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Effects of corrosion environments on the surface finishing of copper chemical mechanical polishing

M.T. Wang[a,*], M.S. Tsai[b], C. Liu[b], W.T. Tseng[b], T.C. Chang[b], L.J. Chen[c], M.C. Chen[a]

[a]*Department of Electronics Engineering, National Chiao-Tung University, Hsinchu, Taiwan*
[b]*National Nano Device Laboratory, 1001 Ta Hsuell Rd., Hsinchu, Taiwan*
[c]*Department of Submicron Technology Development, ERSO/ITRI, Hsinchu, Taiwan*

Abstract

Copper chemical mechanical polishing (Cu-CMP) was investigated using slurries containing alumina abrasive and various types and concentrations of oxidizer, as well as benezotriazole (BTA) additive. We found that the corrosion rate of copper film decreases with increasing BTA concentration in 3 vol.% HNO_3 solution, but the passivation effect of BTA saturates as the concentration reaches about 0.01 M. On the other hand, a small amount of H_2O_2 in H_2O_2/XJFW8099 slurry enhances the corrosion rate dramatically, while an abundance of H_2O_2 in the slurry suppresses the corrosion reaction effectively. The polishing rate and its non-uniformity decrease with increasing volume ratio of H_2O_2 in H_2O_2/XJFW8099 slurry. A very smooth surface with a removal rate of 363.0 nm/min was obtained using the slurry of 1/1 ratio. Depletion of H_2O_2 in the slurry can result in more abrasive residuals as well as a rougher surface; the surface roughness increases from 0.3 to 0.9 nm as the H_2O_2/XJFW8099 ratio decreases from 1/1 to 1/4. Our results indicate that the corrosion rate, polishing rate and surface roughness of copper films are sensitively dependent on the type and concentration of oxidizer as well as the BTA additive. © 1997 Elsevier Science S.A.

Keywords: Corrosion; Chemical mechanical polishing; Benzotriazole; Copper

1. Introduction

Chemical mechanical polishing (CMP) has been proposed as a viable technique to widen the process window and to reduce the defect density in integrated circuit (IC) manufacture [1–3]. Recently, a number of studies on copper chemical mechanical polishing (Cu-CMP) have achieved multilevel interconnections with low electrical resistance, excellent electromigration resistance, and global planarization [4–9]. However, the limited passivation offered by Cu oxide formed on copper surface during CMP process could result in pitting and increased surface roughness. A clear understanding of corrosion effect on polishing rate and surface finishing are therefore extremely important to accomplish Cu metallization.

It has been shown that the use of benzotriazole (BTA) provides a protective and stable film on copper surfaces, which can withstand chemical and thermal environments [10]. For a polishing process using a nitric acid slurry with 6 wt.% alumina (Al_2O_3), it was reported that the average surface roughness increased from an initial roughness of 1.0 nm to 15.0 nm [11]. Moreover, it was found that the use of a different pad structure produced a different polishing rate of copper film for a polishing process using a commercially available Rodel XJFW8099 slurry, which was diluted with hydrogen peroxide (H_2O_2) [12]. Although these studies have provided much valuable information on Cu-CMP, few studies have been done on the effects of corrosion environments on the surface finishing of Cu-CMP process.

The purpose of this study was to investigate the effects of corrosion environments on Cu-CMP. Corrosion rate, polishing rate, surface roughness and micro-scratch of copper film were investigated using various types of oxidizers, such as HNO_3 and H_2O_2. The effects of BTA in nitric-acid-based slurry were evaluated, and various types of slurry were examined. The results of this study may be useful in control of corrosion environments in Cu-CMP processes.

2. Experimental procedures

The corrosion/polishing sample was a two-layer structure

* Corresponding author.

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of Cu/Ta with thicknesses of 900/30 nm, sputter deposited on a 6-in (150-mm) diameter Si wafer which was covered with a 500-nm thick thermally grown SiO_2. The under layer of 30-nm Ta was used as an adhesion promoter for the copper deposition, since copper does not adhere well on the thermal oxide. The wafer was cut into 3×3-cm^2 pieces for corrosion rate experiments, while the entire 150-mm wafer was used for CMP of Cu.

