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# Corrosion electrochemical mechanism of chemical mechanical polishing of copper in $K_3Fe(CN)_6$ solution<sup>①</sup>

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**[Abstract]** Polarization curves of copper were measured in  $NH_3 \cdot H_2O$  media containing  $K_3Fe(CN)_6$ . Components of passive film were analyzed by XPS. Relation of polishing rate with corrosion current density was investigated during CMP. Copper can be passivated in the slurry and main component of passive film is  $Cu_4Fe(CN)_6$ . Relation of polishing rate with corrosion current density is linear direct ratio and expressed as  $R = KJ_{corr}$  during CMP. Coefficient  $K$  varies with different slurry systems but is constant under experimental conditions, which does not vary with  $NH_3 \cdot H_2O$ ,  $K_3Fe(CN)_6$ ,  $\gamma-Al_2O_3$  concentrations, polishing pressures and rotative rate in a slurry system during CMP.

**[Key words]** copper; polishing rate; corrosion current density

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## 1 INTRODUCTION

Chemical-mechanical polishing (CMP) is the most important global planarization technology at present. Specially to polishing of metal used to form interconnections and processes at various stages of integrated circuit (IC) fabrication, only CMP is universally applicable to cause global planarization. Thanks to its low resistivity, copper appears to be a very promising substitute for aluminum in interconnections. For polishing of copper, it cannot get global planarization only by abrasion of abrasives (mechanical polishing) which produces scrape traces and only by chemical corrosion (chemical polishing) which produces corrosion spots on the surface of copper. Only combining chemical corrosion with mechanical abrasion the global planarization can be got. This time, the passive film, which can be abraded on the protruding surface of copper by abrasives and can protect the sunken surface of copper from more corrosion, is formed on the surface of copper by chemical corrosion. On the other side the passive film formed can reduce the surface hardness of copper and make mechanical abrasion more easily. Accordingly, CMP is a process of balancing chemical polishing and mechanical one, a electrochemical corrosion process under abrasion of abrasives. Polishing rate is related not only to concentrations of chemical components but also to polishing pressure and rotative rate. Most of the fruits of CMP technology (specially CMP recipes)

have become business secrets abroad. Preston<sup>[1]</sup> got experience formula of polishing rate according to glass polishing process in 1924 as follows:

$$R = \Delta H / \Delta t = K_p p v$$

where  $R$  is polishing rate (nm/min),  $\Delta H$  is the change in the height of surface (nm),  $\Delta t$  is the elapsed time (min),  $K_p$  is Preston coefficient,  $p$  is pressure on the work piece (kPa),  $v$  is the velocity of the pad relative to the work piece (r/min). When the formula was used in CMP processes, linear<sup>[2,3]</sup> and non-linear<sup>[4]</sup> conclusions about the relation of polishing rate to polishing pressure and rotative rate were got.  $K_p$  is very complex, whose meaning is not clear completely now and may be related not only to components of recipe, pad characters but also to abrasive size, monodispersion.  $K_p$  has been studied quantitatively but it is difficult to apply<sup>[5]</sup>. Because  $K_p$ ,  $p$  and  $v$  are all variables, it is difficult to calculate polishing rate theoretically and more difficult to control polishing time in-situ. In this paper the relation of polishing rate to corrosion current density has been investigated during CMP in recipe containing  $NH_3 \cdot H_2O$ ,  $K_3Fe(CN)_6$  and nano-sized  $\gamma-Al_2O_3$  on the basis of some investigations<sup>[6-8]</sup>.

## 2 EXPERIMENTAL

### 2.1 Main reagents

$NH_3 \cdot H_2O$ ,  $K_3Fe(CN)_6$ , and  $\gamma-Al_2O_3$  abrasive ( $\sim 100$  nm and  $\sim 50$  nm) are all analytic purity.

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Deionized water was used in all tests.

## 2.2 Analysis instrument

Polarization curves and corrosion current density were measured by EG&G Model 273A Potentiostat/Galvanostat. Data were dealt with Model352 Corrosion Analysis Software. Components of passive film was analyzed by KRATOS XSAM800 XPS. Ring-Disk Electrode 636 (US) acted as experimental polishing machine.

