

Study of the Potential Dependence of Co-Adsorption of PEG, Cl⁻, and SPS/MPS on Cu using *In-Situ* Spectroscopic Ellipsometry

In-situ spectroscopic ellipsometry (SE) has been used successfully to characterize additive adsorption onto sample substrates, representative of integrated circuit (IC) chips. These additives adsorb onto the surfaces of trenches and vias in a particular sequence, facilitating defect-free Cu filling of these sub-micrometer structures; this process is called superconformal filling. As device feature sizes shrink, a greater understanding of the interactions of the additives in the baths as a function of potential must be realized in order to formulate baths with greater dynamic range to achieve superconformal filling. Research of this type is important to the microelectronics industry in the effort to achieve the technology nodes of 65 nm and lower.

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Copper (Cu) is the current material of choice for interconnects in integrated circuit (IC) chips ubiquitously used as components in modern day technology. Electrodeposition is the method in which Cu is plated into sub-micrometer structures such as trenches and vias, forming the electrical interconnections between the millions of transistors contained on an IC. This plating process is controlled by specific additives in the electrochemical bath such as polyethylene glycol, Cl⁻ ion, and either 3-mercaptopropyl sulfonate (MPS) or bis-3 sulfopropyl disulfide (SPS).

In-situ spectroscopic ellipsometry (SE) has been used successfully to characterize additive adsorption onto sample substrates. Initial work focused on the co-adsorption of polyethylene glycol (PEG) and Cl⁻ ion onto the coinage metals Cu, Ag and Au in the absence of Cu plating salts at a potential relevant to electroplating, -0.65 V_{MSE} ("MSE" refers to Mercury Sulfate Electrode). It was determined that PEG adsorbed onto the metal substrates in the presence of Cl⁻ ion as a layer of approximately 0.6 nm thick; in the absence of Cl⁻, PEG adsorption was minimal. These two components form the inhibitory layer on the substrate, capable of hindering Cu deposition under true plating conditions. SPS and MPS, "catalysts" or "accelerants", adsorb slower than PEG/Cl⁻ but upon adsorption serve to lift the inhibition caused by PEG/Cl⁻ and thus "accelerate" plating with respect to this layer. This is demonstrated in **Figure 1** in which Cl⁻ and PEG are added, followed the addition of MPS. The growth of the model thickness curve subsequent to MPS addition is the action of MPS on the substrate in conjunction with the

PEG/Cl⁻ layer. The disruption of the PEG/Cl⁻ layer is seen upon a significant reduction in the concentration of additives in the bath by a back dilution process; the more stable thiol remains adsorbed to the substrate.

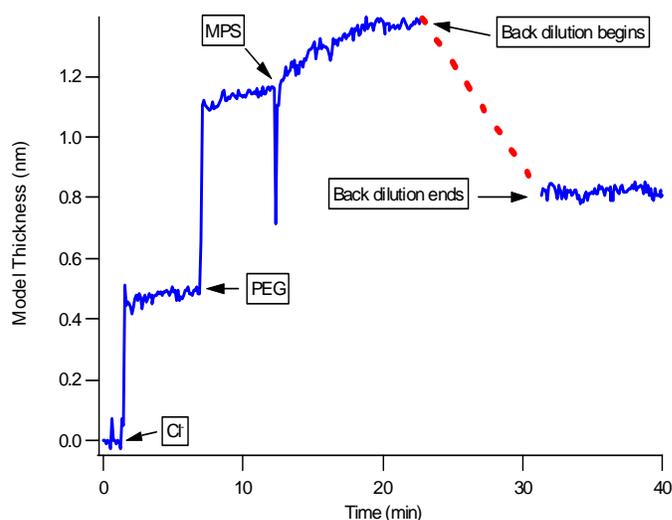
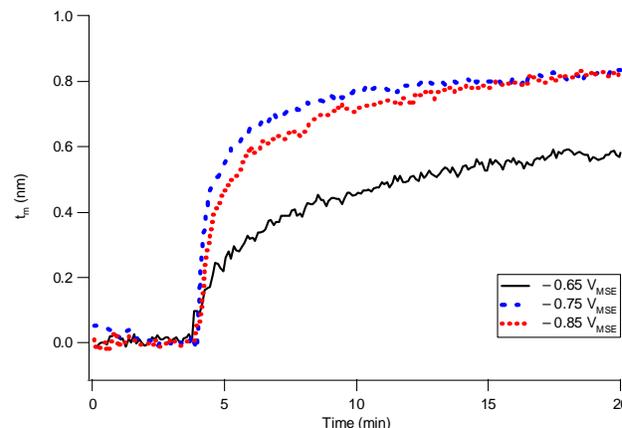


Figure 1. Cl⁻/PEG displacement by MPS. Cl⁻ added at 2 min, PEG at 7 min, MPS at 13 min. Back dilution began at 24 min, resulting in a model thickness nearly comparable to MPS limiting value.

The potential dependence of additive interactions was examined at the potentials of -0.65 V_{MSE}, -0.75 V_{MSE}, and -0.85 V_{MSE}, industrially relevant plating potentials. In **Figure 2** it is shown that there is a **potential dependence of the adsorption of SPS**, the model thickness curve at -0.65 V_{MSE} reflecting a limiting thickness of 0.5 nm ± 0.15 nm versus 0.8 nm ± 0.15 nm at the more negative potentials.



No potential dependence was found for MPS, with the limiting model thickness of the adsorbed layer 1.1 nm, regardless of potential. Upon examination of the interplay between PEG, Cl⁻ and SPS in the bath, it was seen that SPS adsorption was more significant on a shorter time scale at more negative potentials. These findings provide insight as to how potential can play an important role in formulation of electrochemical baths/processes with greater dynamic range needed to superconformally fill vias and trenches with greater aspect ratios as feature sizes shrink.

Publications:

Walker, M. L., Richter, L. J., and Moffat, T. P.,
“Competitive Adsorption of PEG, Cl⁻, and SPS/MPS:
an In-situ Ellipsometric Study on Cu”, J.
Electrochem. Soc. 153, C557-C561 (2006).

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“Potential Dependence of Competitive Adsorption of
PEG, Cl⁻, and SPS/MPS on Cu: An *in-situ*
Ellipsometric Study”, J. Electrochem. Soc., in press.