

Nanometer-Scale Patterning of Metals by Electrodeposition from an STM Tip in Air

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In this paper we describe a method for electrochemically depositing nanometer-scale patterns of Ag from a scanning tunneling microscope (STM) tip in air. Scheme 1 shows that these experiments are carried out in two steps. First, patterns are prepared within a 2-nm-thick self-assembled monolayer (SAM) resist confined to a Au(111) substrate using an STM tip. Next, Ag deposited onto the STM tip prior to resist patterning is electrochemically deposited only into the previously formed patterns; no deposition occurs on the passivated portion of the resist.¹ These results are important because they demonstrate that an STM tip can be used to effect *area-selective* deposition via a faradaic electrochemical process in the absence of intentionally added solvent or electrolyte. The simplicity of the method and the unambiguous demonstration of faradaic electrochemistry are significant.

Deposition of metals onto surfaces from an STM tip has been demonstrated previously. For example, Au clusters were formed in ultrahigh vacuum (UHV) and air by field evaporation from an Au tip.^{2,3} Cu has been deposited onto Au via direct mechanical contact between the STM tip and substrate.^{4,5} Finally, Penner et al. electrodeposited metal clusters onto graphite in solution at STM tip-induced nucleation sites.^{6–8} SAMs have been patterned previously by photooxidation,^{9–11} stamping,^{12–16} STM,^{17–21} electron-beam lithography,^{20,22} and physical abrasion.^{23–25}

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(1) Ag is deposited onto the tip from a solution containing 1 mM Ag(ClO₄) and 0.1 M NaClO₄ by poisoning the potential of the Pt/Ir tip (working electrode) at -400 mV vs an Ag wire pseudoreference electrode for 30–45 s. The SAM is formed by soaking a Au(111) substrate in a 1–2 mM ethanolic hexadecanethiol solution for more than 24 h. All tip-induced etching and deposition were done with the STM in the constant-current mode in air or N₂ at 50–66% relative humidity.

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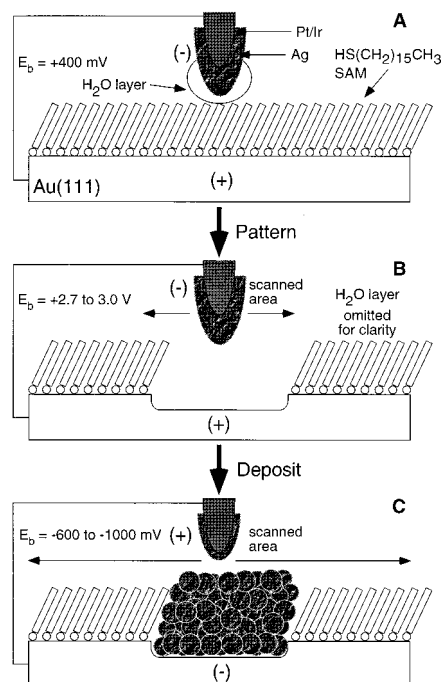
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Scheme 1



Part A of Scheme 1 shows that when the substrate bias (E_b) is +400 mV with respect to the tip, the SAM and the Ag on the tip are stable. Part B illustrates the lithography step in which a well-defined pattern is etched into the SAM by applying a positive bias ($E_b = +2.7$ to $+3.0$ V) to the surface while scanning four times at 40 Hz. A few layers of the Au are also removed during this step. We previously showed that STM-induced SAM patterning is a consequence of a faradaic electrochemical process, which only occurs in humid environments.¹⁹ Others have also speculated that surface modification of graphite^{26–28} and titanium^{29–31} with an STM tip in air were due to chemical^{27,28} or electrochemical processes.^{26,29–31} Finally, part C of Scheme 1 shows that deposition of Ag from the Pt/Ir tip onto the pattern in the SAM occurs by scanning a relatively large fraction of the surface at 3–4 Hz with E_b between -600 and -1000 mV. In this range Ag oxidizes at the tip and redeposits *only* on the exposed Au. Importantly, Ag does not deposit on the unperturbed, highly ordered regions of the SAM. Electrodeposition is facilitated by water condensation between the tip and substrate, which completes the two-electrode nanoelectrochemical cell.³²

Figure 1 shows a series of 500 nm × 500 nm STM images corresponding to Scheme 1. Images were obtained in N₂ containing between 58% and 66% relative humidity. Parts A and B of Figure 1 were obtained before and after patterning,

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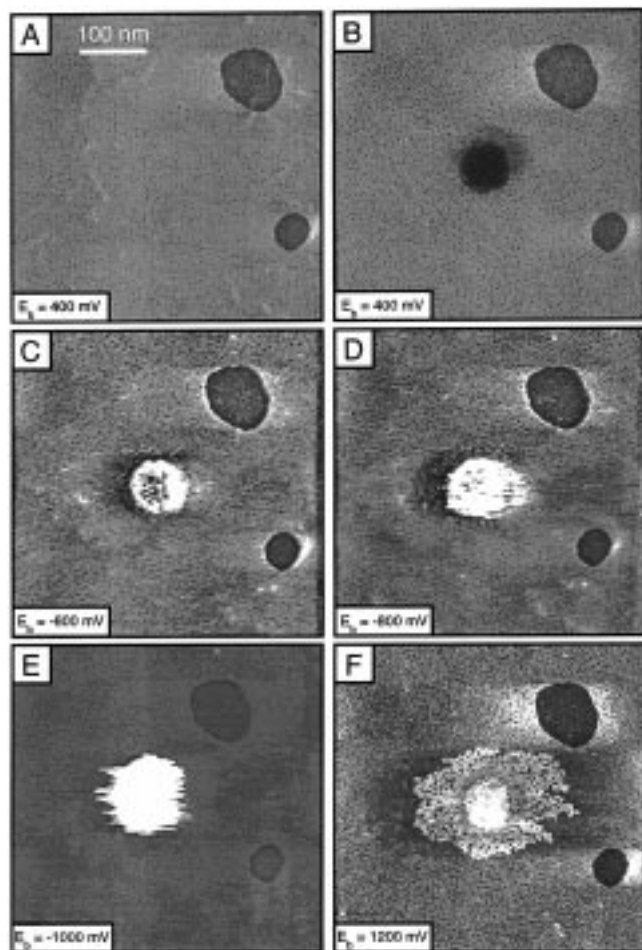


