Vol. 13 № 4 **Trans. Nonferrous Met. Soc. China** Aug. 2003

Article ID: 1003 - 6326(2003)04 - 0977 - 05

Electrochemical characteristic of chemical-mechanical polishing of copper with oxide passive film①

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Abstract: Electrochemical behavior of chemical-mechanical polishing of copper with oxide passive film was studied by electrochemical measurement technologies. Dependences of polarization curves and electrochemical parameters, the rate of formation or removal of passive film of copper on film modifier $KClO_3$ were investigated. The rules of dependences of corrosion potentials and corrosion current densities on polishing pressure and rotation rate were obtained. It is discovered that the rates of formation and removal of passive film of copper are enhanced, while the polishing pressure and rotation rate are reduced. The experiments show that the CMP processes decrease Tafel slope, increase electron transfer coefficient of anode reaction and decrease the activation energy of corrosion reaction of copper, thereby the corrosion processes are accelerated. The results indicate that CMP slurry recipe, which is composed of NaAc-NaOH medium, using $KClO_3$ as passive film modifier and nano-sized γ-Al_2O_3 as abrasive, is feasible and reasonable. The technological conditions are 100 r/min, 16 kPa.

Key words: oxide passive film; chemical-mechanical polishing; electrochemical characteristic
CLC number: O 69; O 646.6 **Document code:** A

1 INTRODUCTION

Thanks to its low resistivity and high electromigration resistance, copper appears to be a very promising substitute for aluminum in interconnections[1]. However, copper is very difficult to pattern, and only chemical-mechanical polishing (CMP) technology can resolve this problem[2]. CMP was initially investigated and opened out from 1980s overseas[3], and it is the best and only global planarization technology at present, but keeps hold of business secrets all the time. Fayolle et al[2] researched CMP process of copper where $Fe(NO_3)_3$ worked as oxidizer, alumina as abrasive and H_2O_2 as modifier. Borst et al[4] compared effects of a variety of surfactants on CMP of copper in business slurry Rodel QCTT1010, indicating that the surfactants were favourable to CMP selectivity. Wrschka et al[5] investigated dependence of polishing rate of copper on alumina or silicon dioxide in Rodel QCTT1010 slurry, indicating that polishing rate by silicon dioxide is slower than that by alumina. Harihanaputhiran et al[6] studied CMP behaviour of copper in H_2O_2-amino acid mixtures slurry, indicating that polishing effect of copper is improved in the presence of H_2O_2. Luo et al[7] reported copper CMP in acidic medium by using $Fe(NO_3)_3$ as etchant for copper and benzotriazole as inhibitor, and found that polishing rate falls when benzotriazole concentration increases.

HU et al[8, 9] studied electrochemical behavior of copper CMP in alkalescence complex media containing $K_3[Fe(CN)_6]$ and γ-Al_2O_3, the feasible recipes and polishing conditions were established by the rules of change of corrosion potential and corrosion current density. HE et al[10-12] invdestigated electrochemical characteristics and polishing rate of copper with $Cu_4[Fe(CN)_6]$ passive film in detail during CMP, a new polishing rate equation and CMP mechanism model of catalytic corrosion were established in definite conditions[10]. A new point of view, in which one of recipe compositions had a characteristic concentration value where the polishing rate was the highest, was put forward[12]. Moreover, electrochemical characteristics and polishing rate of copper with organic passive film were also studied systematically.[13, 14]

Copper can be self-passive to form oxide film besides organic and inorganic films in slurry. In this paper, the characteristics of copper CMP in alkalescence

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① **Foundation item:** Project(59925412) supported by the Science Fund of National Preeminent Youth

Received date: 2002 - 09 - 20; **Accepted date:** 2003 - 01 - 15

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medium containing film modifier is reported when oxide film is formed on the surface of copper and the feasible CMP recipe is got.

2 EXPERIMENTAL

2.1 Reagents

The reagents were ice acetic acid(AR), NaOH (AR), $KClO_3$(AR), γ-Al_2O_3 abrasive(~100 nm), HNN(with definite concentration and pH, made from ice acetic acid and NaOH). Deionized water was used in this test.

2.2 Instruments

Polarization curves, corrosion potential and corrosion current density were measured by EG&G Model 273A Potentiostat/Galvanostat. Data were dealt with Model 352 Corrosion Analysis Software. Components of passive film were analyzed by KRATOS XSAM 800 XPS. Ring-Disk Electrode 636 (USA) acted as experimental polishing machine.