To investigate the effect of BTA addition to HNO_3 solution on the corrosion rate of copper film, we prepared two kinds of solutions: (i) 3 vol.% HNO_3 dilute solutions to which were added various concentrations of BTA ranging from 0.001 to 0.04 M; and (ii) 0.01 M BTA solution to which were added various volume percentages of HNO_3 ranging from 0.001 to 20%. To investigate the effect of H_2O_2 concentration on the corrosion rate of copper film, a Rodel H_2O_2/XJFW8099 slurry with volume ratio ranging from 0 to 4 was used. In this study, commercially available semiconductor grade 30 wt.% H_2O_2 and 70 wt.% HNO_3 were used.

For studying the effects of slurry type on the uniformity and polishing rate of Cu-CMP, three types of slurry were prepared: HNO_3/BTA, H_2O_2/XJFW8099 and Cabot WA355/FE-10, as shown in Table 1. The volume ratio of H_2O_2/XJFW8099 relevant to polishing was varied from 1/1 to 1/4. Cu-CMP was performed with an IPEC/Planar 372M polisher using a Rodel Suba 500 pad. Table 2 gives the experimental parameters and conditions used for Cu-CMP process.

The corrosion tests were performed by dipping the 3×3-cm^2 sample pieces in various corrosion solutions without intentional stirring. To determine the corrosion/polishing rate of copper film, a four-point probe was used to measure the sheet resistance of copper film, and the change of sheet resistance before and after the corrosion treatment or CMP process was used to determine the corrosion/polishing rate. The polishing rate of Cu-CMP was measured at 13 points across a 150-mm diameter wafer (10-mm edge exclusion). Non-uniformity of polishing rate is defined as follows:

$$\text{Non-uniformity}(\%) = 100\% \times \frac{(\text{Max} - \text{Min})\ \text{polishing rate}}{2 \times \text{mean value}}$$

Scanning electron microscope (SEM) was employed to characterize the surface morphology and to measure the thickness of copper film. Atomic force microscope (AFM) was used to characterize the surface roughness before and after the polishing process.

Table 1

General specifications of slurries

Specifications	Slurry type		
	(1–3 vol.%) HNO_3 (0.01 M BTA)	H_2O_2/XJFW8099 (volume ratio: 1/1–1/4)	WA355/ FE-10 (0.01 M BTA)
pH value	0.85	4.20	1.7
Oxidizer	HNO_3	H_2O_2	$Fe(NO_3)$
Abrasive	Al_2O_3	Al_2O_3	Al_2O_3
Solid contents (%)	5	18–28	3

Table 2

Experimental parameters and conditions used for Cu-CMP

Platen/carrier speed	20/42 r.p.m.
Down pressure	3.0 p.s.i.
Back pressure	1.5 p.s.i.
Slurry flow rate	150 ml/min
Temperature	29–30°C
Pad	Suba 500
Pad condition	None

3. Results and discussion

3.1. Passivation effect of BTA on copper corrosion

Nitric acid (HNO_3) is a strong oxidizer which attacks copper very rapidly. Benzotriazole (BTA) is a well known corrosion inhibitor for copper corrosion [13–17]. The mechanism by which BTA is effective in inhibiting corrosion appears to be the formation of a continuous Cu-BTA complex film tightly adhered to the copper surface.

Fig. 1 shows the corrosion rate of copper as a function of BTA concentration in a 3 vol.% HNO_3 solution. The corrosion rate of copper decreases with increasing BTA concentration, but the passivation effect of BTA saturates as the concentration reaches about 0.01 M. Fig. 2 shows the corrosion rate of copper film versus HNO_3 volume percentage with and without 0.01 M BTA. Without any BTA, the corrosion rate increases as the HNO_3 volume percentage increases; with the addition of 0.01 M BTA, a very low corrosion rate was obtained unless the volume percentage was higher than 10%. These results indicate that the 0.01 M BTA is an effective corrosion inhibitor for copper in the region of low HNO_3 volume percentage (<10%).

