

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), polyethelyene glycol (PEG) and bis-(sodium sulfopropyl)-disulfide (SPS), respectively. All of these additives form complexes with Cu(I) and Cl<sup>-</sup> 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<sup>-</sup> displaces surface BTA but not the polymer. This works shows how Cl<sup>-</sup> 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.