Effects of OH Radicals on Formation of Cu Oxide and Polishing Performance in Cu Chemical Mechanical Polishing

Min Cheol Kang,[a] Ho-Seong Nam,[b] Ho Youn Won,[b] Sukhoon Jeong,[c] Haedo Jeong,[c] and Jae Jeong Kim[a,*,z]

[a]*School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Korea*
[b]*Hanwha Chemical, Nano Technology Research Division, Research and Development Center, Daejeon 305-804, Korea*
[c]*School of Mechanical Engineering, Pusan National University, Pusan 609-735, Korea*

The amount of OH radicals generated varied according to the complexing agent or Cu ion, and the accelerating effect of OH radicals on the rate of Cu oxide formation was found in acidic pH. When Cu(I) ions and oxalic acid were added to H_2O_2-based slurry, the decreases in etch and removal rates of Cu were observed because more generation of OH radicals resulted in the formation of thicker Cu oxide compared to additive-free slurry. Therefore, proper control of the formation and dissolution of Cu oxide led to an increase in etch and removal rates.
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Cu has been introduced as an interconnection material due to its low electrical resistance and high resistance to electromigration compared to W or Al.[1-3] The damascene process based on chemical mechanical polishing (CMP), which is used to remove the protruding part and planarize the whole wafer surface, makes it possible to use Cu as an interconnection material.

During Cu CMP, the Cu surface is oxidized by an oxidizing agent through the oxidation of Cu to cuprous or cupric ions (Eq. 1). Among such oxidizing agents, hydrogen peroxide (H_2O_2) is widely used for Cu CMP and its properties have been widely investigated.[4-8] Also, various organic additives were added into the slurry to maximize specific characteristics during the Cu CMP. To inhibit Cu corrosion, benzotriazole (BTA) or 5-aminotetrazole (ATRA) is commonly used.[9-11] An organic additive of the carboxylic group was added as a complexing agent to improve the removal rate of Cu. At present, citric acid,[12-14] oxalic acid,[15] and glycine[16-18] were introduced as the complexing agent and their properties and performance investigated. The complexing agents react with oxidized Cu and form complexes on the Cu surface. In an acidic pH, Cu cations, especially Cu(I) ions, react with H_2O_2 and then H_2O_2 is converted into OH radicals and hydroxyl ions through the so-called Fenton reaction (Eq. 2).[19] The oxidation potential of the OH radical is higher than that of H_2O_2, which is well known to be one of the most powerful oxidizing agents

$$Cu \rightarrow Cu^+ + e \ \ or \ \ Cu^{2+} + 2e \qquad [1]$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH\cdot + OH^- \qquad [2]$$
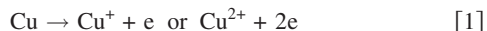
It has been reported that OH radicals enhanced the removal rates of Cu in an H_2O_2-based slurry, including an amino acid at alkaline solution,[16] and that citric acid and oxalic acid improved the removal rate of Cu in the acidic solution. When using citric acid and oxalic acid as the complexing agent in weak acidic pH, the effect of OH radicals in the slurry on Cu CMP performance has not been reported. Therefore, the objective of this study is to understand the effect of OH radicals on Cu CMP.

Experimental

Electrochemical measurements.— For the electrochemical experiments, a 99.9% Cu rod with a surface area of 0.5 cm^2 was used. A Pt electrode and a saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. Potentiodynamic studies were performed with an EG&G model 263 potentiostat/galvanostat corrosion measurement system. The potentiodynamic

* Electrochemical Society Active Member.
z E-mail: jjkimm@snu.ac.kr

polarization measurements were obtained with a scan rate of 10 mV/s and the potential ranged from −1.3 to 1.3 V.

To calculate the thickness of Cu oxide, a chronoamperometry test was conducted. Prior to chronoamperometry tests, 1.5 cm × 1.5 cm Cu wafers were immersed in H_2O_2 solution without and with complexing agent and Cu(I) ion for 10 min. Then a constant current (100 $\mu A/cm^2$) was applied to each Cu wafer. In order to enhance the generation of OH radical in H_2O_2 solution without the complexing agents, 0.001 M copper(I) acetate [$(CH_3COO)Cu$] or copper(II) acetate [$(CH_3COO)_2Cu$][16] was added.

