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Developing Methods for Pattern Transfer in Photoelectrochemical Lithography

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Developing Methods for Pattern Transfer in Photoelectrochemical Lithography

An Honors Thesis submitted in partial fulfillment of the
requirements for Honors Studies in Chemistry

by Ashlyn DesCarpentrie

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Acknowledgements

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Abstract

The microprocessor industry has historically been driven by the goal of shrinking devices. To create features small enough to fit on such devices, photolithography has conventionally been used in the micropatterning of noble metal surfaces. Photolithography is a complicated and expensive process that involves a cleanroom, metallization processes, and photoresist. While this investment makes sense for high revenue applications, a number of microelectronic devices do not require nanometer-scale patterned features. Examples of such applications include specific types of antennae, sensing electrodes, and photocatalysts. Photolithography for these devices is thus too costly in both money and energy. The Coridan lab has developed an easier, photoelectrochemical method of patterning gold by selectively electrodepositing gold on a photodoped cuprous oxide (Cu_2O) electrode. However, most of the applications for microfabricated noble metal surfaces do not work if the metal pattern is on a Cu_2O electrode. A method was developed to selectively deposit small features of gold using a nail polish (nitrocellulose) mask and to chemically isolate the electrodeposited gold pattern off the electrode while maintaining the integrity of its structure, so that it can be placed onto a more helpful substrate. Hydrophilic hydrogel overlayers were found to serve as a medium for etchant to selectively remove Cu_2O and hold onto the gold features left behind.

Introduction

I. Background

Microfabrication of patterned noble metal surfaces has demonstrated utility in a wide variety of applications ranging across microelectronics, electrochemical sensors, miniaturized antennae for communication or sensing devices, semiconductor devices, and electrocatalysts.[1] Gold (Au) has been proven a particularly valuable material for these applications due its high thermal and electrical conductivity, corrosion and oxidation resistance, and ability to be chemically functionalized.[2] The conventional methods to fabricate patterned Au interfaces use photolithography.[3] This process requires the removal of all particulate matter on the substrate to develop a perfectly clean and flat wafer. Then spin-coating is used to create a thin, uniform layer of photoresist on the wafer, which is exposed to UV light through a chromium mask of the desired pattern. Areas of the resist that are under the transparent parts of the mask become more soluble and are washed away with developer solution, leaving behind the desired pattern which undergoes baking to remove remaining solvent. The microprocessor industry has historically been the driving force for improving these photolithography methods, as demonstrated by Moore’s Law which notes that the number of transistors in a computer microprocessor has doubled every two years since 1970.[4] The goal to make small features using photolithography requires an expensive cleanroom, nanoscale photomasks, metallization processes, and polymer photoresist chemistry. While this effort and investment makes sense for high revenue applications, such as fabricating a computer microprocessor, it is too costly both monetarily and in terms of energy and material inputs for many of the applications discussed above. Certain types of antennae, sensing electrodes, and electrocatalysts could benefit from noble metal patterning technology but do not need the nanometer-scale patterned features, and therefore do not necessarily justify the capabilities of conventional photolithography. Therefore, it is of interest to develop a cheaper, energy and atom-efficient method of microfabricating noble metal patterned surfaces that can be performed outside the cleanroom.

II. Motivation and Applications

Flexible electronics are a rapidly growing market as the demand for conformable and wearable technology grows. The idea is to mount electronic circuits on thin, flexible substrates, typically a plastic like polyether ether ketone (PEEK).[5] Over the past few decades, flexible electronics research has been focused on the goals of sustainability, scalability, and low-cost manufacturing. A key to these efforts is the development of a low-cost, energy-efficient method of creating the noble metal features used for interconnections.[6] Below we review some of the notable applications.

Flexible electronics have gained significant attention for their applications to the medical field.[7] For example, significant work has been done to develop skin-like sensor patches for monitoring blood glucose for diabetes patients.[8] This system consists of a biocompatible paper battery that is attached to the skin and drives glucose transport from the interstitial fluid. Then, a thin, flexible biosensor that conforms to the skin surface is placed on top and electrochemically measures the glucose concentrations. Further work is being done to develop a temporary glucose monitor tattoo, which utilizes even larger features for electrochemical glucose measurements.[9] The biosensors in both devices utilize noble metal features, and could thus benefit from a low-cost, benchtop method of patterning noble metals.

Another exciting innovation in flexible electronics is the development of flexible antennae.[10] Antennae are frequently utilized on rigid substrates for telecommunication devices, but the potential for communications with bendable electronics draws attention to the possibilities of flexible antennae. Possible applications for this type of technology include wearable devices integrated into textile substrates for communication and tracking in sports, gaming, and the military.[11] However, the intense requirements of such devices, like high tolerance to degradation while remaining conductive and efficient, lead to challenges in fabrication. Conductive material and substrate must be carefully selected. Noble metals are both durable and highly conductive, providing an excellent source of conductive materials for the features on flexible antennae.