2.3 Methods

Experiments were made by Ring-Disk Electrode. Work electrode copper (purity ≥99.99%, the area is 1.225 cm^2), which was polished by sand paper and rinsed by alcohol and water, acted as polishing wafer. Platinum worked as assistant electrode and Ag/AgCl as reference electrode. Fibred cloth being able to bear acid and alkali was fixed in the glass electrolytic cell and worked as polishing pad. The electrolytic cell was fixed on the pressure sensor to receive pressure quantitatively. Potential scanning rate was 1.0 mV/s.

3 RESULTS AND DISCUSSION

3.1 Polarization curves of copper in HNN media

According to Kaufmann metal CMP model[15], formation of passive film on the surface of metal is precondition of metal CMP. According to Cu-H_2O system Pourbaix graph[16], Cu_2O film can be formed on the surface of copper at pH 7~13 and potential −0.35~0.2 V. These provide some theoretical instructions for copper CMP. Fig. 1 shows the polarization curves of copper in alkalescence HNN medium, and the corresponding electrochemical parameters are listed in Table 1.

Curve (a) in Fig. 1 is self-passive polarization curve of copper in pH 8.5 HNN medium, the electrode reactions may be as follows:

$$2Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e \qquad (1)$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \qquad (2)$$

Curve (b) in Fig. 1 shows that, in the presence of 0.2 mol/L $KClO_3$, copper is still in self-passive state, but the shape of anode part of polarization curve is improved when compared with curve (a), indicating that rate of formation of passive film increases, as a result, it is favourable to protect sunken place from corrosion during CMP. Table 1 indicates that, in the presence of $KClO_3$, fall of corrosion current density of copper J_{corr} and increase of polarization resistance R_p prove the passive film is closer and thicker. Increase of Tafel slope B_a, fall of electron transfer coefficient β_a of anode reaction and enhancement of electron transfer coefficient α_c of cathode reaction show that the activation energy of anode dissolution reaction of copper is increased and the corrosive reaction is more difficult.

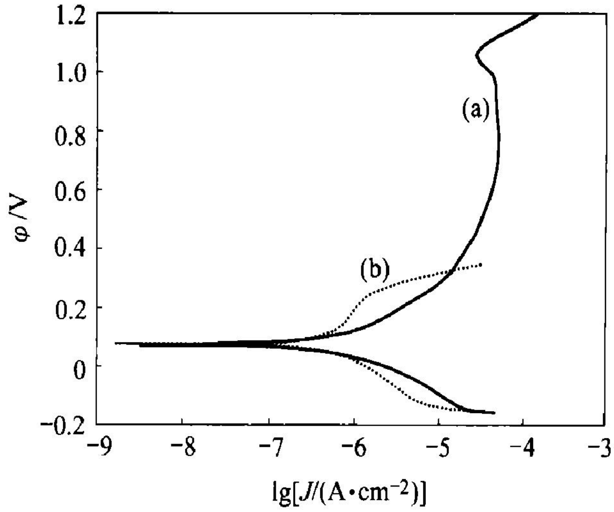

Fig. 1 Polarization curves for Cu in HNN medium
(a) —Absence of $KClO_3$; (b) —Presence of $KClO_3$

Table 1 Electrochemical values of copper in HNN media

Medium	φ_{corr}/V	J_{corr}/($\mu A \cdot cm^{-2}$)	R_p/Ω
(a) —pH8.5 HNN	0.077 4	0.84	51 095
(b) —pH8.5 HNN+ 0.2 mol/L $KClO_3$	0.072 0	0.44	59 032

Medium	B_a	β_a	B_c	α_c
(a) —pH8.5 HNN	0.151	0.20	−0.188	0.314
(b) —pH8.5 HNN+ 0.2 mol/L $KClO_3$	0.394	0.15	−0.230	0.257

Passive film of copper in pH8.5 HNN was analyzed by XPS. The measurement conditions were blazing fountain Mg Kα 1 253.6 eV, 16 mA, 12.5 kV, analyzer mode FRR, mid-distinguishment, C 1s 284.8 eV as energy reference. The vacuum in analysis chamber excelled 2×10^{-7} Pa. The measurement results were Cu 2p binding energy 933.7 eV, Cu LMM 916.7 eV, O 1s 531.6 eV. The analysis indicates the value of Cu is +1, the main component of passive film is Cu_2O. In the presence of 0.2 mol/L $KClO_3$, Cu 2p binding energy 933.7 eV, Cu LMM 916.8 eV, O 1s 531.4 eV, Cl 2p 199.5 eV indicated that the main component of passive film is still Cu_2O

but a small quantity of CuCl may exist. This may be caused by such electrode reaction:

$$Cl^- + 6OH^- \rightarrow ClO_3^- + 3H_2O + 6e \qquad (3)$$

Reaction(3) may be the mechanism of formation of passive film from $KClO_3$.