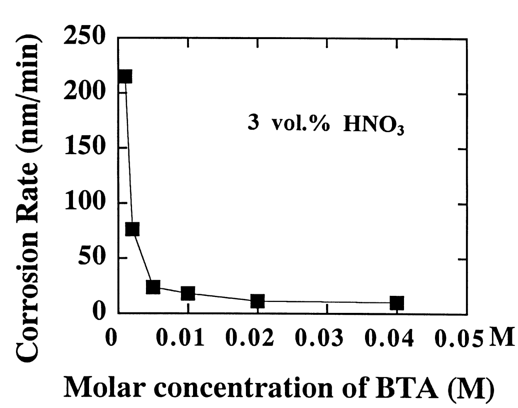

Fig. 1. Corrosion rate of copper film for various BTA molar concentration in 3 vol.% HNO_3.

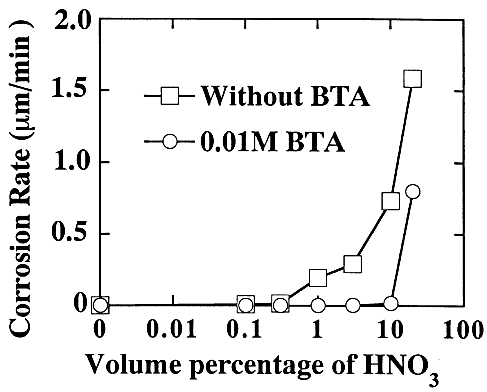

Fig. 2. Corrosion rate of copper film with and without addition of 0.01 M BTA at various HNO_3 volume percentages.

3.2. Effect of BTA on Cu-CMP

Fig. 3 shows the polishing rate distribution of copper film across a 150-mm diameter wafer using a 1–3 vol.% HNO_3 slurry with and without 0.01 M BTA. As shown in Fig. 3a, a higher average polishing rate of 267.4 nm/min as well as a higher non-uniformity of 16.6% were obtained using the 1 vol.% HNO_3 slurry without BTA. With the addition of 0.01 M BTA, both a lower polishing rate of 249.0 nm/min and a lower non-uniformity of 3.5% were obtained. Thus, better polishing rate non-uniformity can be obtained by adding BTA in the slurry. Increasing the volume percentage of HNO_3 from 1 to 3% with BTA added resulted in a slight increase in polishing rate and nearly the same non-uniformity, as shown in Fig. 3b. The polished copper film had a shiny and coppery color surface, and the surface roughness was measured to be less than 1.0 nm. Fig. 4 shows the copper surface before and after polishing. Before CMP, the copper film has an average roughness of 1.4 nm, as analyzed using an atomic force microscope shown in Fig. 4a. After CMP, the surface roughness was reduced to within 1.0 nm, but a micro-scratched surface was obtained, as shown in Fig. 4b.