OH radical trapping experiment.— To analyze the extent of OH radicals, ultraviolet-visible (UV-vis) spectrometry analysis was carried out. *N,N*-dimethyl-*p*-nitrosoaniline (PNDA) as a trapping agent of OH radicals was added into H_2O_2-based solution and the concentration was fixed at 4.15×10^{-5} M.[16] In order to prevent decomposition of PNDA, we measured the absorption intensity at 440 nm using UV-vis as soon as Cu(I) acetate or Cu(II) acetate was added to H_2O_2-based solution.

X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used for surface characteristic analysis.

Static dissolution and polishing test.— To evaluate Cu etch rate, the substrates used in this study were 1.5 cm × 1.5 cm Cu wafers with a structure of Cu [1500 nm, electroplating on seed Cu]/Ta [25 nm, physical vapor deposition (PVD)]/TaN [10 nm, PVD]/poly Si. The Cu etch rate was measured by the sheet resistance change using four-point probe. Cu wafers were dipped into various solutions for 10 min and then sequentially rinsed and dried with deionized water and N_2 gas, respectively. The sheet resistances of wafers were measured at ten points.

The Cu wafers were polished using the R&D CMP Machine POLI-380 (G&P Technologies, Korea) consisting of an 8 in. platen and a 4 in. carrier to determine removal rate. The platen speed was 80 rpm and the carrier speed was 75 rpm. The applied pressure between the platen and the carrier was maintained at 2.5 psi, and the flow rate of slurry was set to 150 mL/min.

Slurry preparation.— The slurry was composed of 2.5 wt % Al_2O_3 (primary particle size: 50 nm) and 2 wt % H_2O_2, without and with 0.02 M citric acid or oxalic acid.

The solution and slurry were fixed at pH 4 using H_2SO_4 or KOH solution.

Results and Discussion

Electrochemical analysis results.— Figure 1 shows the potentiodynamic polarization curve of Cu in H_2O_2 solution with and without complexing agents. Without any complexing agents, the corrosion current density and corrosion potential were 90 $\mu A/cm^2$ and 350
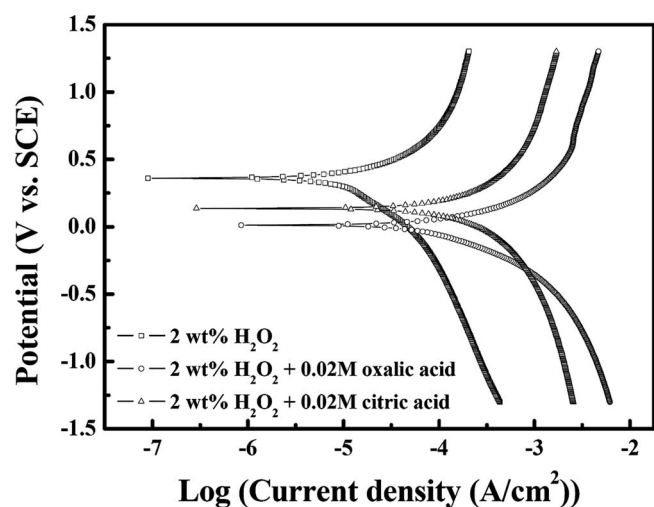
Figure 1. Potentiodynamic polarization curve of the pure Cu rod with a scan rate of 10 mV/s in 2 wt % H_2O_2 solution, without and with 0.02 M oxalic acid or citric acid. Solution pH fixed at 4.

Figure 2. XPS spectra of Cu $2p_{3/2}$ for Cu after immersing for 10 min in 2 wt % H_2O_2 solution without and with 0.02 M oxalic acid or citric acid.

mV, respectively. When citric acid or oxalic acid were added into H_2O_2 solution, the corrosion current density remarkably increased to about 590 and 710 $\mu A/cm^2$, respectively, due to the formation of complex compounds of the complexing agent and Cu ions.[5,12,17,20] Therefore, it is expected that Cu etch rate and the removal rate would increase considerably when complexing agents were added into slurry.

