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# Electrochemical characterization of copper chemical mechanical polishing in L-glutamic acid–hydrogen peroxide-based slurries

**Noyel Victoria Selvam · Ramanathan Srinivasan**

**Abstract** The effect of L-glutamic acid as complexing agent in the presence of hydrogen peroxide as oxidizer in copper chemical mechanical polishing (CMP) slurry is investigated. In the CMP process, the work surface is moved against a pad, with slurry flowing between the surface and the pad. The polish rate was found to be stable over a wide range of hydrogen peroxide concentration. High concentration of either L-glutamic acid or hydrogen peroxide leads to a reduction in polish rate, but a high concentration of both chemicals does not reduce the polish rate. In the absence of hydrogen peroxide, the Cu polish rate was 0 for all the L-glutamic acid concentrations investigated. However, potentiodynamic polarization curves do not show any sign of passivation when L-glutamic acid was present in the solution. In situ open circuit potential measurements show that copper redox reactions as well as hydrogen peroxide redox reactions contribute in determining the electrochemical behavior. We propose that L-glutamic acid inhibits the copper dissolution by adsorption onto the metallic copper, but enhances copper dissolution by complexing copper ions. The results show that it is possible to conduct controllable copper CMP in mildly acidic slurries with hydrogen peroxide as oxidizer and L-glutamic acid as complexing agent.

**Keywords** Copper · CMP · L-glutamic acid · Hydrogen peroxide · Electrochemical characterization

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## Introduction

Copper is widely used as an interconnect material in multilevel integrated circuits because of its lower resistivity and electromigration resistance [1]. The dual-damascene process is employed to form interconnect lines and vias, and it needs planarization of the surface by chemical mechanical planarization or polishing (CMP). Commonly used copper CMP slurries consist of an oxidizer, complexing agents to dissolve the oxide and prevent redeposition of removed copper, and an abrasive material to remove the modified layer [2]. The copper CMP slurries also contain corrosion inhibitors to prevent excess dissolution and corrosion.

Various copper CMP slurry formulations have been evaluated, with each having its own advantages and disadvantages. Hydrogen peroxide is a clean oxidizing agent and hence is used as the oxidizer in most of the copper CMP slurries [3]. The use of organic acids was reported to generate electrostatic repulsion between copper surface and abrasive particle which is favorable to post-CMP processes [4]. Complexing agents such as ammonia [5], acetic acid [6, 7], citric acid [8, 9], glycolic acid [10], oxalic acid [11], arginine [12], and glycine [13–15] have been proposed as suitable candidates. Of these, arginine and ammonium hydroxide are alkaline while all other complexing agents are acidic. In many of the slurries, the polish rate varied significantly with change in hydrogen peroxide concentration. Since hydrogen peroxide is an unstable chemical, this would lead to less stable process conditions. Arginine-based slurries were reported to yield stable polish rates with respect to variations in hydrogen peroxide concentrations [12]. However, alkaline slurries may not be compatible with the low-$k$ materials introduced recently as the intermetal dielectric in microelectronic chip fabrication.

Hence, there is a need to formulate an acidic or a neutral slurry with controllable polishing performance.

The present work is aimed at characterizing L-glutamic acid (Fig. 1) as complexing agent, in conjunction with hydrogen peroxide as oxidizer for obtaining stable Cu CMP removal rates in the acidic pH regime. L-glutamic acid has been employed in shallow trench isolation CMP to suppress silicon nitride polish rate [16] and it has two acidic groups. Potentiodynamic polarization studies were carried out to understand the chemical dissolution and the possible formation of passivation layers. The effect of mechanical action during the CMP process on the copper surface was investigated by in situ open circuit potential (OCP) measurements.

## Experimental procedures

### Copper removal experiments

Struers LaboPol-5 with LaboForce-3 polisher was used for the copper CMP. Fumed silica (M5 Cab-o-Sil from Cabot, with a surface area of 200 $m^2$ $g^{-1}$) was used as abrasive and the abrasive loading was maintained at 1 wt.% in all the experiments. The M5 silica used in these experiments are made of aggregates of very small (5–40 nm) primary silica particles. The L-glutamic acid concentration was varied from 0 to 1 wt.% and hydrogen peroxide concentration was varied from 0 to 10 vol.%. Electrochemical grade copper disk of 25 mm diameter was used for the polishing experiments. A downward force of 10 N (2.9 psi) and a turntable speed of 100 rpm were used while the sample was rotated at 250 rpm. The polish rate was calculated using weight loss method. The static etch rate of copper in various solutions at 40 °C was calculated by immersing the disks in the solution for 10 min and measuring the weight loss. The etch rates were measured at temperature higher than room temperature, since during the CMP process, the local surface temperatures would be higher than the ambient.

