

Effect Of Additives On Deposition and Corrosion:
Vibrational Spectroscopic Measurements
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We used vibrational spectroscopic measurements in conjunction with detailed calculations to understand the basis for the inhibition and acceleration effects evinced by three common electroplating additives: benzotriazole (BTA), polyethylene glycol (PEG) and bis-(sodium sulfopropyl)-disulfide (SPS), respectively. All of these additives form complexes with Cu(I) and Cl⁻ also present in the plating bath.

In the case of BTA, detailed *in situ* infrared visible sum frequency generation (sfg) measurements show the presence of two different types of BTA on the Cu electrode surface. One of these is associated with surface-bound BTA only. The other is BTA which bridges between the surface and the BTA-Cu(I) polymer formed above the electrode. Cl⁻ displaces surface BTA but not the polymer. This work shows how Cl⁻ breaks down the inhibiting film.

In the case of PEG, the Cu(I)-Cl species acts as an inhibitor, because of the relative stability of Cu(I)-O bonds. In the case of SPS, the Cu(I)-Cl complex is relatively easy to reduce, because of the charge delocalization afforded by the bis-thiol species. Extension of this insight to the superfilling process itself will be discussed.

In the case of SPS, spectroscopy of this molecule obtained using *in situ* sfg, infrared-reflection adsorption, or surface enhanced raman (SERS) spectroscopy exhibits insensitivity to the presence of Cl⁻ or Cu in the C-H, thiol, metal-halide, and C-C regions of the spectrum. However, the sulfonate region is strongly perturbed upon halide and Cu addition. On the basis of detailed calculations, we propose a model for the interaction of these components with SPS.