Contactless Electrodeposition and Micropatterning via Bipolar Electrochemical Printing

Trevor M. Braun and Daniel T. Schwartz
University of Washington
BOX 357750

Bipolar electrochemistry is emerging as a new method for electrochemical analysis, locomotion of micro-objects, and fabrication [1-3]. We have previously shown the ability to pattern using Electrochemical Printing (EcP) where the cathode is the electrically conducting surface in a conventional electrodeposition setup [4]. For Bipolar Electrochemical Printing (BEcP), the substrate is no longer actively controlled as the cathode, and instead we have an external cathode in the bulk solution. In this way, current has two paths it can follow, through the electrolyte to deposit on the ring, or through the substrate where bipolar electrodeposition and etching occurs in a spatially controlled manner.

Figure 1 shows the axisymmetric schematic (not to scale) and important dimensions for our BEcP system. Electrolyte flows through a silica nozzle of diameter d and pools on the surface submerging the cathode in bulk electrolyte solution. Deposition occurs in the region below the nozzle while substrate etching occurs in the exterior regions below the cathode. An anode is inserted upstream of the nozzle outlet to complete the circuit.

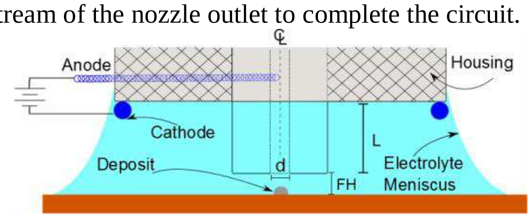

Figure 1. Schematic (not to scale) of the BEcP nozzle and important features and dimensions.

COMSOL simulations of copper deposition on a copper electrode were used to explore the electrochemical behavior of the experimental setup. The simulation employs a secondary current distribution and utilizes the full Butler-Volmer equation as the boundary condition at the conductive surface. Figure 2 shows the current density profile at the electrode surface for two simulations at different nozzle fly-heights. The current density profile corresponds to the overall shape of the expected deposit and we see that by increasing the FH deposit localization decreases and is spread over a wider area. The bipolar crossover point (BCP) is the location along the radial dimension of the substrate where the reaction switches from reduction to oxidation.

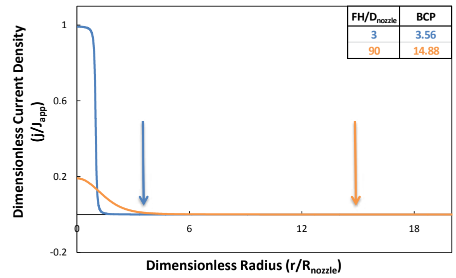

Figure 2. COMSOL simulations show how fly-height (FH) affects the current density distribution on the bipolar electrode. All anodic current is small and distributed over a large area so visibility is minimal on the plot.

We have also experimentally demonstrated the flexibility BEcP has as a microfabrication tool. Figure 3 shows an optical micrograph of a 5x5 copper deposition experiment performed where the fly height was varied along one axis and applied current along the other. At higher currents we see the formation of ring-like deposits where there is minimal copper deposition in the center. Previous work with EcP has demonstrated that a surface pH rise at the deposit center causes craters at high potentials [5]. We have shown efficient use of bipolar electrochemistry for electrodeposition and the potential for a novel approach to micropatterning.

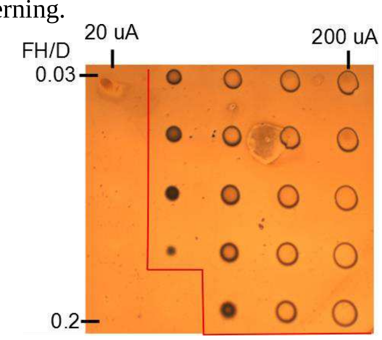

Figure 3. Optical micrograph of copper deposition on a copper substrate using BEcP.

References:
1. Fosdick et al., Parallel screening of electrocatalyst candidates using bipolar electrochemistry, Anal. Chem. **2013** (85) 2493-2499
2. Loget et al., Electric field-induced chemical locomotion of conducting objects. Nat. Commun. **2011**, (2) 535.
3. Loget et al., True Bulk Synthesis of Janus Objects by Bipolar Electrochemistry, Adv. Mat. **2012**, (37) 5111-5116
4. Whitaker et al., Electrochemical printing: software reconfigurable electrochemical microfabrication, J. Micromech. Microeng. **2005** (15) 1498
5. Nelson et al., Characterization of Buffered Electrolytes for Nickel Electrochemical Printing, J. Electrochem. Soc. **2008** (3) D181-D186