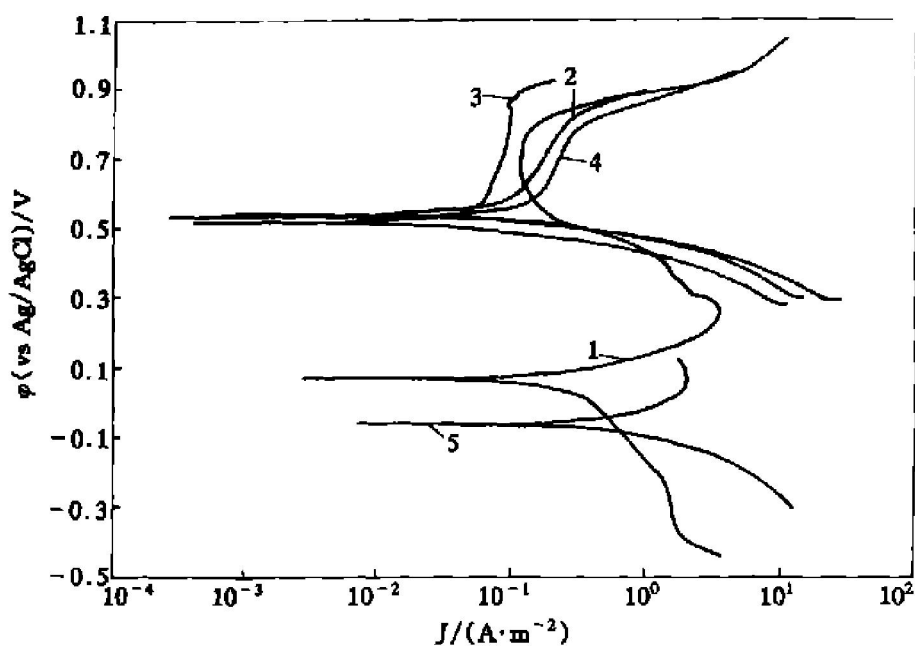
## 2.3 Experimental method

Experiments were made by ring-disk electrode. Work copper electrode (purity  $\geq 99.99\%$ , area  $1.225\text{ cm}^2$ ) which was polished by sand paper and rinsed by alcohol acted as polishing wafer. Platinum worked as assistant electrode and Ag/AgCl as reference electrode. Fibre cloth being able to bear acid and alkali was fixed in the plastic electrolytic cell and worked as polishing pad. The electrolytic cell was fixed on the pressure sensor to receive pressure quantitatively. Potential scanning rate was  $1.0\text{ mV/s}$ . Polishing time was 10 min. Polishing rate was calculated by determining copper contents of slurry after CMP.

## 3 RESULTS AND DISCUSSION

### 3.1 Polarization curves of copper in media of $\text{NH}_3 \cdot \text{H}_2\text{O}$ with or without $\text{K}_3\text{Fe}(\text{CN})_6$

Curve 1 in Fig.1 shows that, because passive potential  $0.25\text{ V}$  is higher than corrosion potential  $0.0682\text{ V}$  of copper when polarization, copper is made self-corrosive in media of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  without  $\text{K}_3\text{Fe}(\text{CN})_6$ . Curve 2 shows that, in the presence of  $1\%$   $\text{K}_3\text{Fe}(\text{CN})_6$ , corrosion potential increases to  $0.536\text{ V}$  and corresponding corrosion current density is debased to  $8.87 \times 10^{-2}\text{ A/m}^2$  ( $\text{pH} = 11.1$ ) greatly, this indicates that copper surface has been passivated and protective passive film is formed on the surface of copper. Curve 3 shows that, when  $\text{NH}_3 \cdot \text{H}_2\text{O}$  concentration is debased to  $0.1\%$  corrosion current density of copper is  $5.041 \times 10^{-2}\text{ A/m}^2$ , it appears that thicker, denser and more protective passive film has been formed. Curve 4 shows that, in the recipe of  $1\% \text{ NH}_3 \cdot \text{H}_2\text{O} + 2\% \text{ K}_3\text{Fe}(\text{CN})_6$  corrosion current density of copper is greater than that of Curve 2 on the contrary, illuminating the protective effect of passive film does not always increase with the addition of  $\text{K}_3\text{Fe}(\text{CN})_6$ . Curve 5 shows that, during CMP under conditions of  $80\text{ kPa}$  and  $300\text{ r/min}$ , corrosion potential debases greatly and corrosion current density increases prominently, the shape of anodic polarization curve changes from the passive state such as Curve 3 into one of corrosive dissolution, these demonstrate that the passive film on the surface of copper has been abraded to make corrosion of copper more fast when without efficient protection of passive film during CMP.