3.2 Effect of corrosion current density on pH and $KClO_3$ concentrations

Corrosion current densities of copper in various pH and $KClO_3$ concentrations are listed in Table 2. In the single HNN medium, pH of the lowest corrosion current density was 8.5. In the presence of $KClO_3$, the corrosion current density did not change obviously in the experimental concentration range. In following experiments $KClO_3$ concentration was kept 0.2 mol/L.

Table 2 Dependence of corrosion current density on pH and $KClO_3$ concentrations

Solution	Corrosion potential/mV	Corrosion current density/($\mu A \cdot cm^{-2}$)
pH7.5 HNN	90.5	1.79
pH8.5 HNN	77.4	0.84
pH9.5 HNN	64.8	1.24
pH10.5 HNN	25.9	4.44
pH12 HNN	5.0	5.32
pH8.5 HNN+ 0.1 mol/L $KClO_3$	75.0	0.45
pH8.5 HNN+ 0.2 mol/L $KClO_3$	72.0	0.44
pH8.5 HNN+ 0.3mol/L $KClO_3$	65.0	0.48

3.3 Effect of corrosion potential on polishing pressure and rotate rate

During CMP, a cyclic change of passivation-abrasion-repassivation-reabrasion happened on the surface of copper, and corrosion potential also changed correspondingly. Fig. 2 shows the curves of corrosion potential with polishing pressure and rotation rate during CMP.

Fig. 2(a) shows that, in the single HNN slurry at the same rotation rate during CMP, corrosion potential decreases to a constant with increasing polishing pressure until it reaches a certain critical value. This indicates that the abrasion quantity of passive film increases to maximum with increasing polishing pressure. The critical pressures were 96 kPa in 100 r/min, 80 kPa in 200 r/min, 64 kPa in 300 r/min, 40 kPa in 400 r/min, respectively. Comparatively corrosion potential in 100 r/min and at the critical pressure was high, indicating that the passive film still keeps some thickness after CMP and the abrasion quantity does not reach maximum. In other rotation rates and at other critical pressures the decrease tendency of corrosion potentials during CMP were similar, showing that the abrasion quantity reaches maximum under these conditions. Thereby, the least polishing rotation rate with the most abrasion quantity is 200 r/min. The conditions with the most abrasion quantity are 200 r/min and 80 kPa, 300 r/min and 64 kPa, 400 r/min and 40 kPa, respectively. At pressure lower than the critical pressure, corrosion potential decreases with increasing polishing rotation rate, which indicates that increase of polishing rotation rate results in increase of abrasion quantity.

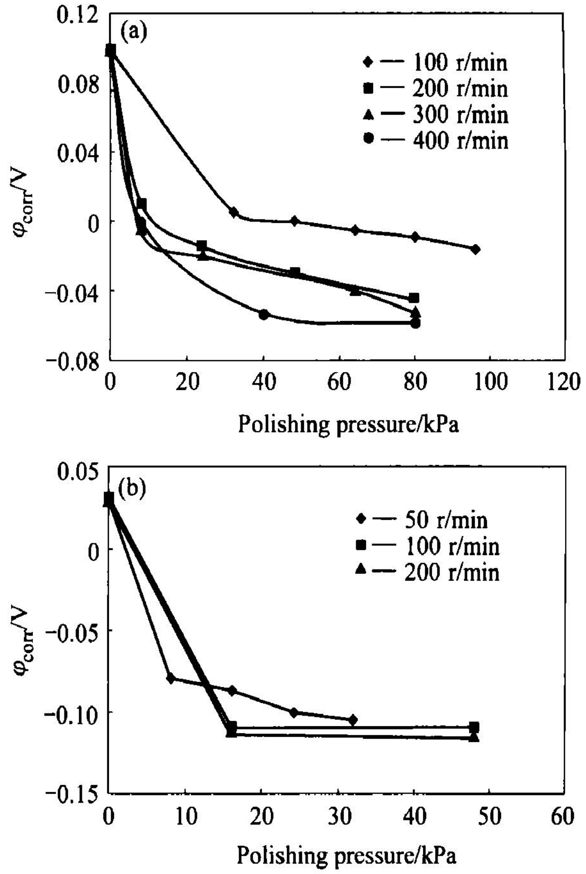

Fig. 2 Corrosion potential with polishing pressure and rotation rate for different recipes