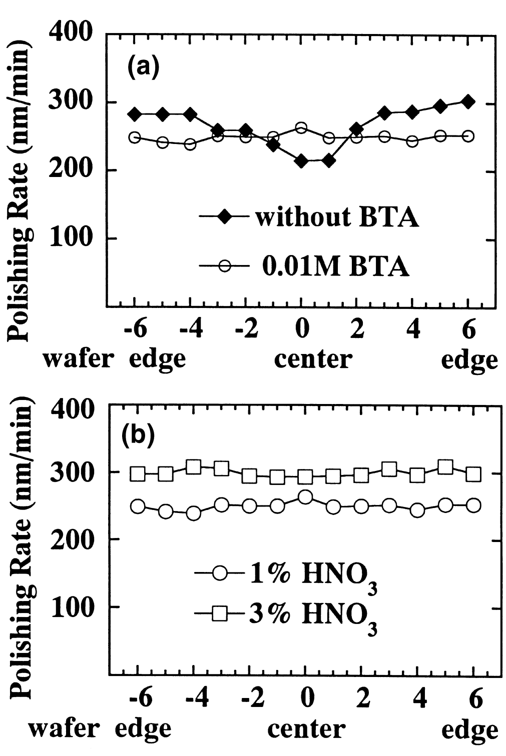

Fig. 3. Polishing rate distribution of copper film across a 150-mm diameter wafer using a slurry of (a) 1 vol.% of HNO_3 with and without addition of 0.01 M BTA and (b) 1 vol.% and 3 vol.% of HNO_3 with 0.01 M BTA.

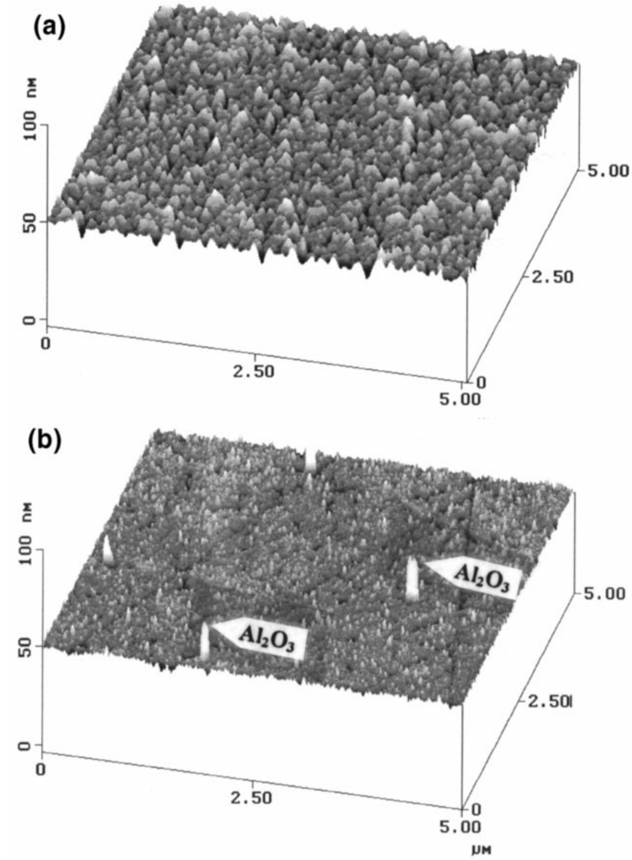

Fig. 4. AFM micrographs showing the features of copper surface (a) before and (b) after polishing.

3.3. Effect of H_2O_2 concentration on the corrosion rate of copper film

The corrosion rate of copper film decreases with increasing volume ratio of H_2O_2 in H_2O_2/XJFW8099 slurry, as shown in Fig. 5. Without H_2O_2 in the XJFW8099 slurry, a very low corrosion rate of 4.0 nm/min was obtained; however, a drastic increase of corrosion rate to 78.0 nm/min was obtained by adding a small amount of H_2O_2 (3 vol.%). This result indicates that the corrosion of copper would be enhanced dramatically when an oxidizer, such as H_2O_2, is present in the environment. Increasing the H_2O_2/XJFW8099 volume ratio to 4 decreases the corrosion rate to 0.54 nm/min. Instead of rapid corrosion in a slurry containing a small amount of H_2O_2, an abundance of H_2O_2 in the slurry could result in a denser and thicker oxide layer formed on copper

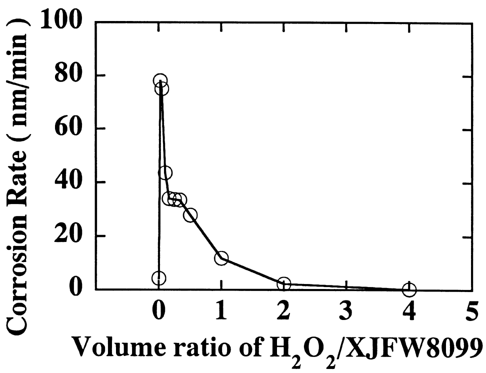

Fig. 5. Corrosion rate of copper film at various volume ratios of H_2O_2/XJFW8099.

surface, which could act as a passivation layer to resist chemical attack. Thus, Cu-CMP should be performed in a slurry containing a sufficient amount of H_2O_2 for passivation of the recessed area.

