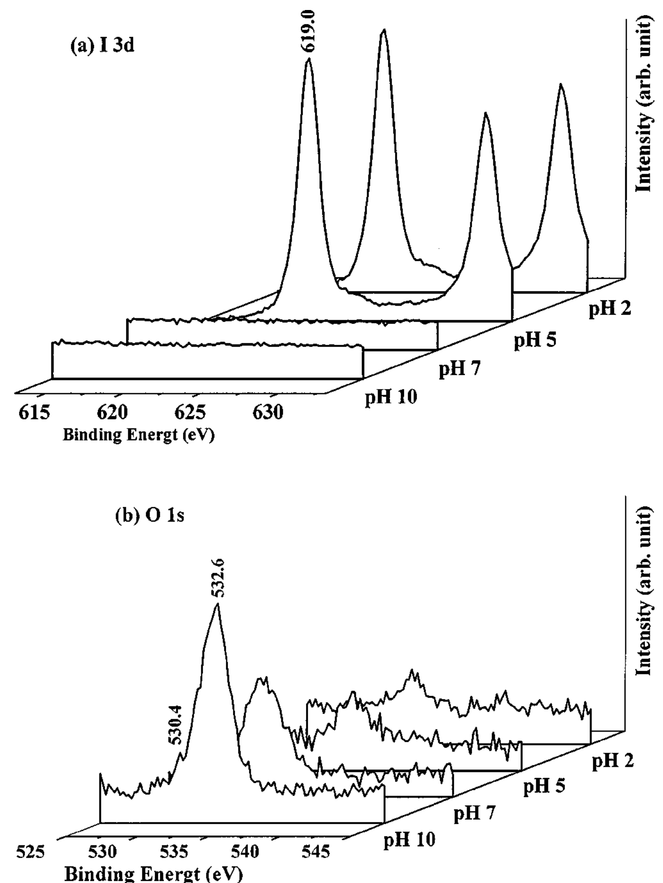

FIG. 6. XPS spectra of copper immersed in 0.1 M KIO_3 slurry with various slurry pHs: (a) I $3d$ spectra and (b) O $1s$ spectra.

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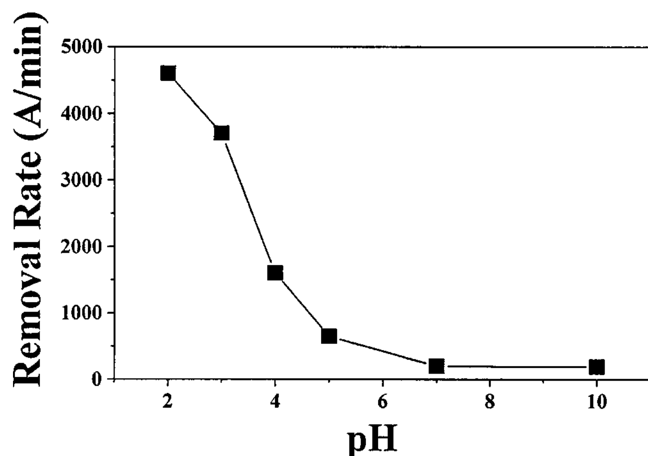

FIG. 7. Effect of slurry pH on the removal rate of copper in 0.1 M KIO_3 slurry under 5 psi downward pressure, 42 and 45 rpm of platen and carrier, respectively, and 150 mL/s slurry flow rate.

D. Cu CMP

The pH of the slurry has a strong influence on the electrochemical reaction and removal rate of the copper. Figure 7 shows the effect of slurry pH on the copper removal rate, which drops significantly with increasing slurry pH. For instance, the copper removal rate is reduced from 4600 to 650 Å/min when the slurry pH increases from 2 to 5, and levels off at $p\mathrm{H}=7$ with a steady-state copper removal rate of 200 Å/min. As a result, the removal rate decreases with increasing pH due to the decrease of the driving force of oxidation by IO_3^-. In addition, the electrochemical measurements show low corrosion resistance and high removal rate of the Cu.

IV. CONCLUSIONS

It may be concluded that the Cu is truly passivated even if in a 0.1 M KIO_3 slurry of pH 2. The electrochemical reaction of copper depends upon the slurry's pH value. The corrosion rate and removal rate decrease with increasing slurry pH. The higher removal rate of copper in acidic slurry is presumably due to the lower protective ability of the Cu surface layer when compared to the oxide layer formed in the alkaline slurries. The results from XPS spectra are consistent with those from the electrochemical measurements. In the case of alkaline slurry, e.g., pH 7–10, the copper is covered with a more protective thin layer of Cu_2O. As in acidic slurries of pH 2–5, the Cu surface is passivated with the formation of CuI.

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