Scanning Probe Microscopy Studies of Dissolution and Deposition Processes on Electrode Surfaces

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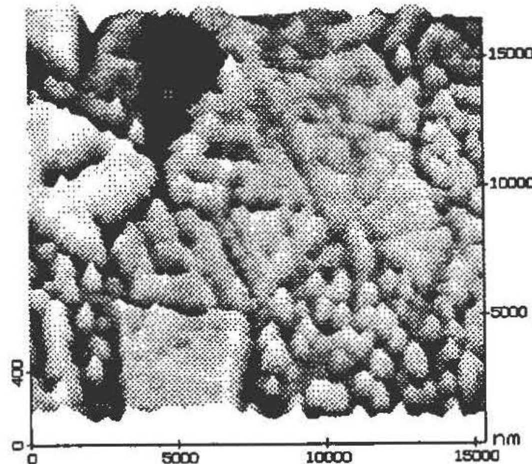
There is substantial interest in the chemistry of immersed copper surfaces because of the importance of this material in energy, catalytic, and microelectronic applications [1]. There has, in particular, been considerable effort directed toward understanding the corrosion and etching of copper [2], and the behavior of underpotentially deposited metal monolayers on the Cu surface [3].

One of the problems in studying the copper material is the relatively poor characterization of the surface while it is in electrolyte. Until recently, there were no direct probes of electrode surface structure at the atomic level. This changed with the advent of the scanning probe [4] and x-ray scattering techniques [5], which have provided substantial insight into the correlation between electrode surface structure and its role in electrochemistry. In particular, we have shown that the Atomic Force Microscope (AFM) is an ideal instrument to monitor electrochemical processes *in situ* [6].

One aspect of our research focused on using the AFM to examine the anodic dissolution of polycrystalline Cu in acidic media with and without a corrosion inhibitor. Dissolution in 0.5 M H_2SO_4 was monitored at two anodic potentials, 30 mV and 100 mV. At the smaller applied potential, an amorphous layer, known to be present on polished copper [7], was observed. The layer was removed by anodic dissolution to expose the underlying copper grain boundaries. It was determined that the layer was 40-60 nm thick, which corresponded closely to the diameter of the final polishing medium (50 nm). Also, at the 30 mV applied



potential, a preferential etching of certain grain surfaces occurred initially followed by dissolution along grain boundaries. At the higher applied potential, crystallographic etching proceeded along regions where grain boundaries were previously evident. The addition of benzotriazole (BTA) formed a protective film that inhibited copper dissolution. At anodic potentials up to 200 mV, the film was stable. At 300 mV anodic of the rest potential, local breakdown of the film resulted in pit-like surface features.

Other areas of our research have concentrated on the Cu(100) surface. This surface has been extensively examined in UHV environments, especially with regard to the structure of adsorbed oxygen [8], but relatively few studies dealing with electrochemical environments have emerged [9]. In particular, there is still uncertainty with regard to the structure of the surface, the potential dependence of this structure, and the presence of any overlayers or ad-lattices. We believe that it is extremely important to understand the bare Cu surface *in situ* before any subsequent corrosion or deposition chemistry is performed.

In 0.1 M H_2SO_4 and 0.1 M $HClO_4$, we discovered that the Cu(100) surface exhibits a $(\sqrt{2} \times \sqrt{2})R45°$ adlattice, in which O or OH^- is chemisorbed in the 4-fold hollow site. This structure may be equivalent to the room temperature O on Cu(100) phase observed in UHV environments [8e,10]. At extremely negative potentials, an atomic spacing indicative of a bare Cu(100) substrate was observed. The $(\sqrt{2} \times \sqrt{2})R45°$ O adlattice observed at potentials between -.45 and -.85 V has implications concerning the chemistry that takes place on a Cu(100) surface in acidic solution.

We have also examined the adsorption and desorption of organic molecules--urea and pyrazine--on Cu(100). Urea and urea derivatives have been proven to be successful corrosion inhibitors for copper and copper alloys in acidic solutions [11]. It is believed that the inhibition is principally governed by the chemisorption of the urea on the copper surface; however, little is known about the structure of the adsorbed urea layer. Using a ph = 6 Na_2SO_4/urea solution, we observe a distorted hexagonal structure best described as a Cu(100)-c(2 x 4)-urea 1/2 monolayer structure at rest potential with the AFM. Upon sweeping the potential cathodic, we first observe a structural transition at -.6 V vs Hg_2SO_4 in which rows with a spacing of 0.43 ± 0.03 nm are observed, followed by desorption of the urea at -.9 V. At this potential, the bare Cu spacing of 0.26 nm is observed. Unfortunately, this process is not reversible, possibly due to complexation of urea with Cu ions in solution.

The structure of pyrazine on single crystal copper surfaces has been studied using LEED [12] and inverse photoemission [13]. The study of pyrazine on copper single crystals is motivated because Cu substrates are used as selective catalysts for reactions of N containing molecules [14]. In the pyrazine solutions, we observe a distorted hexagonal structure at open circuit; although, it is not as ordered as the urea overlayer. We have also imaged a row-like (2 x 1) structure at rest potential. Upon sweeping the potential cathodic, desorption of the pyrazine overlayer at -.6 V vs Hg_2SO_4 is observed revealing a spacing of 0.35 nm $\pm$ 0.02 nm. Upon sweeping the potential back positive, a large structure returns, but it is not as ordered as the original images obtained at open circuit.

In summary, we have shown that the AFM is a versatile instrument for monitoring *in situ* electrochemical experiments with atomic resolution. We observed the removal of the amorphous layer, preferential etching, and corrosion inhibition with BTA on polycrystalline copper; discovered an oxygen adlattice on Cu(100) in acidic media; and studied the adsorption and desorption of organic monolayers on Cu(100).

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