In-situ electrochemical scanning tunneling microscopy (ECSTM) was used to study the corrosion of naked and n-alkanethiol-modified Au(111) surfaces in basic CN⁻ solutions. In these studies, the potential of a naked Au electrode is poised at a sufficiently negative value that no electrochemical etching takes place. Small positive potential excursions from the initial potential permit observation of the initial stages of corrosion. The data indicate that initial corrosion of naked Au(111) occurs only at high energy defect sites such as pits and step edges. At slightly higher overpotentials, pitting occurs in the middle of terraces while continuing at step edges. At even higher overpotentials, etching occurs rapidly and uniformly and the surface becomes very rough. Results from this experiment are compared to those obtained after coating the Au surface with a hexadecan mercaptan self-assembled monolayer (SAM) to determine the extent to which the organomercaptan SAM inhibits Au corrosion. On the SAM-modified Au(111) surface, the onset potential for significant etching is shifted several hundred millivolts more positive than on the naked surface. Additionally, the rate of etching is significantly slower and the corrosion process is very different: etching initially occurs on terraces at defect sites within the monolayer instead of on step edges. We determined that potential, rather than time, is the primary factor that controls the rate of corrosion.

Introduction

We report an in-situ electrochemical scanning tunneling microscopy (ECSTM) study aimed at better understanding the surface chemistry of naked and hexadecan mercaptan-modified Au(111) in basic cyanide solutions. Because self-assembled monolayers (SAMs) of organomercaptans strongly adsorb to and passivate metal surfaces such as Au, Cu, and Ag, we thought these materials might form impervious mass-transfer barriers, thereby providing a simple solution to many corrosion-related problems on the coinage metals. To our knowledge this is the first in-situ examination of corrosion prevention with organomercaptan SAMs as protective coatings.

ECSTM has been a valuable tool for understanding electrochemical processes such as corrosion, deposition, and adsorption. High-resolution studies of molecular and atomic adsorbates, underpotential deposited (UPD) monolayers, and surfacet restructuring and annealing processes on Au substrates have been especially revealing. There are also a number of studies of the oxidation and reduction of Au(111) surfaces that correlate electrochemical data with STM images. Thus, although there have been many ECSTM studies of inorganic materials on metal surfaces, there have been surprisingly few in-situ studies of metals modified with organic monolayers and submonolayers.

Our results show that the presence of the SAM shifts the potential for significant corrosion of Au to potentials several hundred millivolts more positive than its onset on the naked surface. Moreover, the nature of the corrosion process on the naked and passivated surfaces is different. On unpassivated Au, etching begins at step edges and is quite rapid even at cathodic potentials. On the passivated surface etching begins at defects within the SAM, which mainly occur on terraces. Corrosion expands the original etch pits, but the rate is much slower than on the naked surface. We conclude that n-alkanethiol SAMs reduce the rate of corrosion, they are generally too fragile and contain too many defects to be useful for technological applications in highly corrosive environments.

Electrochemical dissolution of Au in alkaline solutions of CN⁻ is thought to proceed as shown in eqs 1–3:

\[ \text{Au} + 2\text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{AuCN}_2^- + 2\text{H}^+ + 2\text{OH}^- \]

\[ \text{AuCN}_2^- + 2\text{H}_2\text{O} \rightarrow \text{Au}^{2+} + 2\text{CN}^- + 2\text{H}_2 \]

\[ \text{Au} + \text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{AuCN}^- + 2\text{H}^+ + 2\text{OH}^- \]

...


\[
\begin{align*}
\text{Au} + \text{CN}^- & \rightarrow \text{AuCN}^\text{ads} \quad (1) \\
\text{AuCN}^\text{ads} & \rightarrow \text{AuCN}^\text{ads} + e^- \quad (2) \\
\text{AuCN}^\text{ads} + \text{CN}^- & \rightarrow \text{Au(CN)}^2_2 \quad (3)
\end{align*}
\]

McCarley and Bard studied the dissolution of Au(111) in dilute CN\textsuperscript-- solutions at open circuit potential and found that the very early stages of Au corrosion and to better understand how protective films act to reduce the rate of corrosion.

**Experimental Section**

**Chemicals.** Hexadecyl mercaptan H(CH\textsubscript{2})\textsubscript{15}CH\textsubscript{3} (Aldrich, 92%) was purified by distillation under reduced pressure. KOH (Johnson Matthey, ultrapure), KCN (Fischer, 99.9%), K\textsubscript{2}SO\textsubscript{4} (Aldrich, 99%), Na\textsubscript{2}HPO\textsubscript{4}, H\textsubscript{2}O (Mallinkrodt), and 100% ethanol were used as received. All electrolyte solutions were prepared with deionized water (Millipore, Milli-Q purification system, resistance \( \approx 18 \) M\textsubscript{Ω}cm).