**Fig. 1** Polarization curves of copper in media of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  with or without  $\text{K}_3\text{Fe}(\text{CN})_6$

(1— $1\% \text{ NH}_3 \cdot \text{H}_2\text{O}$ ,  $E_{\text{corr}} = 0.0682\text{ V}$ ,  $J_{\text{corr}} = 51.66 \times 10^{-2}\text{ A/m}^2$ ;

2— $1\% \text{ NH}_3 \cdot \text{H}_2\text{O} + 1\% \text{ K}_3\text{Fe}(\text{CN})_6$ ,  $100\text{ r/min}$ ,  $E_{\text{corr}} = 0.5361\text{ V}$ ,  $J_{\text{corr}} = 8.872 \times 10^{-2}\text{ A/m}^2$ ,  $\text{pH} = 11.1$ ;

3— $0.1\% \text{ NH}_3 \cdot \text{H}_2\text{O} + 1\% \text{ K}_3\text{Fe}(\text{CN})_6$ ,  $100\text{ r/min}$ ,  $E_{\text{corr}} = 0.5208\text{ V}$ ,  $J_{\text{corr}} = 5.041 \times 10^{-2}\text{ A/m}^2$ ,  $\text{pH} = 10.2$ ;

4— $1\% \text{ NH}_3 \cdot \text{H}_2\text{O} + 2\% \text{ K}_3\text{Fe}(\text{CN})_6$ ,  $100\text{ r/min}$ ,  $E_{\text{corr}} = 0.5382\text{ V}$ ,  $J_{\text{corr}} = 12.78 \times 10^{-2}\text{ A/m}^2$ ,  $\text{pH} = 11.2$ ;

5— $0.1\% \text{ NH}_3 \cdot \text{H}_2\text{O} + 1\% \text{ K}_3\text{Fe}(\text{CN})_6 + 5\% \text{ Al}_2\text{O}_3$ ,  $80\text{ kPa}$ ,  $300\text{ r/min}$ ,  $E_{\text{corr}} = -0.060\text{ V}$ ,  $J_{\text{corr}} = 450.4 \times 10^{-2}\text{ A/m}^2$ )

### 3.2 Analysis of components of passive film on surface of copper

According to Ref. [6], the recipe in which denser passive film could be formed was 0.1%  $\text{NH}_3 \cdot \text{H}_2\text{O}$  + 1%  $\text{K}_3\text{Fe}(\text{CN})_6$ . Fig. 2 shows the components of passive film on the surface of copper by XPS.

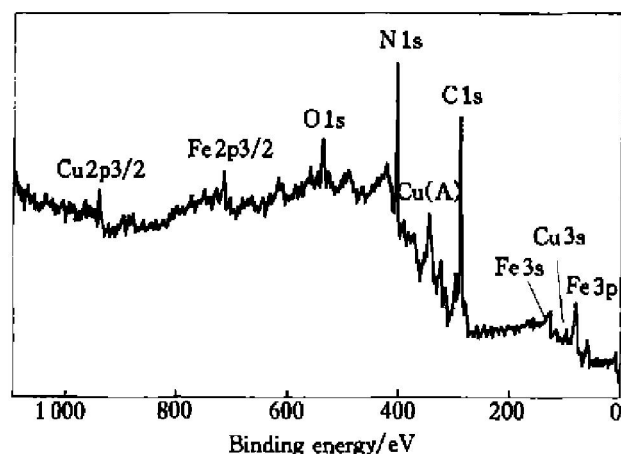


Fig. 2 XPS spectrum of passivative film on surface of copper

The measurement results are Cu 2p 933.3 eV, Cu LMM 916.1 eV, N 1s 398.1 eV, Fe 2p 708.6 eV, O 1s 531.7 eV. According to the results the main component of the passive film on the surface of copper is  $\text{Cu}_4\text{Fe}(\text{CN})_6$  which contains Cu (I) and Fe (II). O is showed to be present on the surface and  $\text{Cu}_2\text{O}$  may be produced because of O from atmosphere or oxidation of copper before measurement.

