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The Effect of Saccharin on Electrodeposited Nickel: An *In-situ* SPM Study

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The performance characteristics and material properties such as stress, microstructure, and composition of nickel coatings and electroformed components can be controlled over a wide range by the addition of small amounts of surface-active compounds to the electroplating bath. A variety of these compounds have been developed over several decades for specific applications. Saccharin is one compound that is widely utilized for its ability to reduce tensile stress and refine grain size in electrodeposited nickel.

While the effects of saccharin on nickel electrodeposition have been studied by many authors in the past, there is still uncertainty over saccharin's mechanisms of incorporation, stress reduction, and grain refinement. *In-situ* scanning probe microscopy (SPM) is a tool that can be used to directly image the nucleation and growth of thin nickel films at nanometer length scales to help elucidate saccharin's role in the development and evolution of grain structure. In this study, *in-situ* atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques are used to investigate the effects of saccharin on the morphological evolution of thin nickel films deposited with direct current and potentiostatic control from borate-buffered acid solutions on single crystal and poly-crystalline gold surfaces. The overpotential dependence of the growth mode, 2-D to 3-D transition, surface roughness, and grain size evolution are described at different metal ion and saccharin concentrations and at different overpotentials and compared with films deposited under similar conditions from an additive-free electrolyte.

We have used AFM to directly measure the roughness and profile evolution (Figure 1) of a particular region on the evolving nickel surface as a function of integrated current to provide the history of surface features beginning with nucleation locations. Saccharin's ability to refine grain is directly observable with this technique. The crystallites formed are faceted and crystalline with triangular features (Figure 2). X-ray diffraction measurements indicate a strong (111) texture for nickel films less than 200 nm thickness when deposited on evaporated polycrystalline gold films that are also preferentially oriented (111). At length scales below the resolution of AFM, we have made STM measurements of the nucleation process and transition from 2-D to 3-D growth. At low overpotentials, saccharin is observable on the Au(111) terraces. In contrast to the observations at higher overpotentials made with AFM, STM measurements at low overpotentials indicate saccharin does not strongly disturb the morphological evolution of nickel relative to that of a deposit from an additive-free bath through at least the first five nickel monolayers (Figure 3). In this talk we will discuss the potential dependence of saccharin's effects on the morphological and grain evolution of electrodeposited nickel.

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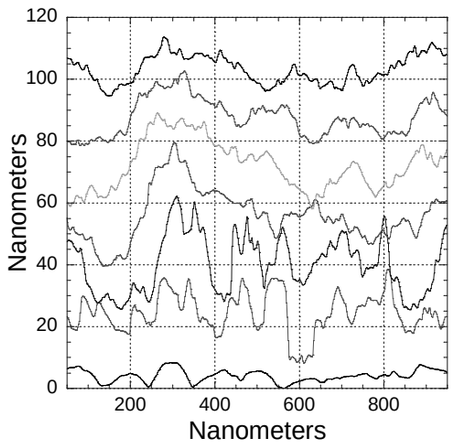

Fig. 1. The profile evolution of a nickel deposit on polycrystalline gold extracted from AFM image data showing a decrease in feature size after the initial nucleation period. The profile traces are offset by a deposit thickness estimated from integrated current.

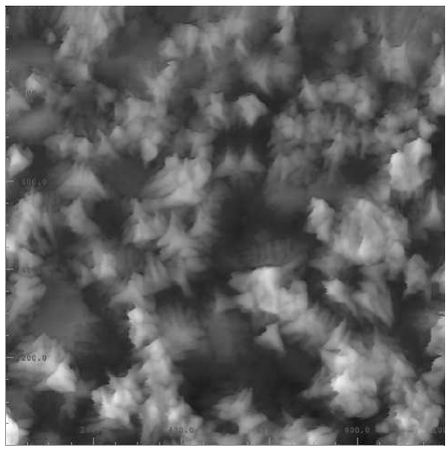

Fig. 2. In-situ 1 X 1 μm AFM image of approximately 50 nm of nickel deposited in the presence of saccharin. Saccharin strongly affects the morphology evolution of nickel films at higher overpotentials.

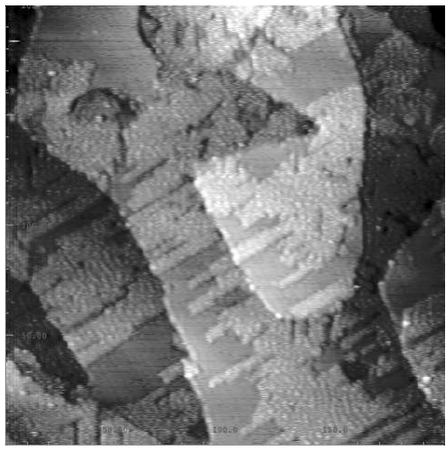

Fig. 3. In-situ 200 X 200 nm STM image of a sub-monolayer of nickel deposited on Au(111) terraces from a modified Watts electrolyte containing saccharin. The highly anisotropic structure of the first nickel monolayer is not strongly affected by the presence of saccharin.