A broader application of noble metal patterned surfaces is the optoelectronics industry, in which light and electrical currents are harnessed for energy conversion, an important topic in sustainable chemistry.[12] Specifically, plasmonic noble metal structures have recently attracted research for applications in solar cells, photodetectors, and light-emitting diodes (LED) due to their ability to guide and manipulate light, subsequently enhancing the efficiency of these devices. Optimizing the size and shape of the noble metal features is key to this improved performance, thus attention should be directed to energy-efficient fabrication techniques like those outlined here.

Previous Work

I. Cu_2O Electrodeposition

The Coridan lab has developed an electrochemical, benchtop method of patterning Au that begins with a cuprous oxide (Cu_2O) substrate. The Cu_2O thin films are prepared via electrodeposition, a low-cost and versatile electrochemical method of coating conductive surfaces with metal and metal oxides by passing electrical current through the system. Typically, a classical three-electrode configuration is used, consisting of a working electrode where the deposition takes place, a reference electrode of known potential against which the potential at the working electrode is measured, and a counter electrode to complete the electrical circuit. This configuration is placed in an electrolyte solution containing the metal ions to be deposited. Using an electronic instrument called a potentiostat, the working electrode is held at a certain electrical potential while current is measured against time. In cathodic electrodeposition, negative potential at the working electrode reduces the metal ions in solution so that they deposit onto the working electrode surface as metal or metal oxides, depending on the specific experimental conditions (pH and potential).

Cu_2O is easily electrodeposited by cathodic reduction of copper (II) lactate ions in alkaline solutions onto fluorine-doped tin oxide (FTO) coated glass at a potential of -0.4 V vs. Ag/AgCl and pH=10:

$$2Cu^{2+} + 2e^- + 2OH^- \rightarrow 2Cu_2O + H_2O \qquad (1)$$

The choice of pH and potential is based on a phase diagram called a Pourbaix diagram, which maps at which pH and potential different redox species are thermodynamically stable and determines which oxidation state of ions in solution will deposit on the working electrode.

Figure 1 is the Pourbaix diagram for Cu in copper sulfate solution. Inside the area designated by the two orange dotted lines, water is thermodynamically stable. Outside of these lines, it will be reduced to hydrogen or oxidized to oxygen. As seen in the figure, the window for Cu_2O deposition is narrow and requires alkaline pH. This is achieved by stabilizing the copper sulfate ions with lactic acid, so that the solution can be titrated with NaOH to bring it to basic pH required for Cu_2O to deposit.

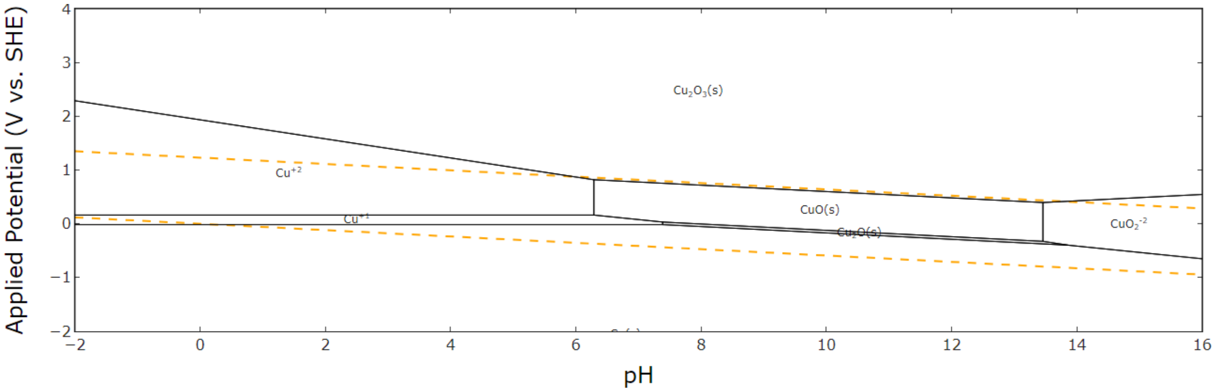

Figure 1: Pourbaix phase diagram for Cu at standard conditions, generated from materialsproject.org.