**Preparation.** SAM-modified substrates were prepared as described previously\textsuperscript{31,36} Briefly, melting a Au wire (0.5-mm diameter, 99.99% purity, Refining Systems Inc., Las Vegas, NV) in a H\textsubscript{2}O\textsubscript{2} flame forms a 1.5–2.0 mm diameter ball at the end of the wire. The ball has a few elliptical Au(111) facets (long axis \( \sim 300 \) μm) on its surface that contain atomically flat terraces up to 1 μm wide. After fabrication, the balls are electrochemically cleaned and annealed by cycling them in 0.1 M HClO\textsubscript{4} between 0.2 and 1.5 V vs Ag/AgCl, 3 M NaCl, for 20 min electrochemically cleaned and annealed by cycling them in 0.1 M HClO\textsubscript{4} between 0.2 and 1.5 V vs Ag/AgCl, 3 M NaCl, for 20 min at these extreme potentials, and the surface no longer consisted of the well-defined Au\textsubscript{crystallites} shown in Figure 1e, indicates further corrosion of the surface. Figure 1f, which was obtained at \( 900 \) mV, where no noticeable dissolution occurred for up to 3.0 min, because it is still cathodically protected at this potential.

When the electrode potential is stepped to \(-850 \) mV, corrosion is very slow and occurs primarily at step edges (Figure 1b), although a few pits appear on the terraces. Figure 1c shows the surface at \(-800 \) mV, where etching proceeds rapidly but still originates from the step edges. At \(-700 \) mV (Figure 1d) the surface once again appears smooth, but this is an effect of the scanning tip, which we have noticed before, and it is not representative of the entire surface. To gain more representative images under these rapid etching conditions, we imaged a nearby region of the surface at \(-500 \) mV (Figure 1e). The surface looks much rougher and is characterized by numerous spherical Au crystals ranging from 30–70 nm in diameter. Figure 1f, which was obtained at \(-400 \) mV in the same region as Figure 1e, indicates further corrosion of the surface. The tip position was offset before capturing the images at \(-200 \) mV (Figures 1g and h) to minimize imaged distortion by the scanning tip. The Au surface continues to roughen at these extreme potentials, and the surface no longer consists of the well-defined Au\textsubscript{crystallites} shown in Figures 1e and f. Enhanced etching at more positive potentials is also reflected in the root-mean-square (RMS) roughness of the surface, which increases from 5.9 nm in Figure 1e to 13.8 nm in Figure 1h. Taken together, these images indicate that corrosion begins primarily on step edges and that the rate of corrosion and surface morphology are defined by the electrochemical potential of the surface.

**CN\textsuperscript-- Etching of Hexadecyl Mercaptan-Modified Au(111).** Figure 2 shows a series of \( 1 \) μm \( \times \) \( 1 \) μm images of a hexadecyl mercaptan-modified Au(111) surface at various potentials and in contact with an electrolyte solution identical to that used for the naked Au etching experiment just described. The Au substrate was introduced into the solution at \(-900 \) mV, rather than \(-1.0 \) V, to prevent electrochemical desorption of the mercaptan, which may occur at more negative potentials.\textsuperscript{37} Figure 2a shows that some etch pits have already formed at \(-900 \) mV. 

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mV even though we did not observe etching on the naked Au surface at this potential. Contamination of the nominally naked Au and the fact that the SAM-modified surface was at this potential almost 7 min longer could account for this observation. The etch pits are most likely points where defects in the monolayer permit intimate contact between CN$^-$ and the Au surface, which is a necessary condition for etching. The origin of the defects is uncertain. They may result from sites within the monolayer that did not contain a molecule at the time of SAM preparation, or the defects might result from molecular desorption during corrosion studies. This issue will be addressed in the future by examining the effect on etching when an excess of n-alkanethiol is present in the CN$^-$ solution and acting as a true corrosion inhibitor.

Unfortunately, we found that the STM tip sometimes damages the SAM surface upon extensive scanning, and

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Figure 3. Sequence of ECSTM images of hexadecyl mercaptan-modified Au(111) in 10 mM KCN + pH 11 buffered Na2HPO4. The electrode was poised at -700 mV for the time durations indicated in the figure. (a) E_{sub} = -900 mV. (b–g) E_{sub} = -700 mV.

therefore it is not always possible to obtain reliable information about surface passivation from exactly the same region of the surface. Rather, it was necessary to change the locations after each image in Figure 2. Although this situation is less than ideal, it is possible to identify some definite trends in the progression of the etch pits. As etching proceeds, the density, width, and depth of the pits increase. The pits indicated by the arrows in Figures 2a–c are all roughly the same diameter (31.4, 30.0, and 31.9 nm, respectively), but their depth increases with increasing etching time and potential (6.5, 13.6, and 24.0 Å, respectively). Because these three etch pits are all about the same width but increasing in depth, we believe that etching proceeds preferentially downward into the Au at low overpotentials (upto -700 mV). At more positive overpotentials, as in Figure 2d–g, the pits also etch outward at a significant rate. This result is consistent with our general conclusion that the SAM inhibits but does not prevent Au dissolution.

