

Incorporation of Cl^- into Copper deposit at Initial Plating Period

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The copper superfilling is achieved by the presence of additives (generally PEG, Cl^- and SPS) in the acid copper sulfate electroplating bath. Moffat et al. have succeeded in predicting the shape evolution of copper electrodeposition by curvature enhanced accelerator coverage mechanism (CEAC). Recently, we demonstrated with Chang et al. that the copper bottom-up electrodeposition can be achieved by addition of only Cl^- and polyethylene glycol (PEG) and halide ion consumption model was proposed¹⁻²). In the model, Cl^- (or Br^-) is assumed to work as an adhesive between PEG and plating surface. If Cl^- is consumed on the plating surface, the concentration of Cl^- will be reduced due to diffusional limitation in the trenches. Then the suppression weakens on the trench bottoms and the rapid deposition is prompted. It was also found that Cl^- concentration in the plating bath affects the superfilling behavior³). That is, strong bottom-up feature was observed with dilute Cl^- , while the shape evolution became just conformal and no bottom-up feature was observed with higher Cl^- concentration, which matches the halide ion consumption model.

Therefore, it is supposed that Cl^- has some key roles in the superfilling mechanism. However, reported Cl^- incorporation into copper deposit with usual superfilling bath is small and it is not high enough to match the halide consumption model. It is empirically known that initial period of the plating is important to obtain good filling feature. In this study, Cl^- incorporation into copper deposit at initial period is investigated.

Experimental

The cell for the filling experiment is a 200ml beaker. The composition of the standard electrolyte is 225 g/dm³ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 55 g/dm³ H_2SO_4 . A flat wafer with a copper sputtered seed layer serves as the working electrode. The reference electrode and the counter electrode are platinum wires. All electrodes are connected to a potentiostat. The wafer chip is covered with a plating tape which has a hole of ϕ 6mm. The electroplating is performed by applying a constant current of 100mA/cm². Following two additive conditions are used for the electroplating.

- A: PEG(Mw.3000, 0.1mM) + Cl^- (2mM)
- B: PEG(Mw.3000, 0.1mM) + Cl^- (2mM)
+ SPS (5.6 μ M)

In order to investigate the interface region between plated copper and seed layer, relatively thin copper layer of 200nm thickness was electroplated. After electroplating, the chips are rinsed by pure water and dried by Ar gas flow. Then SIMS measurement was performed by an analysis company, MST (Foundation for Promotion of Material Science and Technology of Japan).

Results

Fig. 1 shows potential variation at the electroplating and Figs.2-3 shows impurity concentration for O and Cl. Relatively high Cl signal is detected at the initial stage of the electroplating. The peak value of Cl concentration may be much higher, because the surface roughness increases during SIMS investigation. Therefore, this result might suggest that Cl^- consumption at initial period has an important role.

References

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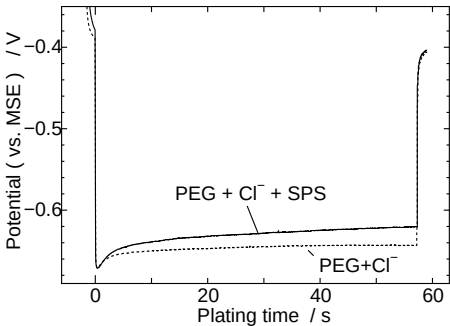


Figure.1 Time variation of overpotential.

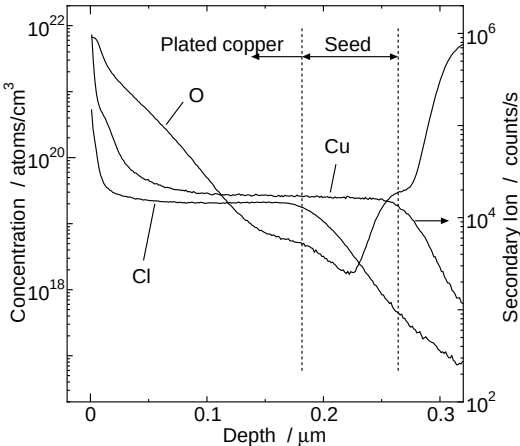


Figure.2 Concentration of impurities with addition of PEG and Cl.

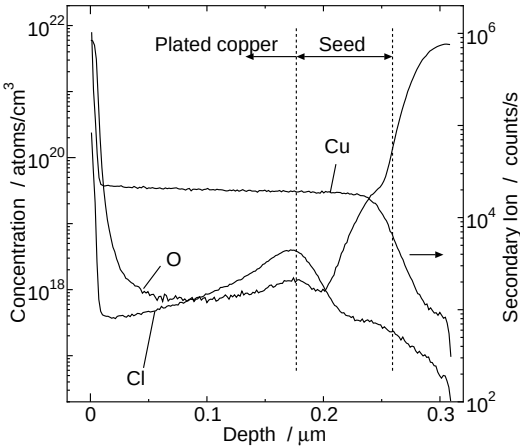


Figure.3 Concentration of impurities with addition of PEG, Cl and SPS.