### 3.3 Relation of polishing rate with corrosion current density

CMP recipe:  $\text{NH}_3 \cdot \text{H}_2\text{O}$  +  $\text{K}_3\text{Fe}(\text{CN})_6$  +  $\gamma$ -

$\text{Al}_2\text{O}_3$ . The experiments ever made show that the conditions of best polishing rate are that:  $\text{NH}_3 \cdot \text{H}_2\text{O}$  concentration is 1%,  $\text{K}_3\text{Fe}(\text{CN})_6$  concentration is 4%,  $\gamma\text{-Al}_2\text{O}_3$  concentration is 20%, rotative rate is 300 r/min, polishing pressure is 80 kPa. Now, to balance chemical polishing and mechanical polishing and not to make single chemical or mechanical polishing prominent, next experiments, in which component concentrations in recipe, polishing pressure and rotative rate are choosed random not exceeding above quantitative conditions, are made. Component concentrations in recipe, polishing pressure, rotative rate and polishing rate, corrosion current density are listed as Table 1. Plot of polishing rate vs corrosion current density is made as Fig. 3 according to data of Table 1.

Two polishing rates by abrasion of two sizes of

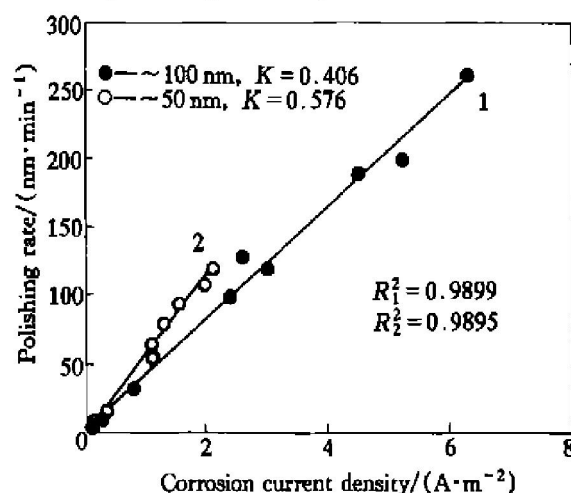


Fig. 3 Polishing rate vs corrosion current density

Table 1 Relation of polishing rate with corrosion current density under abrasion of  $\gamma\text{-Al}_2\text{O}_3$  (~100 nm and ~50 nm)

Composition/ %			Rotative rate /( $\text{r} \cdot \text{min}^{-1}$ )	Pressure /kPa	Polishing rate/( $\text{nm} \cdot \text{min}^{-1}$ )		$J_{\text{corr}}/(10^2 \text{A} \cdot \text{m}^{-2})$	
$\text{NH}_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{Fe}(\text{CN})_6$	$\gamma\text{-Al}_2\text{O}_3$			~ 100 nm	~ 50 nm	~ 100 nm	~ 50 nm
0.1	1	5	50	80	7.0	6.0	22.0	10
1	4	20	200	44	130	54.5	260	110
1	4	20	300	80	260	120	630	210
0.5	1	5	300	80	34	15	80	35
0.1	1	5	300	40	11.5	7	28	11
2	1	5	300	80	14.5	8	33	14
1	4	10	300	80	100	65	240	110
1	2	15	150	40	120	80	300	130
1	3	15	200	80	200	110	520	200
0.5	3	25	200	56	190	95	451	155

$\gamma\text{-Al}_2\text{O}_3$  are compared in Fig. 3 and Table 1. Relation of polishing rate to corrosion current density is linear direct ratio, in the same polishing process the polishing rate made by big size abrasives is greater than that by small ones. The slope of Curve 2 is bigger than that of Curve 1, this may show distribution of small size  $\gamma\text{-Al}_2\text{O}_3$  is better than that of big size one during CMP. The results of Fig. 3 and Table 1 can be expressed by:

$$R = KJ_{\text{corr}} \quad (1)$$

where  $R$  is polishing rate (nm/min);  $J_{\text{corr}}$  is corrosion current density during CMP ( $10^{-2}\text{A/m}^2$ );  $K$  is ratio coefficient and does not vary with component concentrations of the same recipe, polishing pressure and rotative rate but varies with different recipe (for example: different sizes of abrasives). On the other hand, polishing rate is decided by corrosion current density.