### Electrochemical experiments

All electrochemical experiments were conducted using PARSTAT 2263 (Princeton Applied Research). The experimental setup is described in detail elsewhere [12] and a brief summary is given below. A three-electrode cell with saturated calomel reference electrode and platinum wire counter electrode was used. A copper rod of 11 mm diameter fitted inside a Teflon rod was used as the working electrode. For the potentiodynamic polarization experiments, the potential was scanned at 2 mV/s. Sodium sulfate (0.1 M) was used as supporting electrolyte to enhance the conductivity of the solution. The values of corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$) were determined by extrapolating the anodic and cathodic branches of the potentiodynamic polarization plot using the software Powercorr. In order to assess the adsorption of L-glutamic acid on copper, electrochemical impedance spectra were acquired for Cu dissolving in 0.1 M $HNO_3$ at various L-glutamic acid concentrations. The in situ runs were conducted under both static and polishing conditions, with and without abrasives. A force of 10 N (2.9 psi) and a turntable speed of 100 rpm were maintained while the sample holder was kept stationary.

## Results and discussion

### Chemical mechanical planarization

Figure 2 shows the polish rate of copper as a function of hydrogen peroxide concentration at various concentrations of L-glutamic acid. Several notable features are found in the removal rate trend. In slurries without hydrogen peroxide, the copper removal rate is practically 0 for all the L-glutamic acid concentrations investigated. On the other hand, in slurries without L-glutamic acid, the polish rate increases slightly upon addition of hydrogen peroxide concentration and remains more or less the same after-

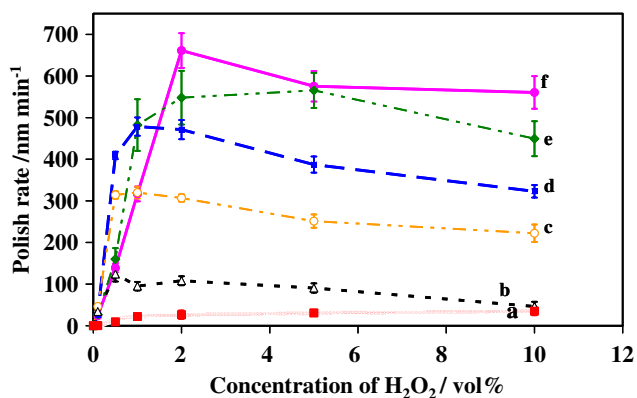**Fig. 1** Structure of L-glutamic acid at various pH
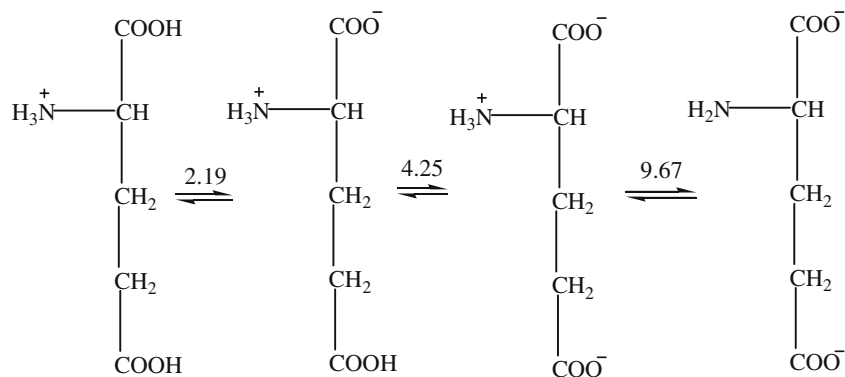
**Fig. 2** Effect of $H_2O_2$ concentration on copper polish rate in slurry with 1 wt.% silica and *a* 0, *b* 0.01, *c* 0.05, *d* 0.1, *e* 0.5, and *f* 1 wt.% L-glutamic acid

wards. Upon addition of a small amount of complexing agent (0.01 wt.%), the polish rate increases to a significant extent (100 nm/min) as seen from Fig. 2. In the pH range of 3–3.5, L-glutamic acid would be present mostly in the zwitterion form which can complex with copper ions or oxides as shown in Fig. 3. Cu–amino acid complexes are known to catalyze the dissociation of hydrogen peroxide to form OH radicals [17]. Hydroxyl radical is a much stronger oxidant than $H_2O_2$ and hence would enhance the oxidation of copper. The copper oxide would in turn be complexed by the L-glutamic acid and this cycle would result in favorable conditions for CMP [18].