To investigate the generation of OH radicals, UV-vis analysis was performed and the absorption intensities at 440 nm are listed in Table I. When the generated OH radicals were reacted with PNDA, the absorption intensity of PNDA at 440 nm decreased. When Cu(I) ions were added into H_2O_2-based solution with and without complexing agents, the absorption intensities at 440 nm decreased from about 1.2 to around 0.56 and 0.9, respectively. The absorption intensity value of the solution containing oxalic acid was lowest, which indicates that the generation of OH radicals was highest in the solution containing oxalic acid. In the case of Cu(II) ion addition, there was no significant increase in generation of OH radicals. In order to generate OH radicals in a H_2O_2–Cu(II) system, first Cu(II) is reduced to Cu(I) by H_2O_2. Then reduced Cu(I) reacts with H_2O_2 and results in the generation of OH radicals (the so-called Fenton-like reaction).[21-23] Kwan reported that the formation rate of OH radicals by the Fenton-like reaction is slower than that of the Fenton reaction.[24] Thus, OH radicals were not detected through UV-vis, because the UV-vis analysis time was not long enough to generate OH radicals.

The results of XPS analysis on the surface of the Cu wafer immersed in various solutions are presented in Fig. 2. In the case of H_2O_2 with and without oxalic acid, the binding energy of the Cu $2p_{3/2}$ peak was observed at 932.5 eV, which was attributed to Cu_2O. As a result, it was confirmed that Cu_2O was formed on the Cu wafer through the immersion in the H_2O_2 and oxalic acid solution. However, in the case of a citric acid-based solution, no peak related to Cu
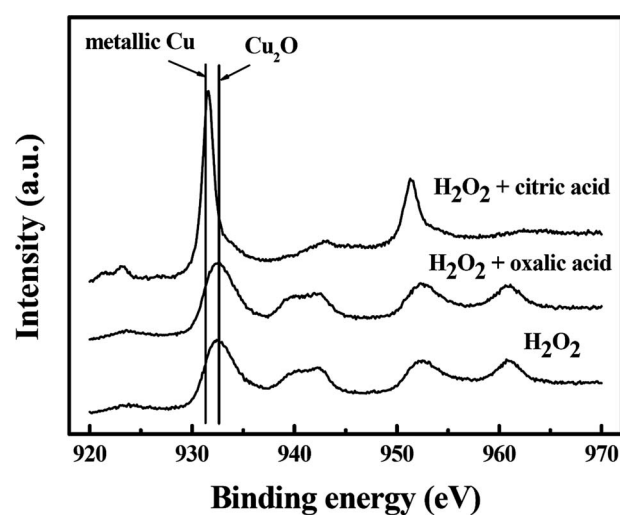
oxide was found on the Cu wafer. Although a large amount of OH radicals was generated in the solution, Cu_2O that formed on the Cu surface was rapidly dissolved by citric acid.

The surface roughness of a dipped Cu wafer in H_2O_2 solution with and without complexing agents is listed in Table II. Except for citric acid-based solution, the root-mean-square (rms) roughness of the Cu wafers increased due to the formation of Cu_2O on the Cu surface. The Cu wafer in oxalic acid-based solution showed the greatest increase in rms roughness, from 7.1 to 66.3 nm, because Cu_2O was formed drastically by OH radicals. In the case of citric acid, the rms roughness of Cu increased from 7 nm to 11.3 nm. The slight increase in rms roughness indicates that the Cu surface was oxidized and the Cu oxide was dissolved. The rms roughness increased normally with dipping time and was about 24 nm after immersing for 30 min. From the previous results of Fig. 2, it can be concluded that the increase in surface roughness can be attributed to the formation of a Cu_2O layer on the Cu surface by generated OH radicals.

