# A Study on the Corrosion Effects by Addition of Complexing Agent in the Copper CMP Process

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Copper CMP in terms of the effect of slurry chemicals (oxidizer, corrosion inhibitor, complexing agent) on the process characteristics has been performed. Corrosion inhibitors, benzotriazole (BTA) and tolytriazol (TTA) were used to control the removal rate and avoid isotropic etching. When complexing agent is added with $H_2O_2$ 2 wt% in the slurry, the corrosion rate was presented very well. In the case of complexing agent, it was estimated that the proper concentration is 1 wt%, because the addition of tartaric acid to alumina slurry causes low pH and the slurry dispersion stability become unstable. There was not much change of the removal rate. It was assumed that BTA 0.05 wt% is suitable. Most of all, it was appeared that BTA is possible to be replaced by TTA. TTA was distinguished for the effect among complexing agents.

*Keywords* : Copper-chemical mechanical polishing (Cu-CMP), Corrosion effect, Complexing agent, Oxidizer, Inhibitors

## 1. INTRODUCTION

Replacement of aluminum by copper for interconnections in the semiconductor industry has raised a number of important issues. The integration of copper interconnection can be carried out by CMP (chemical mechanical polishing) is used to planarize the surface topography[1,2] But there remain many uncertainties and problems occurring from a shortage of experince. Therefore, we investigated the optimization of several conditions with some chemical additives during copper CMP process among them. One of the important consumable for the Cu CMP process is the slurry chemistry[3-5]. The choice of the slurry chemistry, such as pH value and etch rate, influence the metal removal rate, the metal/dielectric selectivity, as well as undesired etching and corrosion of the metal lines[6-8]. In this paper, we investigated the corrosion rate of Cu by the addition of several film forming agents and complexing agents for the effective Cu CMP process. Corrosion rate is not a good indication of polish rate behavior. However, the dissolved Cu species present during CMP process can be used to explain the CMP rates of Cu. In addition, we observed the variation of removal rate of Cu/Ta by variation of the concentration of $H_2O_2$ as the oxidizer and tartaric acid as the complexing agent to find out optimum condition.

## 2. EXPERIMENTAL

The measurements of corrosion rate in this paper were obtained using polarization resistance ($R_p$) method for getting the data that is more accurate. For the polishing, it was carried out on the G&P technology POLI-500CE chemical mechanical polisher. The speed of head and table was both 40 rpm and the down pressure of the head was 7 psi and slurry flow rate was 100 ml/min. The electrochemical curves were recorded with an EG&G 273A potentiostat. First, we have examined suitable volumes (wt%) of tartaric acid as a complexing agent, BTA as a film forming agent and $H_2O_2$ as the oxidizer will put in slurry by means of measurement of removal rate of Cu/Ta layer by the volume of each chemical. With these results, we investigated corrosion rate of copper using 10 kinds of 1 wt% complexing agents and then from the addition of 2 wt% hydrogen peroxide ($H_2O_2$), we also analyzed composition effect of oxidizer and complexing agent.Following, $(NH_4)_2S_2O_8$ 2 wt% is known that it has a large corrosion rate was used with ammonium oxalate 1 wt% as a complexing agent for investigation of corrosion characteristics by a difference of solution oxidizing power.

## 3. RESULTS AND DISCUSSION

Table 1 shows the corrosion characteristics after adding several 1 wt% complexing agents to 2 wt% $H_2O_2$. The corrosion rate of the solution with just $H_2O_2$ 2 wt% without any complexing agent was 0.0513 mpy and it increased generally after the addition of complexing agent.

In order to investigate in detail about the effect by complexing agent, Cu corrosion rate was observed with a solution containing just complexing agent 1 wt% in comparison with the results before, as shown in figure 1.

Table 1. Characteristics of Cu corrosion after adding several complexing agents to 2 wt% $H_2O_2$.

| Complexing agent | pH | Corrosion rate (mpy) | $R_p$ (kΩ) | Icorr (μA) | Ecorr (mV) |
|---|---|---|---|---|---|
| Ammonium Oxalate | 6.70 | 14.56 | 0.6812 | 31.88 | 245 |
| Tartaric acid | 2.13 | 23.21 | 0.4273 | 50.82 | 270 |
| $NH_4OH$ | 10.5 | 14.66 | 0.677 | 32.09 | 121 |
| Citric acid | 2.23 | 17.93 | 0.5532 | 39.25 | 322 |
| Acetic acid | 2.81 | 5.377 | 1.844 | 11.77 | 407 |
| $H_2O_2$ 2wt% only | 5.91 | 0.0513 | 193.5 | 0.112 | 397 |

The corrosion rate of ammonium oxalate was 14.9 mpy at only complexing agent 1 wt%. It means the complexing agent has oxidizing capacity basically. It was seen that tartaric acid and citric acid have good capacity as a complexing agent. Amomonium oxalate also had high value, but there was no difference with $H_2O_2$. In conclusion, tartaric acid was by far the best in capability among the complexing agent and it will be possible to use during real CMP process

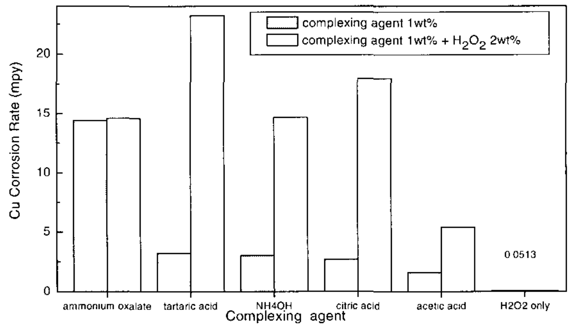


Fig. 1. Corrosion rates of copper as the several complexing agents with the addition of oxidizer.