In the slurry with 0.01 wt.% L-glutamic acid, the plot of polish rate vs. hydrogen peroxide concentrations shows a peak at a hydrogen peroxide concentration of 0.5 vol.%, which is similar to the reported trend for various Cu CMP slurries containing hydrogen peroxide and complexing agents [5, 12, 15, 19]. The reason that the polish rate shows a maximum at a particular concentration of hydrogen peroxide is described as follows [14, 15, 20, 21]: At lower concentrations, hydrogen peroxide increases the oxidation state of copper and hence enhances the polish rate of Cu. The oxidized copper would be removed by the complexing action of L-glutamic acid or any other complexing agent present in the slurry, as well as by mechanical abrasion. At higher concentrations of hydrogen peroxide though, a thick oxide film would be formed over the copper surface which would result in lower removal rates.

It can be seen from Fig. 2 that the peak polish rate and the location of the peak depend on the concentration of L-glutamic acid. In most hydrogen peroxide-based copper CMP slurries, the post-peak polish rate decreases drastically while the decrease was moderate in arginine-based systems [12]. At 0.05 and 0.1 wt.% of L-glutamic acid, the trend remains the same (Fig. 2, lines c and d). At higher L-glutamic acid concentrations (0.5 and 1 wt.%), the removal

rate tends to saturate rather than drop down significantly (Fig. 2, lines e and f). Hydrogen peroxide is an unstable chemical which can degrade in the presence of light and heat [22, 23]. If the polish rate varies drastically with $H_2O_2$ concentration, then the slurry removal rate will not be stable and the process will be difficult to control. Hence, it is preferable to operate in a region where the polish rate variation with hydrogen peroxide concentration is not drastic. Another feature that is noteworthy is the variation of removal rate with respect to the complexing agent concentration. For the sake of clarity, a select set of the data from Fig. 2 is plotted in Fig. 4 as polish rate vs. L-glutamic acid concentration. For slurries containing low concentrations of hydrogen peroxide (0.5% $H_2O_2$), it is interesting to note that the removal rate shows a peak with respect to L-glutamic acid concentration and that the polish rate decreases at higher L-glutamic acid concentrations. Thus, the results indicate that the role of L-glutamic acid is not limited to complexing the copper ions.
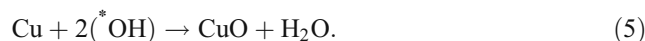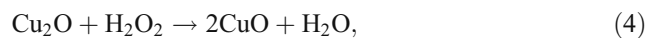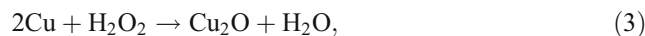
Potentiodynamic polarization studies

Figure 5 shows the potentiodynamic polarization plots for Cu dissolving in solutions containing 0.5 wt.% L-glutamic acid and various concentrations of hydrogen peroxide. Even though CMP rates were essentially 0 in slurries without hydrogen peroxide, the anodic branch of the potentiodynamic polarization curve does not show any sign of corrosion inhibition. With the addition of hydrogen peroxide, the $E_{corr}$ value increases. Copper can directly dissolve into the solution as shown below, but in solutions containing hydrogen peroxide, direct dissolution is unlikely [18]:

$$Cu \rightarrow Cu^{2+} + 2e^-. \tag{1}$$

The following Faradic reactions are expected when Cu reacts with hydrogen peroxide [18]:

$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^- \tag{2}$$

and the non-Faradic reactions would be [18]:

$$2Cu + H_2O_2 \rightarrow Cu_2O + H_2O, \tag{3}$$

$$Cu_2O + H_2O_2 \rightarrow 2CuO + H_2O, \tag{4}$$

$$Cu + 2(^*OH) \rightarrow CuO + H_2O. \tag{5}$$

Correspondingly, dissolved oxygen reduction [18] is one of the cathodic reactions expected:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \tag{6}$$
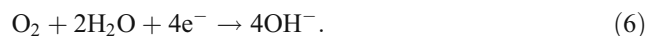
**Fig. 3** Complexation of copper (II) by L-glutamic acid zwitter-ion

$$2 \text{ HOOC-CH}_2\text{-CH}_2\text{-CH-COO}^- + Cu^{2+} \rightleftarrows \underset{NH_3^+}{\text{HOOC-CH}_2\text{-CH}_2\text{-CH-COO}^-}$$
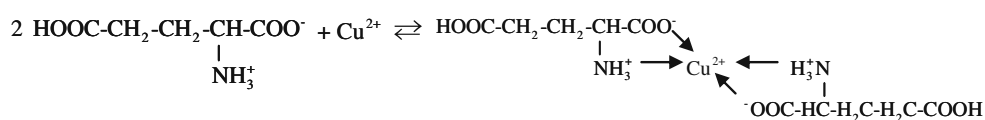
The cathodic reactions [14, 19] involving hydrogen peroxide are given by:

$$H_2O_2 + 2e^- \rightarrow 2OH^-, \tag{7}$$

$$H_2O_2 + e^- \rightarrow OH^* + OH^-. \tag{8}$$

The anodic reaction involving hydrogen peroxide is given by:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-. \tag{9}$$

In the literature, an increase in $E_{corr}$ is frequently associated with formation of a passivating layer [12, 19, 24, 25]. However, the $E_{corr}$ value can change due to changes in the anodic branch as well as the cathodic branch of the polarization curve. Since copper redox reactions and hydrogen peroxide redox reactions occur simultaneously, the increase in $E_{corr}$ cannot be ascribed solely to the formation of a passivating film [14]. In Fig. 5, it is seen that the cathodic branch changes considerably with change in hydrogen peroxide concentration, while the change in anodic branch is relatively less.