The thin films resulting from Cu_2O electrodeposition at the above conditions are transparent with a yellow to orange tint, depending on the thickness of the layer. However, when the electrodeposition process takes place with a 455 nm LED light directed at the working electrode surface (Figure 2), the exposed areas turn black rather than the normal yellow-orange color. The mechanism for this color change was found to be the excitation of electrons at the Cu_2O surface by the incoming photons from illumination, which allows for the reduction of copper in Cu_2O from a 1+ oxidation state to a 0 oxidation state, or copper metal.[13] Rather than a uniform distribution of Cu, the Cu nanoparticles irregularly dope the Cu_2O composite. This "photodoping" makes a thin film that can absorb nearly all non-reflected photons across the visible spectrum, hence the film's black color. In contrast, the regular yellow-orange Cu_2O can only absorb light with wavelengths smaller than 550 nm. The level of photodoping, and consequently the level of blackened color, increases with increasing illumination intensity (Figure 3.b).

The chemical distinctions and resulting color difference between regular and photodoped Cu_2O can be exploited through the use of a laser-printed transparent patterned photomask. By placing the photomask between the LED light and the working electrode, only the areas of the electrode behind the holes in the photomask are exposed to illumination. Thus, the pattern of the photomask is photodoped onto the Cu_2O electrode (Figure 3.a)

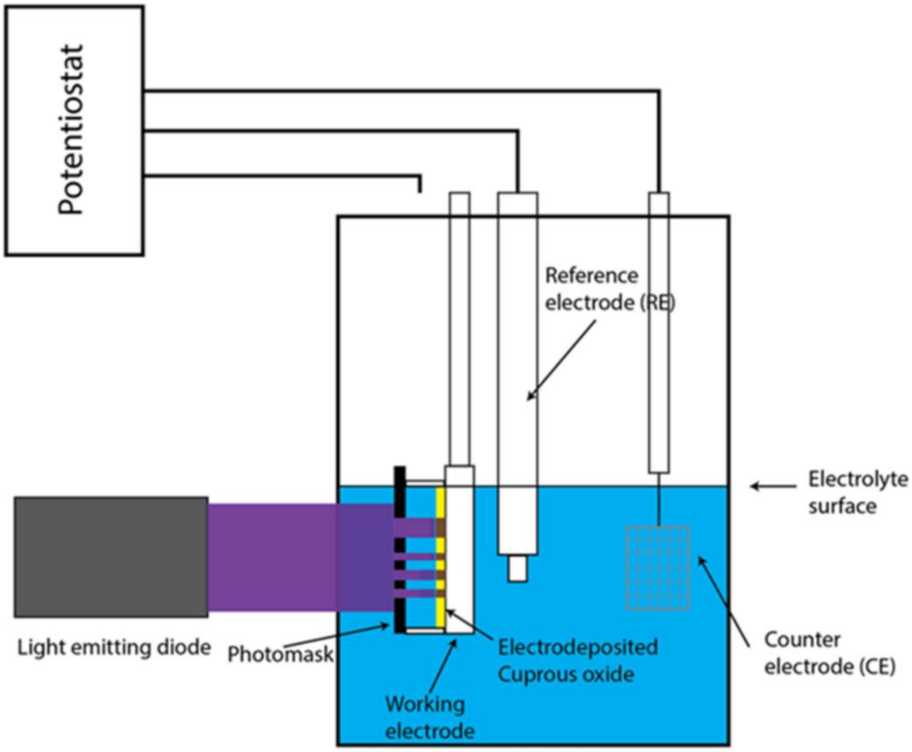

Figure 2: Experimental setup for photoelectrodeposition of Cu_2O onto FTO with use of a photomask.