(a) —HNN(pH8.5) + 5% γ-Al_2O_3

(b) —HNN(pH8.5) + 0.2 mol/L $KClO_3$+ 5% γ-Al_2O_3

Fig. 2(b) shows influence of $KClO_3$ on copper CMP. Compared with Fig. 2(a), polishing pressure and rotation rate needed for abrasion were reduced when corrosion potential was at nadir in presence of $KClO_3$. The critical pressure was 32 kPa in 50 r/min, 16 kPa in 100 r/min or 200 r/min, respectively. Namely in the presence of $KClO_3$, polishing technique conditions were 100 r/min and 16 kPa. Moreover, the corrosion potential at the nadir of Fig. 2(b) was more negative than that of Fig. 2(a), indicating that more polishing abrasion quantity is able to bring results in bigger polishing rate. Therefore, CMP recipe from Fig. 2(b) is even better than that from

Fig. 2(a).

Because formation of superficial passive film was the premise of copper CMP, the rates of formation and growth of passive film influence CMP process. The influencing rules can be explained by corrosion potential curves under various polishing pressures and rotation rates. Fig. 3 shows the curves of corrosion potential under different polishing pressures and rotation rates during CMP.

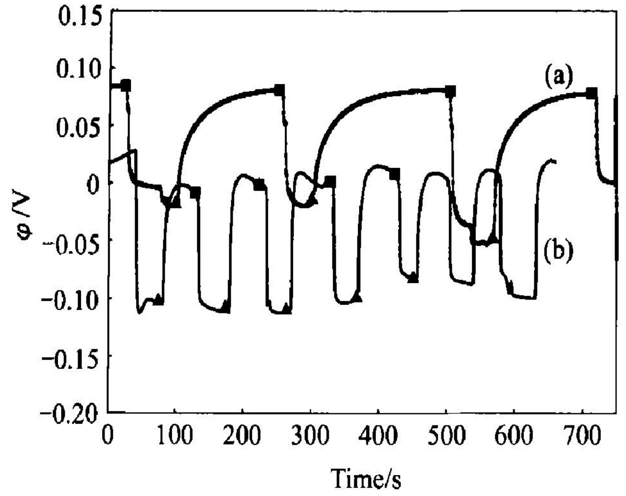

Fig. 3 Corrosion potential curves with polishing pressure and rotation rate

(a) —HNN(pH8.5) + 5% γ-Al_2O_3, 300 r/min, 64 kPa

(b) —HNN(pH8.5) + 0.2 mol/L $KClO_3$+ 5% γ-Al_2O_3, 100 r/min, 16 kPa

■ –Polishing under pressure; ▲ –Stop polishing without pressure

While polishing with pressure and rotation rate, the corrosion potentials of curves (a) and (b) decrease rapidly to the nadir, indicating that the superficial passive films are removed rapidly by abrasives. The removal rate of passive film has been enhanced in the presence of $KClO_3$ because curve (b) decreases more rapidly as shown in Fig. 3.

Withdrawing pressure to stop polishing, corrosion potential of curve (a) increases fast firstly because of copper surface exposing in air, then moved up slowly with increasing thickness of passive film until stable, showing that copper has been repassivated to form Cu_2O but the growth rate of passive film is slow. From Fig. 3(b), it is known that the growth rate of passive film has also been enhanced in the presence of $KClO_3$. This agrees with the results of Fig. 1. Decrease of formation or removal rate of passive film may accelerate polishing rate.

Corrosion potentials of curves (a) and (b) can get back to the values before CMP basically when polishing pressures were withdrawn to make copper repassivated, indicating that the passivation states on the surface of copper kept the same form basically. According to the time needed by descent or ascent of corrosion potential to the stable, the relative removal or growth rate of passive film can be deduced qualitatively. The two curves show the removal rate of passive film is greater than that of the formation one, which can make passive film removed in time and accelerate CMP. However, the removal rate at the beginning of polishing under pressure and the formation rate at the beginning of withdrawing pressure to stop polishing were not only fast but also much at one, thus the balance between mechanical polishing and chemical polishing was kept.

