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Acceleration Effect of Copper Damascene Electrodeposition -2.Monitoring by R.R.D.E-

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Introduction

Recently on-chip metallization has shifted from an aluminum to a copper process. In the copper Damascene process, the copper is electrodeposited into sub µm blind vias and trenches. Recently, larger size vias of several tens of µm have been widely used for build up-PCB because stacked vias can be achieved. Successful via filling requires the use of a combination of additives, e.g. polyethylene glycol (PEG), chloride ions (Cl^-), bis(3-sulfopropyl) disulfide (SPS) and Janus green B (JGB). PEG and Cl^- additives produce an inhibition effect while SPS produces an acceleration effect. 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.

However, most recent report from IBM(3) reports that they succeeded in monitoring of free accelerator, not the adsorbed ones, by ring-disk electrode. Recently, Kondo et al(4) analyzed this free accelerator effect by deposition on a through mask cathode, examination of deposit cross sections. It suggests that the free Cu(I)thiolate complex is indispensable factor for copper damascene electrodeposition. In addition, it was found that 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.1).

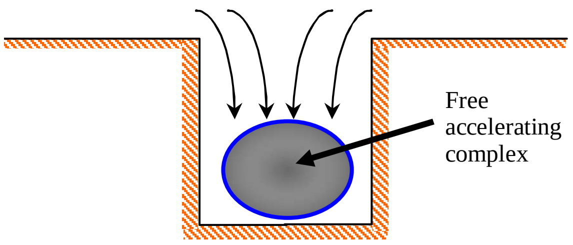

Fig. 1 Schematic illustration of super conformal mechanism by free accelerator.

The purpose of this study is to investigate the acceleration effect mechanism of SPS by both cross section observation of trench and the current-potential curves measurement with rotating ring-disk electrode.

Experimental

The basic 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), and SPS (Bis (3-sulfopropyl) disulfide). The chip with vias was mounted on rotating disk surface and immersed in the copper plating bath with different additive compositions.. After the chips were cathodically polarized, the cross sections were observed by FE-SEM. In addition, cathodic polarization in the bath with PEG, Cl^-, and SPS additives was performed in a rotating ring-disk electrode to detect the existence of free-accelerant complex. The rotating ring-disk electrode consisted of a Glassy-carbon ring and Glassy-carbon disk.

Results and Discussion

1) Figure 2 shows the ring electrode current(I_{ring})-disk electrode potential(E_{disk}) curves in the case of 0.5 and 0.9 V of ring electrode. Fig.2-a is the curve for the bath that SPS concentration is 1 ppm and b is the case of 10 ppm of SPS concentration. SPS oxidation occurs at potential of 0.9V and no SPS oxidation occurs at 0.5 V(3). Next the ring electrode potential (E_{ring}) was fixed at bath 0.5 and 0.9 V. Since a larger I_{RING} was detected at SPS oxidation potential of 0.9 V of E_{ring}, the hatched area in Fig. 1 must correspond to the oxidation of free SPS complex.

2) It is clear that the hatched area increases with SPS concentrations of 1ppm. Larger amount of free accelerating complex forms with SPS concentration of 1ppm. The current increases occur regardless of oxygen concentration in the bath.

3) At the Meeting, important results with effect of the aspect ratio, SPS concentration for the cross sections of Cu deposit in the trench will be addressed.

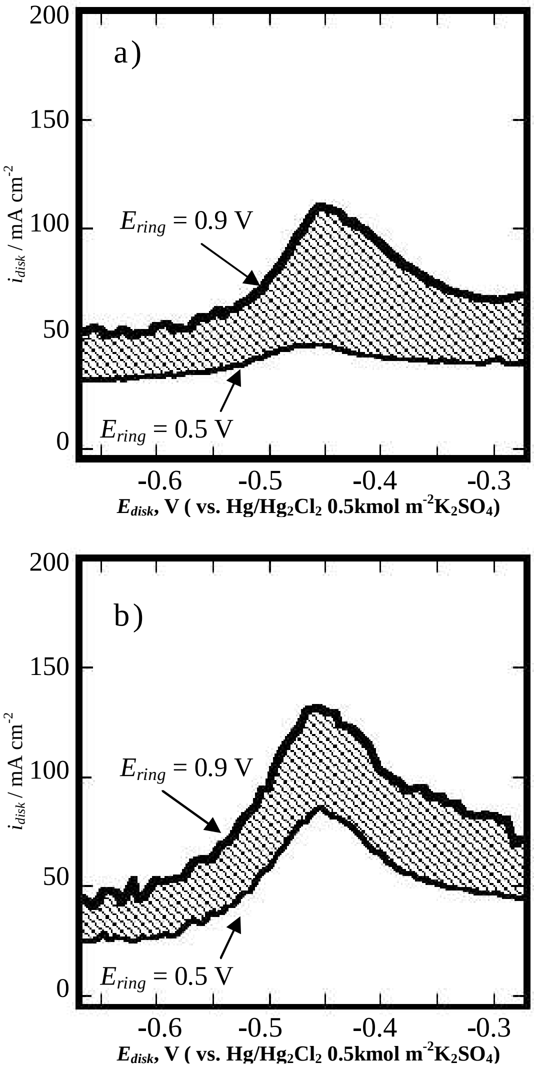

Fig. 2 Rotating ring-disk voltammetry for the Cu electrodeposit bath with different SPS concentration
a) 1 ppm SPS, b) 10 ppm SPS.

Reference

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