In order to investigate the effects of OH radicals on the formation rate of Cu oxide, a chronoamperometry test was performed. Figure 3 shows a potential–time diagram of a Cu wafer in a H_2O_2 solution with and without a complexing agent and Cu(I) ions. The thickness of Cu oxide could be calculated using Faraday's law and transition time at the transition region. The transition region is where Cu oxide is reduced and there is a resulting flat region in the potential–time diagram. As shown in Fig. 3, in the case of H_2O_2 with and without oxalic acid, one transition region, where Cu_2O is reduced to Cu, can be clearly observed. The transition times were 120 and 210 s, respectively. From the observation of one transition region in the potential–time diagram, it was also confirmed that Cu oxide on the Cu surface existed predominantly as Cu_2O. At this time, the calculated thicknesses of Cu oxide, here Cu_2O, were 14.7 and 25.9 nm, respectively. In contrast, in the case of the citric acid-based solution, the transition region cannot be observed. This result indicates that

Table I. Changes of absorbance at 440 nm according to complexing agents and Cu ion in UV-vis spectrometry.

	Absorbance (a.u.)		
	H_2O_2	H_2O_2 + oxalic acid	H_2O_2 + citric acid
No addition	1.23	1.21	1.22
Cu(I) addition	0.90	0.56	0.73
Cu(II) addition	1.22	1.21	1.21

Table II. RMS roughness of Cu after immersing in various solutions for 10 min.

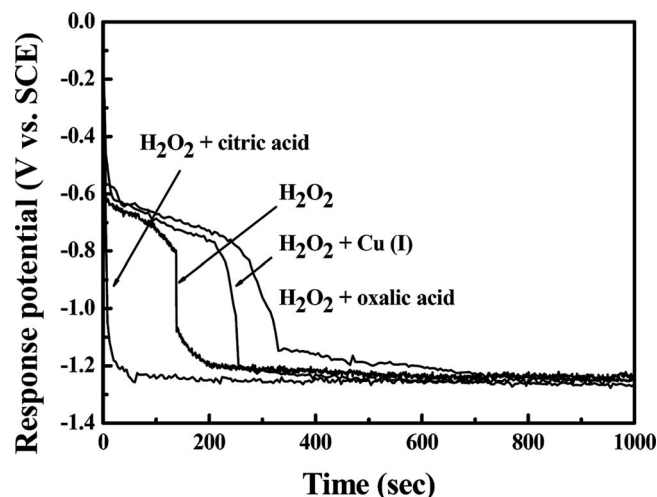|	RMS roughness (nm)
As-prepared Cu	7.1
2 wt % H_2O_2	53.4
2 wt % H_2O_2 + 0.02 M oxalic acid	66.3
2 wt % H_2O_2 + 0.02 M citric acid	11.3
2 wt % H_2O_2 + Cu(I)	61.9

Figure 3. Coulometric reduction of Cu after immersing for 10 min in 2 wt % H_2O_2 solution, with and without complexing agent or Cu(I).

Cu oxide did not exist on the Cu surface. When the Cu wafer was immersed in H_2O_2 solution added with Cu(I) ions, the transition time was longer than in the case of H_2O_2 solution alone, and the transition time and calculated thickness of Cu_2O were 188 s and 23.2 nm, respectively. It was confirmed that OH radicals promoted the formation of Cu oxide. The transition time and calculated thickness of Cu oxide are listed in Table III.

Etch and removal rate tests.— The etch and removal rates of Cu using an H_2O_2-based slurry containing various complexing agents are shown in Fig. 4. The chemical etch rates and removal rates of Cu increased with the addition of complexing agents, which were caused by the acceleration of the anodic reaction of Cu. The etch rate and removal rate of Cu using a slurry containing citric acid increased by about 320 and 180%, respectively, compared to those of oxalic acid. In the case of H_2O_2 and oxalic acid, when Cu(I) ions were added, the decrease in etch and removal rates were observed due to the formation of a thicker Cu oxide compared to those without Cu(I) ions. In the case of citric acid, however, the etch and removal rates slightly increased from 17 to 20 nm/min and from 950 and 990 nm/min with the addition of Cu(I) ions. From the results of a chronoamperometry test, we observed that the more OH radicals were generated, the thicker Cu oxide formed. Citric acid has the ability to dissolve Cu oxide. Therefore, the continuous formation and dissolution of Cu oxide led to an increase in etch and removal rates. There was no significant difference in the etch and removal rates when Cu(II) ions were added because they cannot decompose H_2O_2.

