A Comparison Study of MPSA-Cl-PEG and SPS-Cl-PEG Additive Systems for Copper Electrodeposition

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Introduction

Copper superfilling can be achieved with an acidic electroplating solution containing Cl-, PEG and MPSA [1] or Cl-, PEG and SPS [2], the dimer of MPSA. In this study, experiments were performed to investigate the similarities and differences between MPSA and SPS in plating solutions containing one (SPS/MPSA), two (SPS-Cl/MPSA-Cl) or three (MPSA-Cl-PEG/SPS-Cl-PEG) additives. An understanding of the relationship between MPSA and SPS is critical to a complete understanding of the mechanisms that contribute to superfilling.

Experimental

Galvanostatic and potentiostatic copper electrodeposition experiments were performed on a rotating disk electrode (RDE). Experiments were performed with a copper-plated platinum WE (area of 0.196cm²) and a copper CE. The electrolyte solution consisted of 0.24M CuSO₄·5H₂O and 1.8M H₂SO₄ to which one or more additives from PEG (300ppm), Cl- (50ppm), SPS, and MPSA were added. The electrode rotation rate was 400rpm. Potentials were referred to a saturated sulfate electrode (SSE) reference electrode.

Results

Figure 1 shows the results of galvanostatic experiments performed with solutions containing two additives, either SPS-Cl or MPSA-Cl. The addition of either SPS or MPSA alone to the electrolyte had an inhibiting effect as evidenced by the drop in potential (increase in the overpotential) which occurred over an initial 150 second time period. Subsequent addition of Cl- caused a sharp increase in the potential for both systems. The addition of Cl- appeared to dramatically eliminate inhibition by SPS or MPSA, resulting in acceleration of the plating reaction. However, the additive concentration required to achieve a similar influence on copper electrodeposition was significantly lower for MPSA (1ppm) than for SPS (50ppm).

The results of potentiostatic experiments with the two 3-additive systems are shown in Fig.2 (-0.5V vs. SSE) and Fig.3 (-0.75V vs. SSE). At -0.5V, little acceleration (compared to the Cl-PEG system) was observed for SPS-Cl-PEG system. In contrast, a significant accelerating effect was observed for MPSA-Cl-PEG system, even though the MPSA concentration was very low. At a potential of -0.75V, both the SPS and MPSA additive systems exhibited a slow transition from a low to high acceleration, a transition that is critical for superfilling [3]. The observed difference in the potential dependent behavior of the two systems suggests that acceleration in the Cl-PEG-SPS system may be due to (1) the formation of MPSA via the electroreduction of SPS (SPS + 2e⁻ → 2MPSA) [4] and/or (2) potential dependent adsorption of an SPS-related accelerator.

Summary

The experiments described above, as well as others, examine the behavior of SPS and MPSA additive systems that exhibit superfilling. A comparison of the two additive systems provides insight into the mechanisms that govern the superfilling process.

References