Acceleration Effect of Copper Damascene Electrodeposition

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Introduction

The copper super conformal filling is essential technology for on-chip metallization and also for PCB. This super conformal filling is achieved by combination of acceleration and inhibition effects. Josell et al(1,2) suggested acceleration model on super conformal filling. This model is based on the adsorption of accelerator and formation of curvature at the via bottom (See Fig.1). However, most recent report from IBM(3) says that they succeeded in monitoring of free accelerator, not the adsorbed ones, by ring-disk electrode.

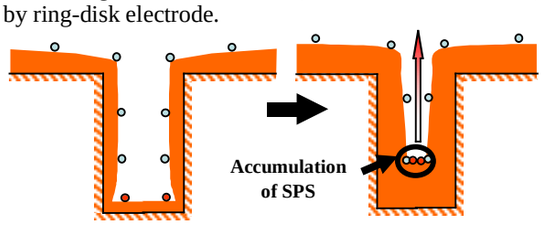

Fig. 1 Schematic illustration of super conformal model by Josell etal.

In this report, this free accelerator effect is discussed in details. With through mask plating of electrode just at the bottom of the cavity, we have examined the current-volt curves and we further observed the deposit cross sections to find out the curvature

Experimental

The through mask plating substrate was formed by photo resist on copper. The patterns consist of 1 μm of photo resist height and 2 to 30 μm in width of through mask copper surfaces. The bath consists of 0.6 kmol m^{-3}-$CuSO_4$ and 1.85 kmol m^{-3} - H_2SO_4, respectively. The additives are Cl^-(chloride ion), PEG (Polyethylene glycol), HCl, JGB (Janus Green B), and SPS (Bis (3-sulfopropyl) disulfide). The through mask plating substrates were cathodically polarized at constant voltage. After through mask plating, the cross sections were observed by FE-SEM.

Results and Discussion

1)Figure 2 shows the current-voltage curves on the through mask substrates. Fig.2-a is without JGB leveler and b is with JGB. It is clear that the current density increases with decreasing the width of through mask copper surfaces. These current increases occur regardless of JGB. These current increases are due to the acceleration effect of SPS.

2) Figure 3 shows the cross sectional view of deposit by through mask plating with additives of PEG+JGB+SPS+Cl^- (Fig2-a). The deposits are always flat regardless of width of through mask copper surfaces.

3)The deposits in Fig.3 should show curvature with smaller width judging form Josell et al acceleration mode(1,2), since more acceleration with smaller width(Fig.2). Unfortunately, only the flat deposits have been obtained and no curvature has been found. According to Farndon et al(4), the complex of Cu(I)thiolate can be formed during copper plating and this complex can be the accelerator. With higher aspect ratio copper damascene via, i.e. with smaller width, the accumulation of the free complex of Cu(I)thiolate is enhanced at the via bottom(Fig.4). This free complex accumulation is and indispensable factor for the super conformal filling of copper Damascene.

4)At the Meeting, important results with our ring-disk electrode experiment will be addressed.

Reference

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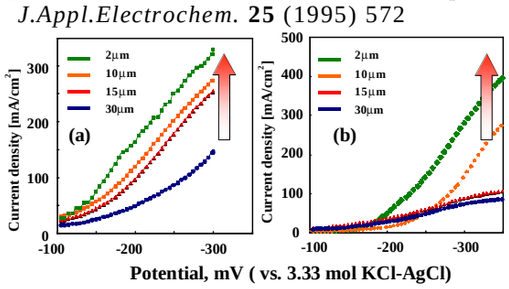

Fig. 2 Cathodic polarization curves on through mask substrate. Without and With JGB.
a) PEG+SPS+Cl^-, b) PEG+JGB+SPS+Cl^-.

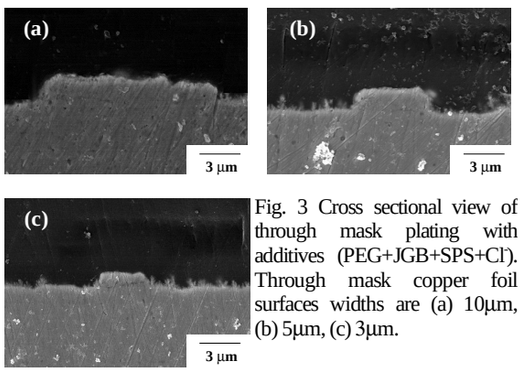

Fig. 3 Cross sectional view of through mask plating with additives (PEG+JGB+SPS+Cl^-). Through mask copper foil surfaces widths are (a) 10μm, (b) 5μm, (c) 3μm.

1/2 SPS + H^+ + e^- → MPS

2 MPS + Cu^{2+} → Cu(I)thiolate + 1/2 SPS + 2 H^+

+ Cu(I)thiolate + H^+ + e^- → Cu + MPS

Cu^{2+} + 2e^- → Cu

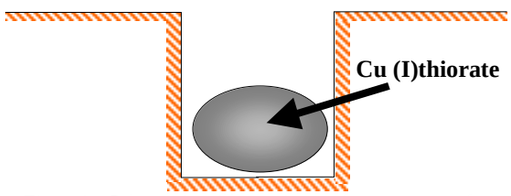

Fig. 4 Schematic illustration of super conformal mechanism by free accelerator.