3.4. Effect of H_2O_2 concentration on Cu-CMP

Cu-CMP was performed using H_2O_2/XJFW8099 slurry of various volume ratios of H_2O_2 to XJFW8099 with the polishing conditions shown in Table 2. The polishing rate increases with decreasing volume ratio of H_2O_2 in the H_2O_2/XJFW8099 slurry, as shown in Fig. 6; the increasing polishing rate also accompanied the increase of non-uniformity. There are two possible explanations for this observation as follows. (i) Solid contents of abrasive (Al_2O_3) decrease as the volume ratio of H_2O_2/XJFW8099 is increased, and the lower abrasive content could result in lower polishing rate. (ii) Chemical corrosion can be suppressed in the slurry containing a sufficient amount of H_2O_2, as concluded from Fig. 5. This implies that higher contents of H_2O_2 in the H_2O_2/XJFW8099 slurry provides better passivation for the recessed surface of copper during the CMP process; thus, the polishing rate and non-uniformity are reduced.

Fig. 7 shows the morphology of the polished surface using the H_2O_2/XJFW8099 slurry with different volume ratios of H_2O_2 to XJFW8099. A very smooth surface with a removal rate of 363.0 nm/min was obtained using the slurry of 1/1 ratio, as shown in Fig. 7a. On the other hand, depletion of H_2O_2 in slurry can result in serious corrosion of copper thus generating a rougher surface, which in turn results in more abrasive residues, as shown in Fig. 7b. Surface roughness increases from 0.3 to 0.9 nm as the H_2O_2/XJFW8099 ratio decreases from 1/1 to 1/4. Generally, micro-scratches with a depth ranging from 0.5 to 3.0 nm were always found even though a shiny surface was obtained.

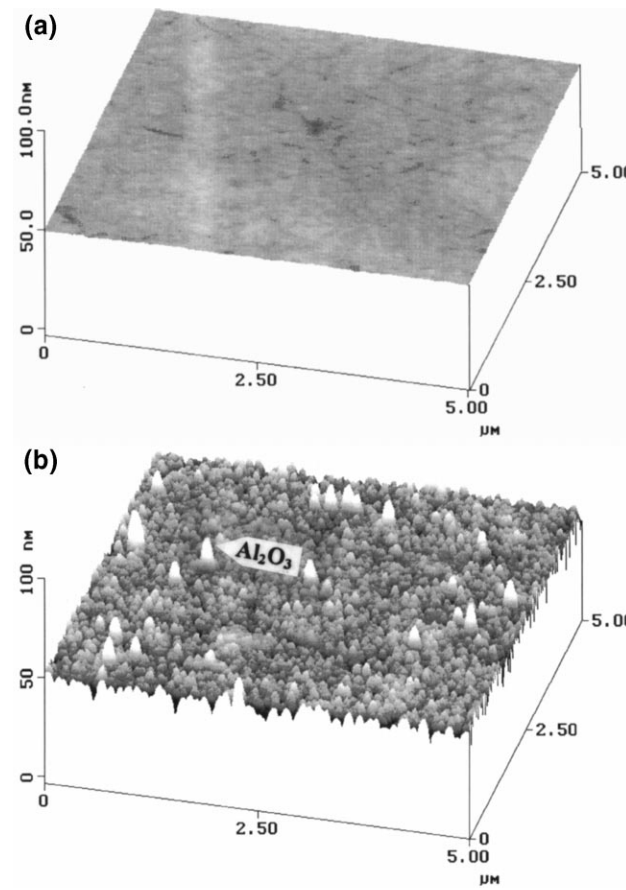

Fig. 7. AFM micrographs showing the morphology of polished surface using H_2O_2/XJFW8099 slurry with H_2O_2 to XJFW8099 volume ratios of (a) 1/1 and (b) 1/4.

