

Analysis of Organic Plating Additives Using Boron-Doped Diamond Electrodes

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The wide potential window of water stability and low background currents on boron-doped diamond electrodes permit investigations of previously inaccessible chemistries (1-3). In the present studies, cyclic voltammetry was used to investigate diamond as a sensor electrode for several commonly used organic copper plating additives.

Boron-doped diamond film electrodes were fabricated by hot-filament chemical vapor deposition (4-6). XPS and ATR-FTIR were used to examine the oxygen concentration and functionality on the diamond surface. Cyclic voltammetry in 0.5M H₂SO₄ verified that the electrodes displayed the characteristic wide potential window and low baseline current of high-quality diamond electrodes.

Cyclic voltammograms were measured, Fig. 1, on platinum and polycrystalline diamond in CuSO₄/H₂SO₄ solutions containing polyalkylene glycol and disodium (bis(3-sulfopropyl)) disulfide (SPS). The insets of Fig. 1 show full scans for platinum and diamond, 1 mA scale; only portions of the platinum scan are visible at lower current scales, because of its large baseline current. For polyalkylene glycol on platinum, Fig. 1a, oxygen evolution occurred at +1.4 V vs. SHE; no peaks corresponding to polyalkylene glycol oxidation or reduction were observed. Identical voltammograms were obtained regardless of the glycol concentration. The larger baseline current density on platinum compared to diamond is clearly visible.

However, on diamond, Fig. 1a, two oxidative peaks of the glycol were observed at approximately +2.05 V and +2.4 V; the peak heights increased linearly (R²=0.98) with increasing glycol concentration. Oxygen evolution was visible beyond +2.4 V.

For measurement of SPS on platinum, Fig. 1b, only the cathodic sweep (+1.6 V to 0.5 V) is visible, since the anodic current (+0.5 V to 1.6 V) is off the scale (see inset for full scan). Oxygen evolution occurred at +1.4 V; no peaks corresponding to SPS oxidation or reduction were visible. As with polyalkylene glycol, identical voltammograms were obtained on platinum regardless of the SPS concentration. On diamond, Fig. 1b, SPS displayed two oxidative peaks at +1.65 V and +2.1 V; the peak heights increased linearly with increasing SPS concentration.

In Fig. 2 are voltammograms on diamond of CuSO₄/H₂SO₄ solutions containing polyethylene glycol (PEG) of 20, 100 and 200 mg/L concentrations and 4000 and 10000 molecular weight (MW). The solid lines correspond to 4000 MW PEG; the dashed lines, 10,000 MW PEG. An oxidation peak appears at +2.1 V, with a shoulder approximately at +2.3 V; the oxidation peak increases in height with increasing PEG concentration of either MW. For equivalent concentrations of different MW PEG, the 4000 MW displayed higher peak currents than the 10000 MW.

Voltammograms in CuSO₄-free, acid solutions of glycols and SPS on diamond display different oxidation peak positions and heights than for the CuSO₄ solutions. This data are suggestive that CuSO₄ interacts

with these organics in solution, a view consistent with the purpose of these organics as additives in copper plating.

Acknowledgments

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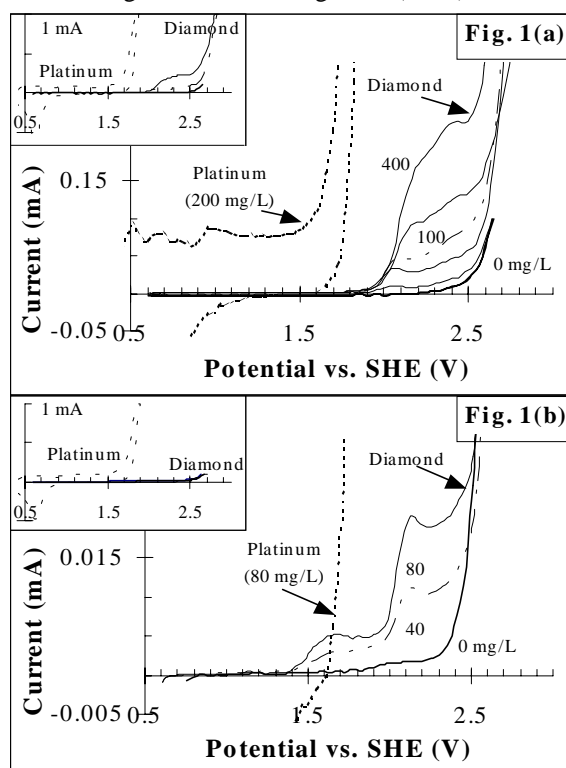


Fig. 1: Cyclic voltammograms of CuSO₄/H₂SO₄ solutions containing (a) polyalkylene glycol and (b) SPS, respectively, on platinum (dashed) and diamond (solid). Insets show full scans on 1 mA scale.

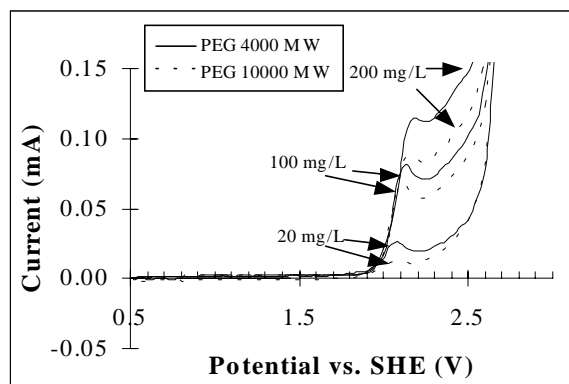


Fig. 2: Voltammograms on diamond of CuSO₄/H₂SO₄ solutions containing PEG of 4000 MW (solid) and 10,000 MW (dashed).