The corrosion current ($I_{corr}$) values were estimated by extrapolating the cathodic and anodic branches of the polarization curves and are summarized in Table 1. The data at the extremes of the polarization curves were not included in the analysis. The results of static etch rate experiments at room temperature and at 40 °C are also included for comparison. From the table, it is clear that the overall corrosion current increases with the hydrogen peroxide concentration. As expected, the etch rate was higher at 40 °C, but the overall trend remained the same at

both temperatures. For a solution containing 0.5 wt.% L-glutamic acid, the static etch rate increases with the addition of hydrogen peroxide. On the other hand, for a solution containing 1 vol.% hydrogen peroxide and no L-glutamic acid, the etch rate was found to be 0 while the $I_{corr}$ is moderate (25 μA/cm$^2$). Similarly, a comparison of the results at 10 vol.% hydrogen peroxide shows that the static etch rate increases by about 127% when the L-glutamic acid concentration was increased from 0.5 to 1 wt.%. However, the $I_{corr}$ increases by about 36-folds for the same change. Unfortunately, it is not possible to distinguish between the current associated with hydrogen peroxide redox reactions and that associated with copper redox reactions. Thus, in this system, the static etch rate experiments which are used to determine the chemical dissolution rate do not have a one-to-one correspondence with the corrosion currents estimated from potentiodynamic polarization studies.

Figures 6 and 7 show the potentiodynamic polarization curves for Cu dissolving in 1 and 10 vol.% of H$_2$O$_2$, respectively, at various concentrations of L-glutamic acid. The addition of L-glutamic acid leads to an increase in corrosion current for 0.5 wt.% as well as 1 wt.% of L-glutamic acid. On the other hand, CMP experiments show that, in presence of 1 wt.% H$_2$O$_2$, the Cu polish rate is higher for 0.5 wt.% and that it decreases to a moderate value for 1 wt.% L-glutamic acid (Fig. 4, line b). This apparent contradiction needs to be resolved. It is worth noting that, in Fig. 6 also, the cathodic branch changes considerably upon addition of L-glutamic acid. In Fig. 7, for a solution containing 10 vol.% H$_2$O$_2$, in the absence of
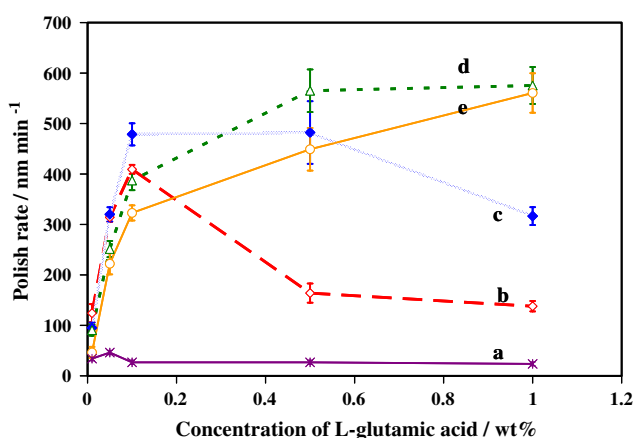


**Fig. 4** Effect of L-glutamic acid concentration on copper polish rate in slurry with 1 wt.% silica and *a* 0.1, *b* 0.5, *c* 1, *d* 5, and *e* 10 vol.% H$_2$O$_2$
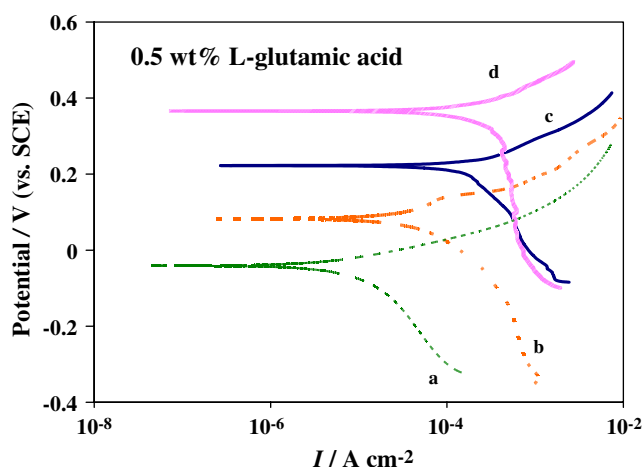