### 3.4 Catalytic corrosion model of CMP

CMP mechanisms are very complex, which are not very clear now<sup>[9,10]</sup>. There are many dependent factors on polishing rate, which include components of recipe, abrasive size and mono-distribution, velocity between pad and wafer, polishing pressure, hardnesses of wafer and passive film, and so on. Additionally, because the surface of the wafer is not smooth, the area of fact interface between wafer and pad increases with CMP processing, and fact pressure on the wafer cannot be calculated at some time. These factors are divided into ascertainable factors and unascertainable factors in this paper. The ascertainable factors include component concentration, polishing pressure, rotative rate, and so on. The unascertainable factors include characters of passive film, area of fact interface between pad and wafer, monodistribution and dispersion of abrasives, abrasive distribution between pad and wafer, characters of pad, moving forms of slurry and so on. It is the unascertainable factors to make explaining mechanisms of CMP processes and establishing polishing rate equation very complex and difficult by mechanical friction<sup>[11,12]</sup>. However, when these problems are studied with electrochemical theories all factors including ascertainable and unascertainable ones can be ignored. The polishing rate equation can be established by way of electrochemical parameter—corrosion current density which can show overall effect caused by all those factors because wafer and slurry have constructed electrochemical corrosion system.

Corrosive rate equation of copper in corrosive electrochemistry is as follows:

$$J_{\text{corr}} = \Delta WzF / (StA) \longrightarrow R = (0.0445/z) J_{\text{corr}} \quad (2)$$

where  $W$  is corrosion quantity of copper (g),  $z$  is transfer counts of electron in corrosion reaction,  $F$  is Farady constant ( $96500\text{C/mol}$ ),  $S$  is area of copper electrode ( $\text{cm}^2$ ),  $t$  is corrosion time (s),  $A$  is relative atomic mass of copper,  $R$  is corrosion rate (nm/min),  $J_{\text{corr}}$  is corrosion current density ( $10^{-2}\text{A/m}^2$ ). If  $z$  is 1 the ratio coefficient of Eqn. (2) is 0.0445. The forms of Eqs. (2) and (1) from results of Fig. 3 are the same, all  $R \propto J_{\text{corr}}$ . This shows that Eq. (1) accords with the principle of corrosion electrochemistry. However, the ratio coefficient of Eq. (1) is greatly bigger than that of Eq. (2), and  $J_{\text{corr}}$  is also different. Fig. 1 has showed that  $J_{\text{corr}}$  (Curve 5) during CMP is greatly bigger than that (Curve 1) in single chemical corrosion. These express that CMP is a process accelerating electrochemical corrosion—a catalytic corrosion process. The catalytic powers root in that as follows: 1) worse hardness of passive film formed on the surface of copper; 2) high speed mechanical abrasion to passive film by nano-sized abrasives, which make the protruding surfaces of copper absent protection from passive film and entirely bared in the corrosive slurry and make copper corrosion more easily and fast. The passive film and abrasive can be regarded as catalyzers which accelerate corrosion dissolution of copper.

## 4 CONCLUSIONS

1) Main component of passive film on the surface of copper is  $\text{Cu}_4\text{Fe}(\text{CN})_6$  in  $\text{NH}_3 \cdot \text{H}_2\text{O}$  slurry containing passivator  $\text{K}_3\text{Fe}(\text{CN})_6$ .

2) Under the conditions of the experiments, polishing rate of CMP  $R = KJ_{\text{corr}}$ , namely relation of  $R$  to  $J_{\text{corr}}$  is linear direct ratio.

3) Relation of polishing rate to corrosion current density accords with the principle of electrochemical corrosion rate during CMP all the same under experimental conditions. Formation of the passive film on the surface of copper and mechanical abrasion by nano-sized abrasives accelerate corrosive dissolution of copper. In fact, CMP can be regarded as a catalytic corrosion process.

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