It is interesting to note that etching first appears mostly on the terraces for the SAM-coated surface. This is in contrast to the observation that on the naked Au surface etching first occurs along step edges. We think that the SAMs adsorb onto the Au at the step edges more strongly than the terraces because the former are higher energy sites. This observation is consistent with previous observations that SAMs passivate better on rougher Au surfaces and that other adsorbates that coordinate through metal–sulfur interactions bond preferentially at step edges. Alternatively, the SAMs may nucleate first at step edges and then grow outward into the terraces where defects in packing are present at phase–domain boundaries.

Parts d and e of Figure 2 show the surface at -600 mV and -500 mV, respectively. The number density of etch pits has increased from about 12/µm² in Figure 2c to 24/µm² in Figure 2e. They are also much wider (50–100 nm) and deeper (>35 Å) and have grown into very well-defined triangular and hexagonal shapes in Figure 2e, reflecting the symmetry of the underlying Au(111) surface. At -400 mV (Figure 2f) and -200 mV (Figure 2g), the pits coalesce as they continue to become wider and deeper.

When comparing the images of the SAM-modified Au surface to those obtained on the nominally naked Au, it is clear that the SAM decreases the corrosion rate considerably. This is demonstrated by comparing the RMS roughness values of images obtained at the same potential (Figure 2e–g with Figure 1e–g). Figures 1e and 2e were both obtained at E_{sub} = -500 mV and similar t_{tot}, but the RMS roughness on the naked Au is 5.94 nm compared to 0.86 nm on the SAM-modified Au. Similarly, the RMS roughness values for the naked Au at E_{sub} = -400 mV (6.20 nm) and -200 mV (13.7 nm) are much larger than those for the SAM-modified Au at the same potentials (3.15 nm and 4.19 nm, respectively).

As mentioned previously, it was not possible to reliably image the same area throughout the experiment because of the effect of the tip on the monolayer. The SAM is ~23 Å thick, and significant electron tunneling can probably only occur through distances of ~10 Å under the conditions used here; therefore, it is likely that the tip pushes through the monolayer while scanning. This probably disrupts the film, allows CN⁻ to penetrate, and thereby enhances etching under the tip. Figure 2h clearly demonstrates this effect. The eight approximately 1 µm × 1 µm areas marked are those scanned during this experiment. These features are 30–50 nm deep.

The images shown in Figure 2 convolute time and electrode potential. That is, both time and potential change in the sequence of images. To confirm our hypothesis that etching is governed principally by potential, we obtained a series of 900 nm × 900 nm images (Figure 3) of a hexadecyl mercaptan-modified Au(111) surface in contact with an electrolyte solution identical to that used for the two previously described experiments (Figures 1 and 2). The Au substrate was introduced into the electrochemical cell at -900 mV and then stepped to -700 mV, where images were captured at constant potential but at different times. The times given in the figure are referenced to the instant before the substrate is stepped to -700 mV. At -900 mV (Figure 3a) some etch pits have already formed, as in Figure 2a. The images in Figure 3b–f show that minimal etching occurs for up to 23.8 min at -700 mV, although most of the pits enlarge slightly and a few new pits form (indicated by the circles in Figure 3b and f). By comparing the topography of Figures 2g and 3f, which we obtained at roughly the same times (20.5 and 23.8 min, respectively) but very different potentials (-200 and -700 mV, respectively), we conclude that electrode potential is the dominant factor affecting the rate of corrosion.

Conclusions

We have demonstrated that the rate of Au(111) corrosion on an organomercurcapron-modified surface is slower than...
that on a nominally naked Au surface. However, the SAM-modified surface only passivates the surface well at quite negative potentials, and even then etching at defect sites within the SAM proceeds at a fairly rapid rate. The mechanism of corrosion on the naked Au(111) is different from that of the hexadecyl mercaptan-modified surface. Initially, the naked surface etches at high energy sites such as step edges while the SAM-modified surface etches at SAM-defect sites on terraces. The naked Au(111) then etches more rapidly and uniformly to yield circular crystallites; eventually the surface becomes very rough. The SAM-modified Au(111) etches out from defect sites to form triangular and hexagonal-shaped pits. The extent of etching on the SAM-modified surface depends primarily on substrate potential rather than time; at modestly positive potentials the rate of etching is slow. Overall, the SAM-modified surface is more resistant to corrosion for longer periods of time and at more positive (etching) potentials than the nominally naked surface.

We conclude that even under the best of circumstances, however, n-alkanethiol SAMs are insufficiently stable and contain too many defect sites to be technologically useful protective coatings for most applications. At the present time we are exploring the use of polymerizable SAMs41,42 as more effective passivating films.

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