**Fig. 5** Potentiodynamic polarization plots of Cu in solutions containing 0.5 wt.% L-glutamic acid and *a* 0, *b* 0.1, *c* 1, and *d* 5 vol.% H$_2$O$_2$

**Table 1** Values of corrosion potential, corrosion current, and static etch rates for copper in solutions containing various concentrations of L-glutamic acid and hydrogen peroxide

| Concentration of $H_2O_2$ (vol.%) | Concentration of L-glutamic acid (wt.%) | $E_{corr}$ (mV) | $I_{corr}$ ($\mu A\ cm^{-2}$) | Static etch rate (nm min$^{-1}$) | |
|---|---|---|---|---|---|
| | | | | Room temperature | 40°C |
| 0 | 0.5 | −41 | 11 | 7 | 8 |
| 0.1 | 0.5 | 83 | 55 | 30 | 32 |
| 1 | 0.5 | 222 | 302 | 69 | 101 |
| 5 | 0.5 | 360 | 351 | 83 | 217 |
| 1 | 0 | 99 | 27 | 0 | 1 |
| 1 | 1 | 204 | 1,302 | 166 | 198 |
| 10 | 0.5 | 375 | 22 | 110 | 260 |
| 10 | 1 | 366 | 799 | 248 | 318 |

L-glutamic acid, a kink is observed in the anodic branch of the polarization curve. Near the kink, the anodic current decreases a little and then, with further increase in the potential, the current also increases. This indicates that there may be a film formation on the copper surface but, while the film reduces the corrosion, it does not completely passivate the surface. The film probably consists of oxides and hydroxides of copper [19, 26–28]. Upon addition of L-glutamic acid, the kink disappears. The corrosion current cannot be estimated accurately for the case of Cu dissolving in a solution containing 10 vol.% $H_2O_2$ and no L-glutamic acid, since the kink appears early in the anodic branch. For the other two cases, the corrosion current increases with the increase in L-glutamic acid concentration. In this case, the CMP experiments also show that the removal rate increases when the L-glutamic concentration is increased from 0.5 to 1 wt.% in the presence of 10 vol.% $H_2O_2$ (Fig. 4, line e).
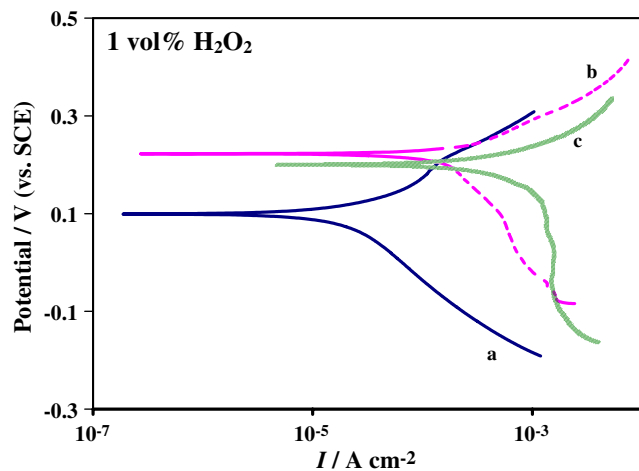
### In situ OCP measurements

Figure 8 shows the in situ OCP under static and polishing conditions for a slurry with 0.5 wt.% L-glutamic acid and 1 wt.% silica abrasives, with and without $H_2O_2$. In the absence of hydrogen peroxide, the OCP increases slightly when polishing is stopped. When polishing is restarted, the OCP decreases and this decrease is probably due to the mechanical removal of the oxidized copper species. In the presence of 1 vol.% hydrogen peroxide, the OCP is slightly higher under polishing conditions. When polishing is stopped, the OCP increases slowly and continues to increase even after 120 s. In the slurry containing 10 vol.% hydrogen peroxide, the OCP is significantly higher under polishing as well as static conditions. However, when polishing is stopped, the OCP moves up to its steady-state value relatively quickly. When the slurry contains 1 vol.% hydrogen peroxide, the region near the copper surface may be starved of hydrogen peroxide in static conditions. The rate of consumption of hydrogen peroxide by reaction may
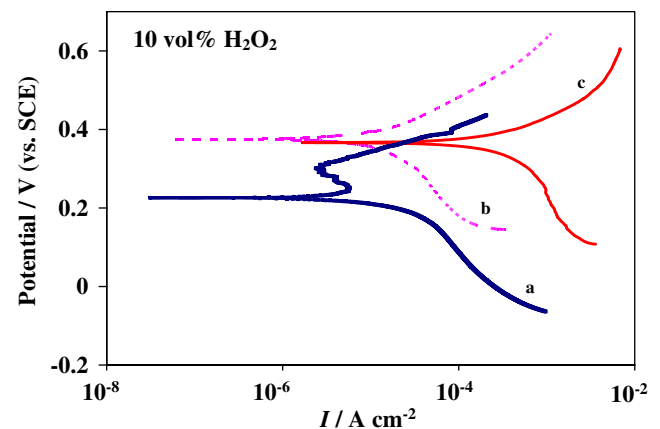


