Atomic layer etching (ALE) processes are critically important for the precise tailoring of materials and structures in nano-electronics. For atomically precise etching of metals, plasma-based approaches are available which generate nonvolatile etch products thereby contaminating the metal surface. Hess and co-workers have developed a two-step process that etches copper (Cu) films with chlorine and hydrogen plasmas at low temperature (below 20 °C). This process generates a volatile etch product that minimizes surface contamination. In most plasma-based approaches, the metal etching rate is higher than 1 nm per etch cycle. Such high etch rates do not provide the requisite atomic-scale control over etching required in ALE. While plasma-assisted ALE processes for oxides are mature, ALE of metals is still in its infancy and numerous development efforts are currently underway.

In this communication, we report on an electrochemical approach for the layer-by-layer etching of Cu with atom-scale control over the etching rate. The two-step approach consists of surface-limited electrochemical sulfidization of Cu followed by selective etching of the resulting copper sulfide (Cu2S) monolayer. Surface-limited sulfidization has been used previously for fabricating semiconductors. Feasibility of the electrochemical ALE of Cu is demonstrated and process performance parameters (etch rate, surface roughness) are characterized.

Cyclic voltammetry and chronoamperometry.—Surface-limited sulfidization of Cu was studied using cyclic voltammetry (CV) performed using a three-electrode cell consisting of a sputter-deposited Cu substrate as the working electrode, a platinum (Pt) wire as the counter electrode, and a saturated Ag/AgCl reference electrode (Fisher Scientific). The electrolyte contained 0.1 M potassium hydroxide (KOH, Fisher Chemical) and 0.5 mM sodium sulfide (Na2S, Sigma-Aldrich) and was prepared using de-aerated DI water. A VersaSTAT 3 potentiosat was used for all electroanalytical measurements. All potentials reported below are referenced to the standard hydrogen electrode (SHE). The Cu substrate was rinsed first with ethanol and then with DI water before drying with N2. The cleaned substrate was immersed in 2 M sulfuric acid (H2SO4, Fisher Scientific) for 1 min to remove surface Cu oxides. A potential of −1.2 V vs. SHE was applied for 100 s to further reduce Cu oxides before the working electrode potential was scanned (at 20 mVs) from −1.2 V to −0.6 V vs. SHE and back. Chronoamperometry was performed at an applied potential of −0.75 V vs. SHE.

Electrochemical atomic layer etching.—Electrochemical ALE (e–ALE) of Cu was performed on a Cu substrate fabricated using electrochemical atomic layer deposition (e–ALD) detailed elsewhere. Cu e–ALD for 10 cycles was performed on a sputter-deposited Cu substrate to form a ~2 nm Cu film with RMS surface roughness of ~0.2 nm. Surface-limited sulfidization of Cu was performed at −0.75 V vs. SHE in an alkaline Na2S-containing electrolyte (composition reported above). The substrate was then removed from the sulfidization electrolyte, rinsed with de-aerated DI water, dried under N2, and transferred immediately to the etching electrolyte. The Cu2S layer formed during sulfidization was selectively etched by immersion in de-aerated 2 M HCl for 30 s. This process did not etch the underlying Cu. After selective etching, the Cu substrate was again rinsed with de-aerated DI water and dried under N2 before it was transferred back to the sulfidization electrolyte. The sulfidization and selective etching steps were repeated to achieve layer-by-layer removal of Cu with atomic precision. The surface-limiting signature of the sulfidization step was confirmed by performing e–ALE on sputter-deposited Cu substrates.

Anodic stripping coulometry.—After e–ALE was performed, the Cu remaining on the electrode was electrochemically stripped in 50 mM H2SO4 by first scanning the electrode potential from OCP (~0.4 V) to 0.6 V vs. SHE at 20 mV/s and then holding the potential at 0.6 V until the stripping current dropped to zero. Since hydrogen evolution was thermodynamically prohibited at 0.6 V, the stripping current measured was solely due to Cu dissolution. The integrated stripping charge density provided via Faraday’s law the mass of Cu remaining after various number of e–ALE cycles. Substrate RMS roughness before and after e–ALE was measured using Dimension 3100 (Veeco Digital Instruments) AFM.

Results and Discussion

Surface-limited sulfidization of copper.—CV of a Cu substrate in an electrolyte containing 0.5 mM Na2S and 0.1 M KOH (pH = 13.2) is shown in Fig. 1a (blue). The background CV without Na2S in the electrolyte is also shown (red). The positive limit of the potential scan was set at −0.6 V to prevent surface CuO formation. Hydrogen evolution was observed at potentials negative with respect to −1.0 V. In the anodic scan direction, an oxidation peak was observed near −0.68 V corresponding to bulk CuO film formation. A relatively small oxidation peak located at −0.98 V corresponding to surface-limited sulfidization of Cu was also observed consistent with prior reports of sulfur adlayer formation on Cu at such potentials. In the cathodic (reverse) scan direction, a peak appeared at −0.93 V indicating reduction of bulk CuS.

To demonstrate surface-limiting characteristics of the proposed sulfidization scheme, we performed chronoamperometry on Cu...
Figure 1. (a) Cyclic voltammogram of a Cu substrate in 0.5 mM Na₂S + 0.1 M KOH (blue) and in Na₂S-free solution of 0.1 M KOH (red). Scan rate was 20 mV/s. (b) Current density (left axis) and integrated charge density (right axis) during sulfidization at –0.75 V vs. SHE.

at –0.75 V. This potential is anodic with respect to the small oxidation peak at –0.98 V but cathodic with respect to bulk Cu₂S formation at around –0.68 V (Fig. 1a). As seen in Fig. 1b, after an initial unsteady state behavior which can be attributed to transient diffusion and electro-nucleation processes, the current eventually (after ∼35 s) decays to nearly zero. This indicates self-terminating behavior once the electrode surface is covered with a monolayer of Cu₂S. The integrated charge density associated with this self-limiting surface sulfidization was \[ Q_{\text{sat}} \approx 300 \ \mu \text{C/cm}^2 \] and in agreement with previous reports. Assuming surface molar density of Cu(111) to be about \( N = 2.96 \ \text{nmol/cm}^2 \), the measured charge density \( Q_{\text{sat}} \) corresponds to a Cu oxidation state of \( n = Q_{\text{sat}}/NF = 1.05 \) where \( F \) is the Faraday’s constant. This suggests the formation of a monolayer of Cu₂S (\( x \approx 2 \)) on Cu.

