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# Bis-(3-sodiumsulfopropyl disulfide) Decomposition with Cathodic Current Flowing in a Copper-Electroplating Bath

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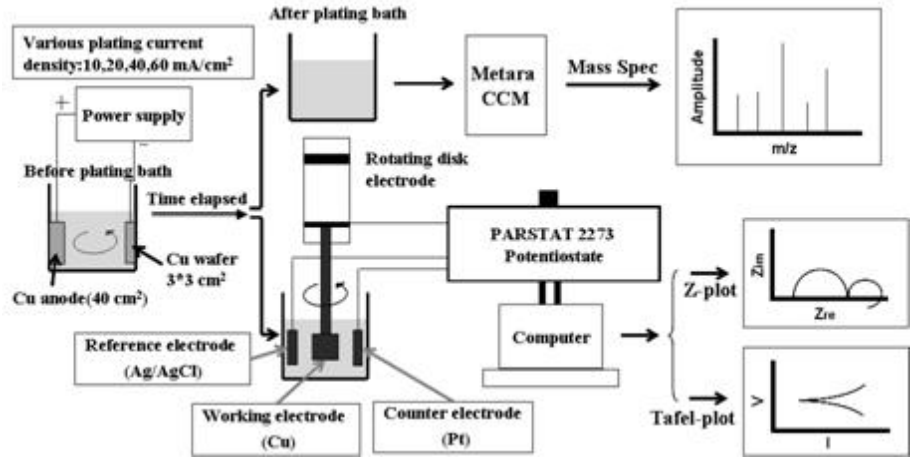
Electroplating is a promising method for forming copper (Cu) interconnections in dual-damascene structures due to its excellent gap-filling capacity and high throughput. External additives used for state-of-the-art damascene manufacturing of semiconductor logic and memory devices involving the electroplating of Cu metallization have been widely studied.

The gap-filling capability of Cu electroplating and the defect performance after Cu chemical-mechanical-polishing (CMP) processes are affected by SPS molecules which are decomposed or oxidized during the aging of the plating bath. Hence, the decomposition effect of SPS deserves investigation. However, little information is available on the byproducts of SPS decomposition in an electrolyte with a Cu metal.




In this study, the decomposition effect of SPS with cathodic current flow was investigated using mass spectroscopy Metara Sentry CCM$^{TM}$ tool. The electrolyte with a cathodic current flow increased SPS decomposition. The mass spectrum shows that 1,3-propanedisulfonic acid (PDS) was the most stable species among SPS byproducts. The mass spectrum also shows many other peaks, including MPS(O) $[O_3S(C_3H_6)SOH]^-$, MPS($O_2$)$[O_3S(C_3H_6)SO_2H]^-$, SPS(O) $[O_3S(C_3H_6)SOS(C_3H_6)SO_3]^{2-}$, and SPS($O_2$) $[O_3S(C_3H_6)SO_2S(C_3H_6)SO_3]^{2-}$. These peaks are due to the break down of SPS or MPS and reaction with dissolved oxygen. The peak of PDS shifted and that the peaks of the oxidations of SPS or MPS slightly transformed. The concentration of PDS increased with time and current while the concentration of SPS decreased.

The polarization curves indicate that the components of the bath after the electroplating process improve the

efficiency of Cu electroplating due to the generation of more Cu ions and Cu(I)thiolate species. The equivalent circuit of Cu electroplating was developed and examined using electrochemical impedance spectroscopy (EIS), which were obtained by a potentiostat/galvanostat (Princeton Applied Research PARSTAT$^{TM}$ model 2273), to characterize the properties of the aged bath with the decomposition of SPS. The Nyquist plot shows that there were three semicircles in the electrochemical analysis of plating baths containing SPS. An equivalent circuit simulated using the EIS data shows that the electrochemical system consisted of three resistances, two capacitances, and one inductance. The values of the circuit's components, which were obtained by fitting the Nyquist spectra, revealed the properties of the aged bath with the decomposition of SPS.