3.4 Polarization curves of copper during CMP

Copper with passive film was bare step by step to make corrosion dissolution more severe during CMP while pressure and rotation rate were applied. Polarization curves of copper during CMP in slurry are shown in Fig. 4. Curves (a) and (b) are polarization curves in the single HNN medium, indicated that the surface state of copper changes from passivation before CMP (curve (a)) to corrosion during CMP (curve (b)), which results in decrease of corrosion potential and increase of corrosion current density, indicating that passive film on the surface of copper is abraded to make copper change from passive state to active one. Polarization resistance R_p decrease from 51 125 Ω before CMP to 2 600 Ω after CMP and electron transfer coefficient of anode reaction β_a increase from

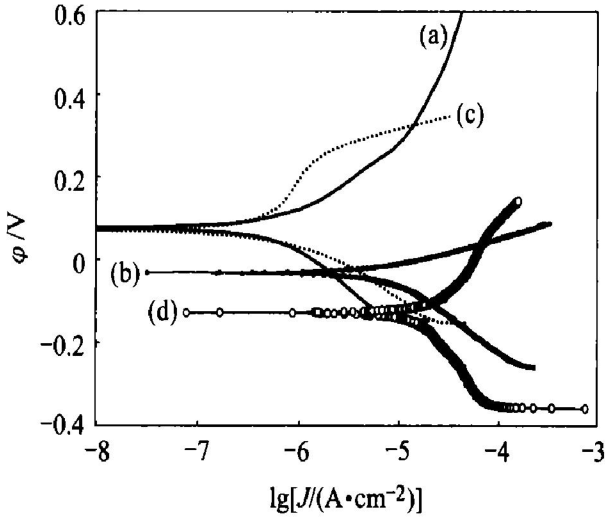

Fig. 4 Polarization curves of copper during CMP

(a) —HNN(pH8.5) + 5% γ-Al_2O_3, 0 r/min, 0 kPa, φ_{corr} 0.078 V, J_{corr} 0.62 μA/cm^2, R_p 51 125 Ω, B_a 0.30, β_a 0.20, B_c − 0.26, α_c 0.23;

(b) —HNN(pH8.5) + 5% γ-Al_2O_3, 300 r/min, 64 kPa, φ_{corr} − 0.0 321 V, J_{corr} 10.92 μA/cm^2, R_p 2 600 Ω, B_a 0.066, β_a 0.89, B_c − 0.14, α_c 0.42;

(c) —HNN(pH8.5) + 0.2 mol/L $KClO_3$+ 5% γ-Al_2O_3, 0 r/min, 0 kPa, φ_{corr} 0.077 V, J_{corr} 0.41 mA/cm^2, R_p 59 095 Ω, B_a 0.39, β_a 0.15, B_c − 0.23, α_c 0.257;

(d) —HNN(pH8.5) + 0.2 mol/L $KClO_3$+ 5% γ-Al_2O_3, 100 r/min, 16 kPa, φ_{corr} − 0.13 V, J_{corr} 25 mA/cm^2, R_p 873 Ω, B_a 0.20, β_a 0.30, B_c − 0.39, α_c 0.15

0.20 to 0.89, indicating that the activation energy of anode dissolution reaction decreases and the corrosion rate quickens and the corrosion current density of the corrosion reaction increases. These changes indicate that CMP processes make copper more corrosive.

Curves (c) and (d) show the changes of polarization curves before and after CMP in the presence of 0.2 mol/L $KClO_3$. Compared with curve (c) that indicates copper is in self-passive state, curve (d) during CMP indicates copper is in corrosion state. Large decrease of corrosion potential and polarization resistance, large increase of corrosion current density from 0.41 $\mu A/cm^2$ to 25 $\mu A/cm^2$, made out that the passive film is removed rapidly to bring on corrosive rate of copper to multiply. Because β_a and α_c have all changed in one way of reducing activation energy, namely β_a increases and α_c descendes, the corrosion current density is greater than that in absence of $KClO_3$ during CMP so as to make corrosion more rapidly. Thereby, the polishing rate at this time can be expected to be greater. Along with CMP processing, the protruding surface of copper was polished to dissolve and the sunken place was protected from being polished. Because the sunken place did not effectively contact with polish pad(0 kPa) and passive film was not removed. So, the surface of copper can be made global planarization.

4 CONCLUSIONS

The polarization curve of copper is reformed, the formation or removal rate of passive film is quickened, the corrosion current density of copper is enhanced and the polishing pressure and rotation rate as well are reduced during CMP in the presence of $KClO_3$. The CMP processes reduce Tafel slope B_a and increase electron transfer coefficient of anode reaction β_a, thereby reduce the activation energy of corrosion reaction of copper and are favourable to accelerate polishing rate. The CMP slurry recipe which is composed of NaAc-NaOH medium, using $KClO_3$ as passive film modifier and nano-sized γ-Al_2O_3 as abrasive, is feasible and reasonable. The technological conditions are 100 r/min and 16 kPa.

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(Edited by YANG You-ping)