Conclusion

In this work, the effect of OH radicals on Cu CMP was investigated according to complexing agents. Cu was oxidized to Cu(I) by H_2O_2, and formed Cu(I) ions that decomposed H_2O_2 into OH radi-
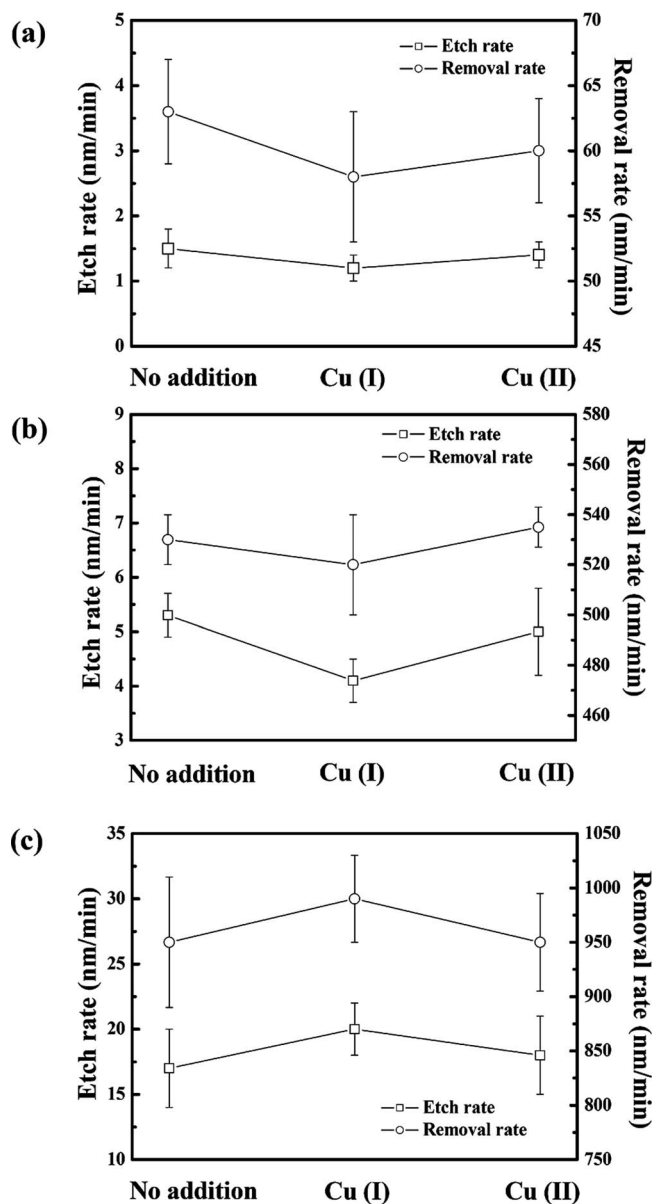

Figure 4. Cu etch rate in 2 wt % H_2O_2 solution and removal rate of Cu in 2.5 wt % Al_2O_3-based slurry including 2 wt % H_2O_2 (a) without complexing agent, (b) with oxalic acid, and (c) with citric acid according to types of Cu ion.

cals, which has a stronger oxidizing ability than H_2O_2. The amount of OH radicals generated varied with the complexing agent type. The formation rate of Cu oxide increased as the amount of generated OH radicals increased. When oxalic acid was added, the amount of generated OH radicals was the largest, resulting in an increase in formation rate of Cu oxide.

In contract, although a significant amount of OH radicals was generated in the citric acid solution, no Cu oxide existed on the Cu surface due to dissolution of Cu oxide by citric acid. Moreover, the repeated formation and dissolution of Cu oxide led to an increase in etch and removal rates of Cu.

Table III. Transition time in diagram of potential–time and calculated thickness of Cu oxide.

	Transition time (s)	Calculated thickness of Cu oxide (nm)
H_2O_2	119	14.7
H_2O_2 + oxalic acid	210	25.9
H_2O_2 + citric acid	–	–
H_2O_2 + Cu(I)	188	23.2

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