**Fig. 6** Potentiodynamic polarization plots of Cu in solutions containing 1 vol.% $H_2O_2$ and *a* 0, *b* 0.5, and *c* 1 wt.% L-glutamic acid



**Fig. 7** Potentiodynamic polarization plots of Cu in solutions containing 10 vol.% $H_2O_2$ and *a* 0, *b* 0.5, and *c* 1 wt.% L-glutamic acid
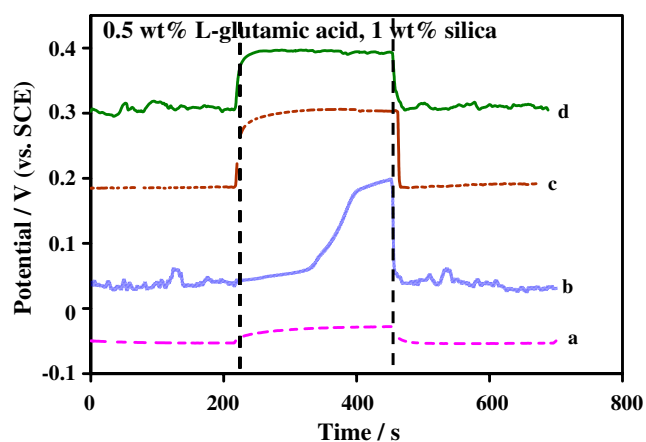
**Fig. 8** In situ OCP for copper in slurries containing 1 wt.% silica, 0.5 wt.% L-glutamic acid, and *a* 0, *b* 1, *c* 5, and *d* 10 vol.% $H_2O_2$

be more than the rate of diffusion of hydrogen peroxide from bulk solution and hence mass transfer limitations may explain the slow rise of the OCP. During polishing, fresh slurry will flow to the interface and the concentration of hydrogen peroxide near the interface will be more than that under static conditions. Hence, the OCP drops quickly when polishing is restarted in this slurry. The OCP value is altered by the presence of oxide and hydroxide films on the copper surface. If the films are mechanically removed, the OCP will reflect the change. The OCP is also altered by the hydrogen peroxide redox reactions occurring on the electrode surface. Thus, when polishing is stopped, the change in OCP would be due to the lack of mechanical removal as well as the mass transfer limitations of hydrogen peroxide. In slurries containing 10 vol.% hydrogen peroxide, the concentration of hydrogen peroxide near the Cu–slurry interface will be high even under static conditions. Thus, the OCP rises to the steady-state value quickly in these slurries and mass transfer will not be a limitation. A report on OCP monitoring of Ta and Cu in slurries with glycine, hydrogen peroxide, and alumina abrasives also indicates that pH and mass transfer effects influence the OCP trends [29]. It was reported that in the slurries without glycine, at a pH of 2, the OCP of copper increased during static conditions while at a pH of 10 or higher, there was almost no difference in the OCP between static and polishing conditions. On the other hand, in the presence of glycine at a pH of 2, the OCP decreased slightly during the static period and the probable reason was an accumulation of the ionic species at the disk/pad interface.

Amino acids have been reported to act as corrosion inhibitor for metal in acidic medium [30–36]. Specifically, L-glutamic acid was found to inhibit copper corrosion in 0.5 M HCl by physically adsorbing onto the copper surface and the adsorption was reported to follow the Langmuir isotherm model [31]. A few amino acids such as glycine are