Figure 1. A series of $500 \text{ nm} \times 500 \text{ nm}$ STM images of hexadecanethiol-modified Au(111) obtained in N_2 (relative humidity 58–66%). (A) Before STM-induced SAM removal. (B) After STM-induced SAM removal. The dark square is the patterned region where the SAM and a few Au layers have been removed by scanning a $50 \text{ nm} \times 50 \text{ nm}$ region four times at 40 Hz with the substrate biased at $+2.7 \text{ V}$. (C)–(E) Electrochemical deposition of Ag from the STM tip into the $50 \text{ nm} \times 50 \text{ nm}$ pattern at negative biases of (C) -600 mV , (D) -800 mV , and (E) -1000 mV . (F) Most of the Ag deposit is removed at positive biases ($+400$ to $+1000 \text{ mV}$) and presumably redeposited onto the tip. Part F shows the surface after E_b is reversed ($+1200 \text{ mV}$). Some Ag within the pattern and a monolayer of Ag surrounding the pattern cannot be removed at biases up to at least $+1200 \text{ mV}$. This enhanced stability, compared to the vast majority which is easily removed, suggests that this “monolayer Ag” resides beneath the SAM.^{34–38} We are

respectively, a $50 \text{ nm} \times 50 \text{ nm}$ region of the SAM at $E_b = +2.7 \text{ V}$. The dark square in part B is the pattern. Ag deposits into the pattern when E_b is held at sufficiently negative potentials (parts C–E of Figure 1). At low overpotential ($E_b = -600 \text{ mV}$, part C), Ag deposits at the edge of the pattern consistent with flux enhancement at electrode edges.³³ At -800 mV (part D), the amount of Ag deposited increases. At -1000 mV (part E), the deposit grows larger ($\sim 27 \text{ nm}$ tall). Most of the Ag in part E is removed at positive biases ($+400$ to $+1000 \text{ mV}$) and presumably redeposited onto the tip. Part F shows the surface after E_b is reversed ($+1200 \text{ mV}$). Some Ag within the pattern and a monolayer of Ag surrounding the pattern cannot be removed at biases up to at least $+1200 \text{ mV}$. This enhanced stability, compared to the vast majority which is easily removed, suggests that this “monolayer Ag” resides beneath the SAM.^{34–38} We are

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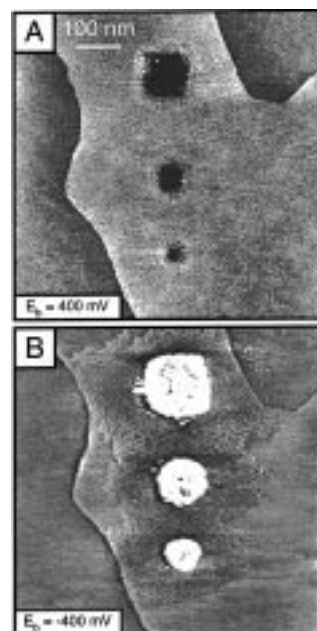


Figure 2. (A) $100 \text{ nm} \times 100 \text{ nm}$, $50 \text{ nm} \times 50 \text{ nm}$, and $25 \text{ nm} \times 25 \text{ nm}$ patterns formed on a hexadecanethiol-modified Au(111) surface in humid air (relative humidity 50–55%) by STM lithography. (B) Same surface as (A) after Ag from the STM tip is deposited into the patterns. A monolayer of Ag, which has diffused beneath the SAM, surrounds the three patterns. The z -scale is (A) 2 nm and (B) 15 nm .

not certain why Ag remains within the pattern, but perhaps the SAM reorganizes to stabilize this material by capping it.⁶ In experiments performed more quickly than those shown here, practically all the Ag was removed from the patterns at positive biases. This suggests that the Ag becomes more stable with time, which is consistent with reorganization of the SAM. Importantly, it is not possible to define the pattern in the resist, nor is it possible to deposit a significant amount of metal at low relative humidity.

Figure 2 demonstrates that various sizes of metal patterns can be fabricated. Part A shows three square patterns formed in the SAM, which are nominally 100 , 50 , and 25 nm on a side. Part B was obtained at $E_b = -400 \text{ mV}$ (after the entire image area was scanned twice with E_b between -400 and -600 mV), showing again that Ag deposits only on the exposed Au (note, however, that the monolayer Ag is still observed).

In summary, we have demonstrated controlled, faradaic electrochemistry in humid atmospheres using a two-electrode nano-electrochemical cell in which one electrode is an Ag-coated STM tip and the others are Au electrodes having critical features as small as 25 nm .³⁹ The key finding is that it is possible to perform rapid, high-resolution electrochemical deposition of metals within water nanodroplets that condense onto surfaces from humid air. The STM tip is multifunctional: it is used for lithography, deposition, and imaging. There is relevancy of this method to practical applications of lithography and presently unresolved fundamental issues involving electrochemical processes on nanoscopic length scales.

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