

**Electrochemistry of Copper in the Chemical Mechanical Planarization (CMP) Slurries Containing Glycine and Hydrogen Peroxide**

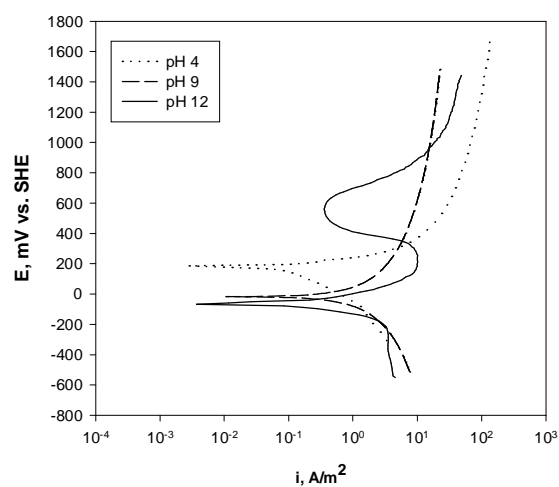
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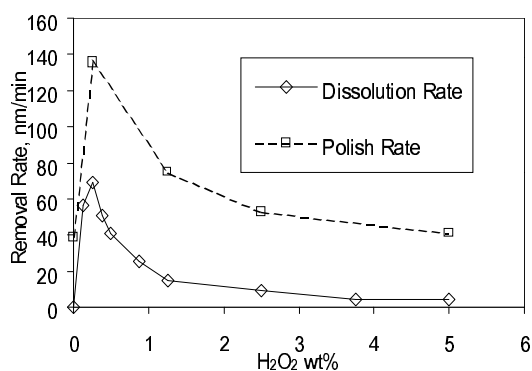
Copper has recently started to replace aluminum as the interconnect metal in integrated circuits. Copper metallization offers faster and more reliable integrated circuits, due to its higher electrical conductivity and superior electromigration resistance (1). The damascene technique, which allows successful integration of copper, utilizes CMP to remove the overburden material and achieve global planarization for further processing. Early studies on copper CMP by Carpio and coworkers (2) showed that the principal components of a successful CMP slurry includes oxidizing agents and complexing agents as well as corrosion inhibitors and buffering agents. Favorable polishing results were obtained using a mixture of glycine and  $H_2O_2$  as the main components of a slurry for copper CMP in both alkaline (3) and neutral (4) pH regimes. In the present study, we examined the roles of glycine and  $H_2O_2$  in reactive slurries representative of those that might be used in copper CMP, with the aim of improving our understanding of the mechanisms at play.

We first investigated the electrochemistry of copper in aqueous glycine solutions in the absence of  $H_2O_2$  by comparing the polarization behavior with the appropriate potential-pH diagram for the copper-water-glycine system (5). Figure 1 shows that copper dissolves actively in 0.01 M glycine at pH's 4 and 9 while it exhibits an active-passive behavior at pH 12 due to the formation of  $Cu_2O$  and  $CuO$ . Very similar behavior was observed in solutions containing  $10^{-2}$  M glycine and  $10^{-5}$  M cupric nitrate solutions. The polarization behavior shown in Figure 1 was reasonably consistent with the potential-pH diagram at a total dissolved copper activity,  $\{Cu_T\}$ , of  $10^{-5}$  and total glycine activity,  $\{L_T\}$ , of  $10^{-2}$  (5).

We then carried out weight loss and polishing experiments to examine the electrochemistry and polishing behavior of copper in aqueous  $10^{-2}$  M glycine solutions and slurries with different amounts of  $H_2O_2$ . The polishing slurries contained 5 wt % alumina particles and the polishing tests were conducted at a constant pressure of 27.6 kPa and a rotational speed of 200 rpm. According to the Figure 1, additions of  $H_2O_2$  to  $10^{-2}$  M aqueous glycine solutions at pH 4, should increase the dissolution rate. Figure 2 shows that small additions of  $H_2O_2$  up to about 0.25 wt % indeed increased both the dissolution and the polish rate. However, further increases in the concentration of  $H_2O_2$  inhibited the dissolution and lowered the polish rate. Several other researchers reported a similar behavior for copper in the mixtures of different complexing agents with  $H_2O_2$  (3, 4, 6). In addition to common copper oxides  $Cu_2O$  and  $CuO$ , copper is known to form higher copper oxides such as copper sesquioxide ( $Cu_2O_3$ ) and copper peroxide ( $CuO_2$ ) at high concentrations of  $H_2O_2$  (7). Therefore, the passivation behavior exhibited in Figure 2 at high  $H_2O_2$  concentrations might be due to formation of  $Cu_2O_3$  and  $CuO_2$ .



**Figure 1.** Effect of pH on the polarization behavior of copper in  $10^{-2}$  glycine at a scan rate of 2 mV/sec and rotational speed of 200 rpm.



**Figure 2.** Dissolution/polish rates in aqueous  $10^{-2}$  glycine solutions/slurries at pH 4 at different  $H_2O_2$  concentrations.

## References

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