reported to adsorb onto the copper electrode and reduce the corrosion in nitric acid [36]. On the other hand, in the presence of hydrogen peroxide, some of them have been shown to be removal rate enhancers for copper polishing [12, 13]. Although, according to the Pourbaix diagram [37], copper oxides and hydroxides would not be stable at acidic pH range, in the presence of hydrogen peroxide, they may be present on the surface. It was reported that L-glutamic acid acts as an inhibitor for copper dissolution in 0.5 M hydrochloric acid, which is characterized by decreased $I_{corr}$ values with increase in concentration of glutamic acid [30, 31]. Citric acid, which has been reported to act as inhibitor for copper dissolution in the nitric acid system [38], also presents the same trend and has been used as complexing agent for Cu CMP in the presence of hydrogen peroxide [8]. The adsorption of an additive on the metal surface can be measured by analyzing the electrochemical impedance spectra of copper in solutions of various concentrations of the additive [31, 39]. The impedance spectra of copper in 0.1 M nitric acid at various concentrations of L-glutamic acid is presented in Fig. 9. The data for blank solution without L-glutamic acid and 0.05 wt.% L-glutamic acid are expanded and shown in the inset for clarity. The spectra are modeled using the standard circuit involving Warburg impedance shown in Fig. 10. Here, $W$ represents the Warburg impedance, $R_s$ the solution resistance, $R_t$ the charge transfer resistance, and $Q$ the constant phase element. The fractional surface coverage $\theta$ at different concentrations of L-glutamic acid can be determined according to the formula: $\theta = \frac{R_{t(inh)} - R_t}{R_{t(inh)}}$ where $R_{t(inh)}$ and $R_t$ are the charge transfer resistances in the inhibited and uninhibited solution, respectively. Initially, the surface coverage increased with L-glutamic acid concentration in the solution and then saturated at higher concentrations, as shown in Fig. 11. The data was fit to the Langmuir adsorption isotherm model shown in the following equation: $\theta = \frac{Kc}{1+Kc}$, which is frequently written in the form: $\frac{c}{\theta} = \frac{1}{K} + c$. Here, $c$ is the L-glutamic acid concentration in the solution and $K$ is the adsorption isotherm constant given by $K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$ where 55.5 mol $L^{-1}$ is the concentration of water in the solution, $\Delta G_{ads}$ is the free energy of adsorption, $R$ is the universal gas constant, and $T$ is the temperature in kelvin [40]. The value of $\Delta G_{ads}$ is −37.7 kJ $mol^{-1}$, which is of the same order of magnitude as that reported for the adsorption of amino acid on Cu in 0.5 M HCl. The results corroborate the hypothesis that L-glutamic acid adsorbs onto the copper surface.

Since the removal rate is 0 in the absence of hydrogen peroxide, it is clear that L-glutamic acid does not dissolve copper to a significant extent and possibly inhibits copper dissolution. On the other hand, oxidized species of copper are complexed by L-glutamic acid. The following picture emerges from this analysis. Both hydrogen peroxide and
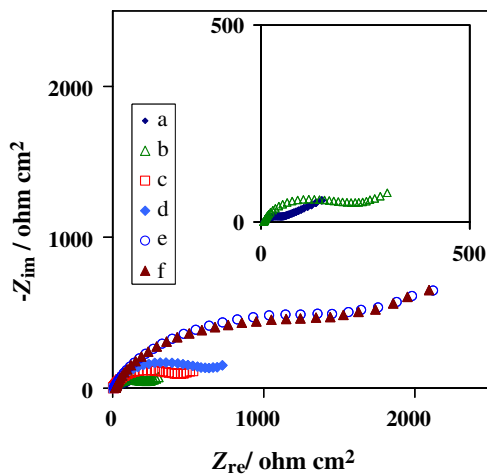
Fig. 9 Electrochemical impedance spectra of copper in solutions containing 0.1 M HNO$_3$ and *a* 0, *b* 0.05, *c* 0.1, *d* 0.3, *e* 0.5, and *f* 1 wt. %L-glutamic acid. The expanded version is shown in the *inset*



Fig. 11 Comparison of experimental and Langmuir isotherm model for adsorption of L-glutamic acid on Cu. The *points* represent the data and the *line* represents the model best fit

L-glutamic acid interact with the copper surface. At low concentrations, hydrogen peroxide oxidizes the surface and, at higher concentration, it leads to the formation of relatively thicker copper oxide. The oxide may reduce the polish rate although it may be porous and hence does not result in complete inhibition of dissolution. If the oxidized species are not present, L-glutamic acid will adsorb onto the bare copper surface and will inhibit dissolution. If oxidized species of Cu are present, then L-glutamic acid complexes them and hence will facilitate the removal of the oxide layer.

