

## The Role of SPS in Damascene Copper Electroplating

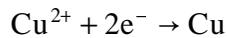
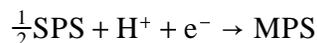
Philippe M. Vereecken, Hariklia Deligianni,  
Keith T. Kwietniak and Panayotis C. Andricacos  
*IBM, T.J. Watson Research Center  
Yorktown Heights, NY 10598*

Robert A. Binstead, Janet Wu,  
Robert Mikkola and Jeffrey M. Calvert  
*Shibley Company, Marlborough, MA 01752*

Since the development of copper damascene plating [1] and the subsequent implementation of copper interconnects in microelectronics, a renewed interest in the role of the organic additives in copper electroplating has emerged. Typical copper sulfate based electroplating chemistries consist of an organic polymer (e.g., polyethylene glycol (PEG)) as a suppressor additive, bis(sodiumsulfopropyl)disulfide (SPS) or similar molecule as an accelerator/brightening agent, and possibly an additional organic molecule that acts as a leveling agent to produce mirror-like plated surfaces. In combination, these additives can also achieve accelerated, bottom-up electrodeposition of copper into submicron inlaid features which permits void-free interconnect wiring in damascene structures.

In recent years several models have been proposed in an attempt to describe the roles of these additives in the so-called superconformal or superfilling mechanism [1-3]. Whereas these models seemingly contradict one other, each model satisfactorily reproduces the behavior of experimental data obtained under different limiting conditions. The existence of several models is not surprising given the complex nature of the superfilling mechanism, which depends on bath composition, additive concentration, feature size and current density.

The copper plating chemistries used to fill early generation damascene structures were characterized by a relatively high leveler content. In this case the superfilling mechanism was found to be dominated by diffusion and adsorption of the leveler [1]. In the case of the more recently developed two component (suppressor and accelerator) or three component (with low leveler concentration) copper plating chemistries, it has been found that competition between the accelerator and suppressor for adsorption sites can describe the superfilling of sub-micron features [2]. The accumulation of accelerator due to a rapid change in surface to volume ratio inside a trench or via is believed to be responsible for the observed bottom-up filling [2,3]. We support the latter concept, but believe that competitive adsorption/desorption alone does not explain the acceleration effect of SPS or MPS (mercaptopropane sulfonic acid). SPS and its monomer, MPS, are known to be both chemically and electrochemically active in the copper plating solution [4,5]. The reduction of SPS to MPS provides a possible catalytic pathway for copper deposition through the formation of cuprous thiolate [5]:



The total reaction equals the electrochemical reduction of  $\text{Cu}^{2+}$  to Cu, showing the catalytic action of SPS. From the above reaction sequence it follows that a surface excess of MPS is necessary to initiate the catalytic reaction. The initial formation of MPS may explain the observed induction time for bottom-up fill in some plating chemistries. Accumulation of adsorbed MPS due to the volume decrease in the patterned structures, and slow diffusion of free MPS out of these features, can then explain the large difference in copper deposition rate in a trench or via as compared to the wafer surface. In this paper we present electrochemical results supporting the above reaction mechanism.

The electrochemical behavior of SPS on gold, platinum and glassy carbon disk electrodes was investigated with cyclic voltammetry and rotating disk voltammetry. Irreversible reduction and oxidation waves for SPS were observed at all electrode materials for concentrations larger than 10 mM. Quasi-reversible reduction of SPS was observed at high scan rates (10-1000 V/s) on Au in 10% sulfuric acid. Owing to strong adsorption of SPS on Au and Pt, no obvious reduction or oxidation waves could be measured in this medium for concentrations  $\leq 1$  mM. However, diffusion limited oxidation of SPS was observed on glassy C for concentrations of 0.1 and 1 mM SPS. The latter enables the detection of small concentrations of SPS in commercial copper plating solutions. Here, we present a rotating ring-disk technique to measure the consumption rate of SPS during copper plating.

### References:

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. Res. Develop.*, **42**, 567 (1998).
2. A. C. West, S. Mayer, and J. Reid, *Electrochem. Solid-State Lett.*, **4**, C50 (2001).
3. D. Josell, D. Wheeler, W. H. Huber, J. E. Bonevich, and T. P. Moffat, *J. Electrochem. Soc.*, **148**, C767 (2001).
4. J. P. Healy, and D. Pletcher, *J. Electroanal. Chem.*, **338**, 167 and 179 (1992).
5. E. Farndon, F. C. Walsh, and S.A. Campbell, *J. Appl. Electrochem.*, **25**, 572 (1995)