

Suppression effect of Low-Concentration Bis-(3-sodiumsulfopropyl disulfide) on Copper Electroplating

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From 1997, copper (Cu) has been used as the interconnection metal as a replacement for aluminum by a dual damascene process invented and developed at IBM because the Cu metal has higher electromigration resistance and lower resistivity. Different from the metal-etching patternization in the aluminum metallization process, the Cu metal lines are produced by the dual damascene process including the deposition of diffusion barriers and Cu metals and the removal of overburden metals by chemical mechanical polishing (CMP). For the Cu metallization, electroplating has been a promising method for forming fine Cu interconnects due to its excellent gap-fill capability and high deposition rate for dual-damascene structures.

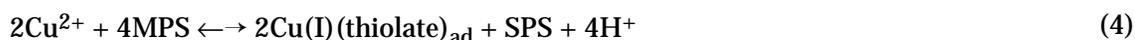


The Cu electroplating process is usually carried out in an acid Cu electrolyte that generally contains cupric sulfate as the source of cupric ions, sulfuric acid as a supporting electrolyte to provide conductivity of the solution, and relatively small amounts of additional agents to modify plating kinetics and to regulate film properties. Besides, external additives, including polyethylene glycol (PEG) or polyalkylene glycols (PAG), a sulfonate-terminated thiol or disulfide catalyst such as bis-(3-sodiumsulfopropyl disulfide) (SPS) or NaSH(CH₂)₃SO₃ (MPS), and polymer leveler, are used for several reasons such as the formation of void-free and seam-free Cu conductors to realize superfilling.

According to the two-step electron transfer mechanism for Cu electroplating with cuprous ions as an intermediate, the reaction equations are:



Therefore, if Cu electroplating rate wants to be accelerated, it should speed the reaction of the Eq. 1 because it is the bottleneck of cupric reduction. SPS is widely studied and proved that it had an acceleration function in the Cu-electroplating process because SPS can accelerate the reaction of the Eq. 1.



According to Eq. 3 and 4, SPS is believed to form MPS by cathodic reduction and then MPS is able to reduce Cu^{2+} ions to Cu(I)thiolate complexes to accelerate the Cu-electroplating rate. It is important that SPS has been proven to be unable to reduce Cu^{2+} to Cu^+ in aqueous solutions. This suggests that SPS species have to consume energy to form MPS as well as the reduction reaction from Cu^{2+} ions to Cu(I)thiolate complexes.

In this study, we discuss the effect of the SPS concentration on Cu electroplating using electrochemical analyses, including potentiodynamic (PD) polarization curves, cyclic-voltammetry stripping (CVS), and electrochemistry-impedance spectroscopy (EIS). The results show that the Cu-electroplating rate has a strong correlation with the concentration of SPS. Adding a few SPS species to the plating bath inhibits the Cu-electroplating rate. This is because the SPS concentration is too low. The formation of Cu(I)thiolate complexes is too low to accelerate the Cu-electroplating rate while the added SPS still consumes energy from the system. When the SPS concentration is larger than the threshold value (~100ppm), it can promote more $\text{Cu(I)(thiolate)}_{\text{ad}}$ and Cu(thiolate)Cl formation at the Cu surface, accelerating the Cu-electroplating rate. Furthermore, the Cu-electroplating rate reaches to a limit as the SPS concentration continues to increase. Tan et al. also demonstrated that the transition time (defined as the time required to reach 70% of the steady-state value) of Cu electroplating decreased and reached a limit when the SPS concentration increased from 0.05 to 1000 ppm.

Therefore, in this study, we prove that SPS had a suppression function in the Cu-electroplating process when its concentration is lower than ~100ppm. Even if the SPS concentration continues to increase, the Cu-electroplating rate will reach to be saturated because effective reduction site on the Cu surface has been fully occupied and recess $\text{Cu(I)(thiolate)}_{\text{ad}}$ and Cu(thiolate)Cl formation can't grow to accelerate the Cu-electroplating rate.

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