If hydrogen peroxide is present in relatively lower concentration and L-glutamic acid is present at higher concentration, then some of the surface will be oxidized by hydrogen peroxide. Part of the glutamic acid will adsorb onto the copper surface and prevent its interaction with hydrogen peroxide, while the glutamic acid in solution will dissolve the copper oxides formed thus facilitating removal. This also explains why the potentiodynamic polarization curves do not show any kink in the presence of L-glutamic acid. When the potential of the electrode is increased above the OCP values, copper is electrically oxidized and the oxidized species would be complexed by the L-glutamic acid and will dissolve. In that sense, L-glutamic acid is not a strong corrosion inhibitor like benzotriazole or potassium sorbate which inhibit copper dissolution in anodic potentials also. Thus, too high a concentration of either one of
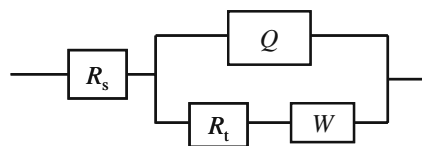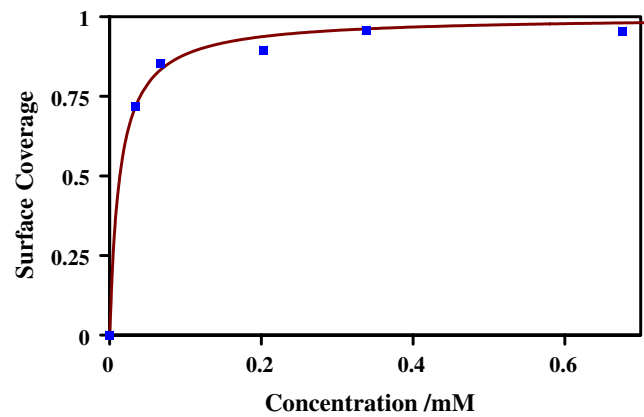
the chemicals (hydrogen peroxide and L-glutamic acid) would reduce the polish rate. However, the mechanism is different for these two cases. A high concentration of hydrogen peroxide will lead to a thick oxide formation which reduces further oxidation of copper, while a high concentration of L-glutamic acid will lead to a reduction in oxide formed on the surface. The competitive nature of the interaction processes ensures that the polish rate will increase continuously only when both the complexing agent and the oxidizing agent are increased simultaneously at the correct proportion.

In order to verify that oxide forms on the surface at high concentration of hydrogen peroxide, experiments were conducted by immersing Cu disk in a solution containing 10 vol.% hydrogen peroxide and 0.01 wt.% L-glutamic acid for 20 min. The copper disk turns black, which indicates that the surface is covered with cupric oxide, whereas if the film is cuprous oxide, the color would change from purple to blue, green, yellow, and red depending on the thickness of the oxide [41]. The solution remains clear throughout the experiment. When the Cu disk was immersed in a solution containing 10 vol.% hydrogen peroxide and 1 wt.% L-glutamic acid for 20 min, the disk remained bright, while the solution turned blue. The results indicate that, when the L-glutamic acid concentration is low, a high concentration of hydrogen peroxide leads to the formation of cupric oxide on the surface.

While the results show that L-glutamic acid can be used as a complexing agent to formulate a Cu CMP slurry with stable polish performance in a pH regime that is compatible with low-*k* dielectric, further optimizations with patterned wafers are necessary. A suitable corrosion inhibitor also needs to be incorporated into the slurry to minimize dishing. Further analysis with electrochemical and non-electrochemical techniques such as scanning electrochemical microscopy and in situ spectroscopy would help to



Fig. 10 Equivalent circuit of an electrode with Warburg impedance

confirm the hypothesis that L-glutamic acid acts as an inhibitor for copper surface as well as complexing agent for copper ions.

## Conclusions

The CMP of copper in slurries containing L-glutamic acid and hydrogen peroxide was investigated using CMP and electrochemical techniques. It was found that the slurry provides a stable Cu polishing performance in a pH range that is compatible with low-$k$ dielectrics. For a fixed hydrogen peroxide concentration, the polish rate vs. L-glutamic acid concentration shows a maximum. In the absence of hydrogen peroxide, the polish rate was 0 for all the concentrations of L-glutamic acid studied. However, the potentiodynamic polarization curves do not show any sign of passivation even at high L-glutamic acid concentration. In situ experiments show that the copper redox reactions along with the hydrogen peroxide redox reactions contribute to the electrochemical results. The growth of oxide and hydroxide films on the copper surface is slow when the polishing is stopped in slurries containing low concentrations of hydrogen peroxide. It is proposed that L-glutamic acid adsorbs onto the copper surface and inhibits its dissolution. However, L-glutamic acid complexes with the oxidized copper species and hence enhances the Cu polish rate in the presence of hydrogen peroxide. The hypothesis successfully explains the removal rate trends and the electrochemical results.

## Symbol list

$E_{corr}$    Corrosion potential
$I_{corr}$    Corrosion current
$R_s$    Solution resistance
$R_t$    Charge transfer resistance in uninhibited solution
$R_{t(inh)}$    Charge transfer resistance in inhibited solution
$Q$    Constant phase element representing the double layer
$W$    Warburg impedance
$\theta$    Surface coverage of adsorbed species
$K$    Adsorption isotherm constant
$c$    Concentration of L-glutamic acid in solution
$\Delta G_{ads}$    Free energy of adsorption
$R$    Universal gas constant
$T$    Temperature in kelvin

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