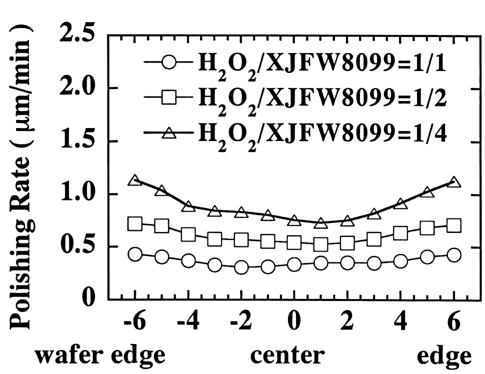

Fig. 6. Polishing rate distribution across a 150-mm diameter wafer using H_2O_2/XJFW8099 slurry and Suba 500 pad.

3.5. Cu-CMP using WA355/FE-10 slurry

We also examined the performance of commercially available Cabot WA355/FE-10 slurry composite of ferric nitrate oxidizer and abrasives for Cu-CMP. A high level of non-uniformity, as high as 35.8%, and a worse surface were observed. With a 0.01 M BTA added to this slurry, non-uniformity can be reduced to 5.1% and a polishing rate as high as 1.22 μm/min can be achieved. However, the WA355/FE-10 slurry, either with or without BTA, produced a worse surface roughness, as characterized in Fig. 8. The polished surface has a brown color and is not shiny. The ferric-ion-base slurry appear to be unsuitable for Cu-CMP

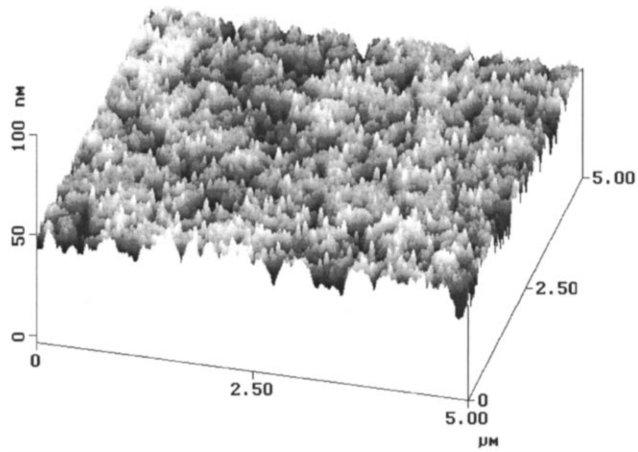

Fig. 8. AFM micrographs showing the increased surface roughness resulting from WA355/FE-10 slurry with 0.01 M BTA.

process, although the addition of a higher concentration of BTA might improve the surface finishing.

4. Conclusions

The effects of corrosion environments on Cu-CMP process using various types and concentrations of oxidizer have been investigated. Our results show that the addition of 0.01 M BTA in nitric-acid-based slurry resulted in an efficient corrosion inhibition for the copper film. With 0.01 M BTA in 1 vol.% HNO_3 slurry, a polishing rate of 249.0 nm/min and non-uniformity of 3.5% were obtained. For H_2O_2/XJFW8099 slurry, a small amount of H_2O_2 in the slurry enhanced the corrosion rate dramatically, while an abundance of H_2O_2 in the slurry suppressed the corrosion rate effectively. The polishing rate decreased but non-uniformity was improved with increasing volume ratio of H_2O_2 in the slurry. Using either H_2O_2/XJFW8099 or $TiNO_3$/BTA slurry, we obtained a shiny surface with a surface roughness of less than 1.0 nm, although surface micro-scratch was observed by atomic force microscope. The WA355/FE-10 slurry, however, did not produce an adequate polished surface.

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