The following is the characteristics of copper corrosion by difference of oxidizers for same complexing agent (ammonium oxalate). Figure 2 shows the difference between adding $H_2O_2$ 2 wt% and adding $(NH_4)_2S_2O_8$ 2 wt% to the ammonium oxalate 1 wt%. The corrosion rate of $H_2O_2$ increased from 0.0513 mpy to 14.56 mpy under the influence of complexing agent. However, in the case of $(NH_4)_2S_2O_8$, rather it decreased from 257 mpy to 29.71 mpy. From these results, we founded that complexing agent disturbs the oxidizer with very high oxidizing power. In contrast, it was ascertained that the addition of complexing agent is essential in case of oxidizer with low oxdizing power like $H_2O_2$.

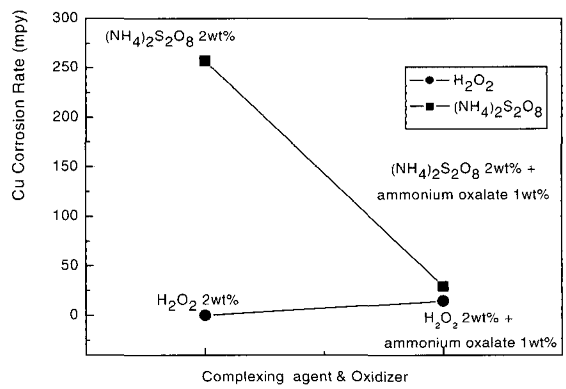


Fig. 2. Characteristics of copper corrosion for complexing agents by difference of oxidizers.

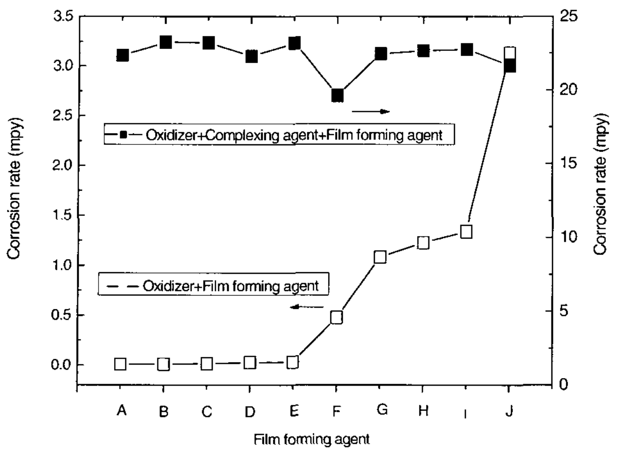


Fig. 3. Corrosion rates of copper as the several film forming agents with the addition of complexing agent.

Table 2. Corrosion rates of copper obtained by adding several film forming agents in slurry.

| Oxidizer+Film Forming agent +Complex agent (mpy) | | Film forming agent | Oxidizer+Film Forming agent (mpy) |
|---|---|---|---|
| 23.16 | A | TTA | 0.0067 |
| 23.26 | B | BTA-1 | 0.0099 |
| 23.24 | C | BTA-2 | 0.0143 |
| 22.3 | D | Xylitol | 0.0232 |
| 23.21 | E | Reference | 0.0292 |
| 19.61 | F | Triethanolamine | 0.4754 |
| 22.47 | G | Gallic acid | 1.084 |
| 22.59 | H | Benzoic acid | 1.228 |
| 22.77 | I | Succinic acid | 1.341 |
| 21.66 | J | Citric acid | 3.135 |

Subsequently, we examined the corrosion rate of copper obtained by adding several film forming agents in slurry. Table 2 and figure 3 show the Cu corrosion rate by the existence of a complexing agent after adding of the several film forming agents of 0.05 wt% with $H_2O_2$ of 2 wt%. First there was not much change of the corrosion rate in comparison to the reference wasn't added film forming agent when the tartaric acid is added. When the tartaric acid is added with $H_2O_2$ + film forming agent in slurry, it changed from 0.0292 mpy to 23.21 mpy. Because the complexing agent promoted the dissolution of copper by the function as a chelating agent. It was assumed that the acidic agent improved the activity of the copper surface and enhanced the dissolution of $Cu^{2+}$. At additional experiment except tartaric acid under previous result, the corrosion rate decreased than reference in case of TTA, BTA and Xylitol and the others increased.

## 4. CONCLUSION

In this work, we applied $R_p$ method to corrosion analysis to obtain reliable data. The removal rate of Cu/Ta was remarkably low at $H_2O_2$ and tartaric 0%, but it was increased dramatically in proportion to rise in concentration. We chose the appropriate concentration of $H_2O_2$ and tartaric acid to be each 2.0 wt% and 1.0 wt%, at which a high removal rate were obtained within the scope which does not cause trouble in slurry stability. Cu corrosion rate was larger with tartaric acid and citric acid than others. The acetic acid was presented that it will be useful for $2^{nd}$ step. Besides, it was ascertained that the addition of complexing agent is essential in case of oxidizer with low oxidizing power. In the case of TTA among film forming agents, the results of potentiostat appeared similarly to BTA which is the most common chemical used for Cu corrosion. Consequently, TTA is expected that it can be used as substitute for BTA.


## ACKNOWLEDGMENTS

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