Electrochemical atomic layer etching (e–ALE) of copper.—A schematic representation of the Cu e–ALE sequence is provided in Fig. 2. In this sequence, surface-limited sulfidization of Cu and selective etching of the formed Cu₂S by HCl are repeated sequentially:

(i) **Surface-limited sulfidization of Cu**: In Na₂S-containing electrolytes, solution-phase equilibrium favors formation of hydrosulfide species (HS⁻ₐq). At suitable electrode potentials, i.e.,

\[ 2 \text{Cu} + [\text{HS}^-]_{\text{aq}} \rightarrow [\text{Cu}_2\text{S}]_{\text{solid}} + [\text{H}^+]_{\text{aq}} + 2\text{e}^- \quad [1] \]

When the surface Cu atoms are oxidized completely to Cu₂S, Reaction 1 self-terminates as observed in Fig. 1b.

(ii) **Selective etching of Cu₂S by HCl**: Following step (i), the formed Cu₂S can now be etched selectively using HCl as the etchant because the presence of chloride ions facilitates formation of stable aquo-chloro-complexes with Cu⁺ from the Cu₂S layer. During etching, the following complexation chemistry proceeds spontaneously:

\[ [\text{Cu}_2\text{S}]_{\text{solid}} + 6[\text{Cl}^-]_{\text{aq}} \rightarrow 2[\text{CuCl}_2^-]_{\text{aq}} + [\text{S}^-]_{\text{aq}} \quad [2] \]

The chloro-complex formed in Reaction 2 may also exist as CuCl₂⁻ as described elsewhere. Note that, in the absence of dissolved oxygen, Cu⁰ cannot be oxidized. Thus, as Cu₂S is etched via Reaction 2, the exposed underlying Cu remains protected. When the surface Cu₂S is entirely removed, Reaction 2 is also terminated and the subsequent e–ALE cycle begins.

The e–ALE sequence described above was characterized by electrochemical techniques. First, the surface-limited sulfidization signature, i.e., the decay of the oxidation current to zero in ∼35 s, is confirmed via chronoamperometry during step (i) of the 1st–5th cycles of e–ALE (Fig. 3). During each e–ALE cycle, the integrated sulfidization charge density (Fig. 3 inset) remained fairly constant.
Figure 4. Normalized Cu stripping charge density \(Q/Q_0\) is a linear function of the number of e–ALE cycles with a slope corresponding to a Cu etch rate of \(\sim 10\%\) (equivalent to \(\sim 1\) Cu monolayer) per e–ALE cycle. The inset shows AFM line scans of the Cu electrode before and after 6 cycles of e–ALE.

(except for the 1st cycle) indicative of quite repeatable sulfidization and etching steps. Anodic stripping coulometry was also performed to determine the amount of Cu remaining after various e–ALE cycles. The integrated Cu stripping charge density \(Q\) after various e–ALE cycles normalized to the charge density of the original un-etched Cu electrode prepared by e–ALD \(Q_0\) is shown in Fig. 4. It is observed that \(Q/Q_0\) decreases linearly with increasing e–ALE cycles. From the slope of this curve, an equivalent etch rate was computed to be 0.103 (10.3\%) per etch cycle. Since the original un-etched electrode was prepared by depositing 10 atomic layers of Cu via e–ALD,5 one expects \(\sim 10\) cycles of e–ALE to be required to etch this film completely which is consistent with the measured etch rate of \(\sim 10\%\) per e–ALE cycle. This suggests an etch rate of \(\sim 1\) Cu monolayer per e–ALE cycle.

Table I shows surface RMS roughness (from AFM) after various e–ALE cycles. The RMS roughness of the original un-etched Cu surface was \(\sim 0.2\) nm.5 After 4 and 6 cycles of e–ALE, the measured RMS roughness of the electrode remained in the \(\sim 0.2\) nm range and thus relatively unchanged compared to the un-etched Cu surface. In control experiments, Cu samples subjected to step (ii) but not to step (i) exhibited significant roughness amplification. These observations confirm that e–ALE facilitates atomic layer-by-layer etching of Cu with negligible surface roughness amplification.

### Conclusions

Feasibility of the electrochemical atomic layer etching of Cu is demonstrated. The e–ALE process consists of two steps: (i) surface-limited sulfidization of Cu to form Cu3S followed by (ii) selective etching of Cu3S in HCl. The e–ALE process provides an etch rate of close to 1 Cu monolayer per e–ALE cycle. Furthermore, substrate RMS roughness is not amplified during e–ALE suggesting a layer-by-layer etching mode. The e–ALE approach presented herein opens new avenues for atomically precise tailoring of surfaces in advanced nano-electronics.

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| Number of e–ALE cycles | Average RMS roughness | RMS roughness [min, max] |
|------------------------|-----------------------|--------------------------|
| 0 (un-etched)          | 0.22 nm               | [0.19, 0.23] nm          |
| 4                      | 0.21 nm               | [0.19, 0.25] nm          |
| 6                      | 0.23 nm               | [0.15, 0.28] nm          |