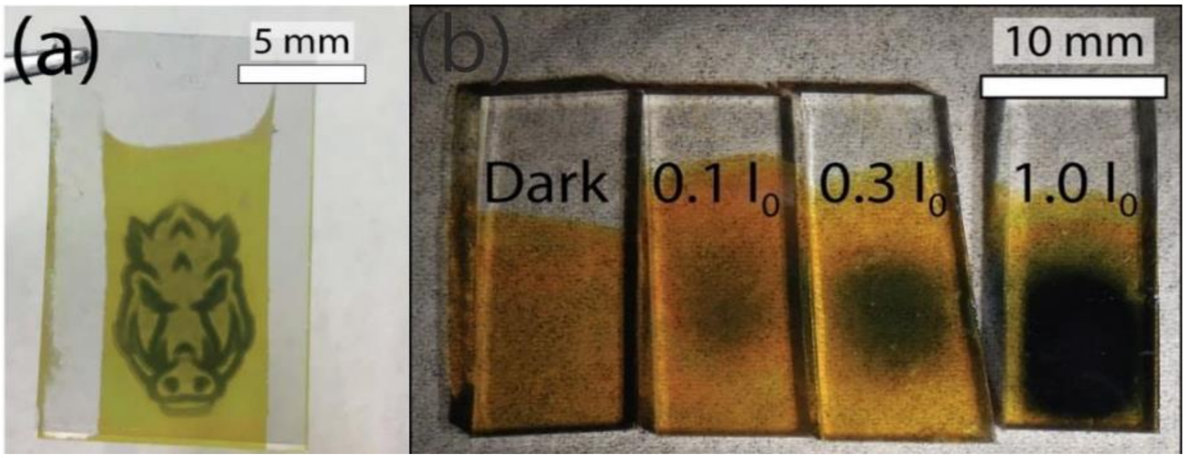

Figure 3: (a) Electrodeposited pattern using a razorback-patterned photomask between the electrode and the 455 nm light during growth. The black areas are photodoped Cu_2O, and the yellow areas are regular Cu_2O. (b) Cu_2O films demonstrating increasing levels of photodoping (increasing levels of black color) due to increasing intensity of illumination (from left to right) during electrodeposition. From Lowe, et al. 2017.[13]

II. Electrochemical Patterning of Au

It was previously found that regular (non-photodoped) Cu_2O can act as a substrate for direct Au electrodeposition in a tetrachloroaurate solution at pH=10 and at a potential of -0.5 V vs. Ag/AgCl. When this process occurs, it is observed that the Cu_2O substrate becomes plain Cu metal underneath the Au areas, suggesting that the mechanism allowing for Au electrodeposition involves the complete reduction of Cu^{1+} in Cu_2O to Cu^0. However, Au electrodeposition can additionally be driven by local heating. If red light at 660 nm is shown onto a Cu_2O electrode that has been patterned with photodoped areas, only the black areas of the electrode, which can absorb broadband illumination, will be able to absorb the light. This consequently generates selective local heating in the pattern. Implementing this localized photothermal heating into an Au electrodeposition process with a patterned Cu_2O electrode as the working electrode substrate directs the Au ions to the heated areas, and the metal Au deposits mainly onto the pattern (Figure 4). Hence, a pattern of gold is electrodeposited on top of the same pattern of photodoped Cu_2O, giving a cheap, efficient alternative to conventional photolithography for the patterning of gold.

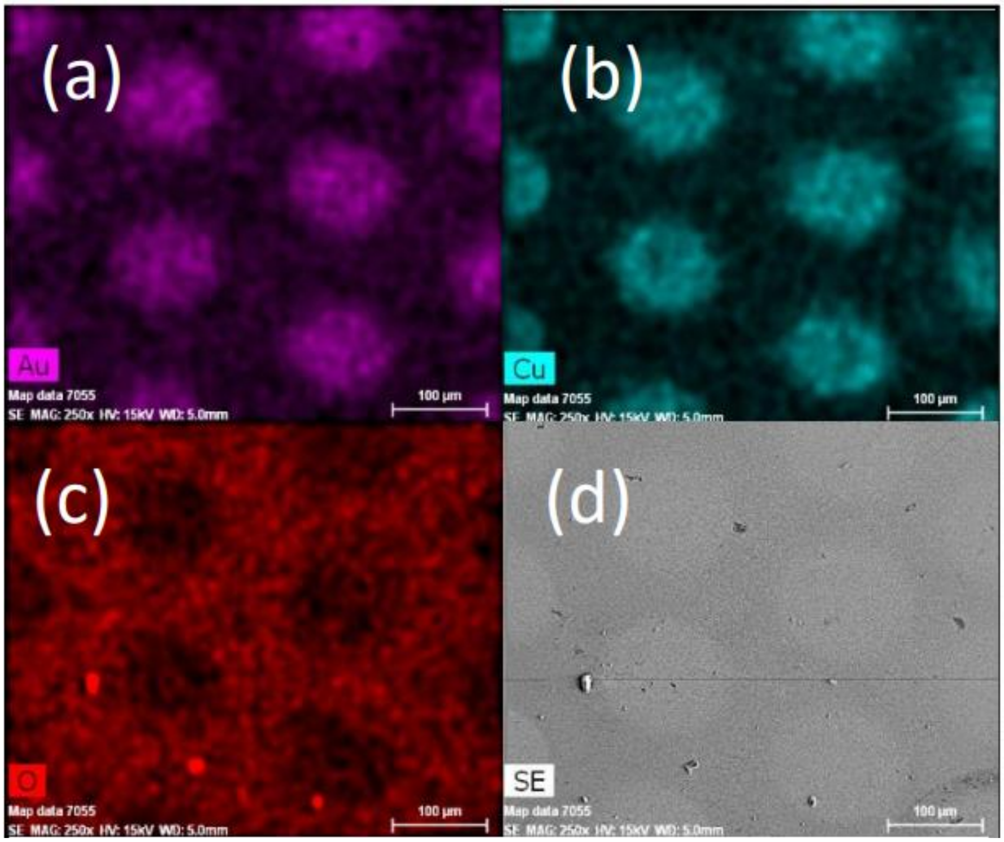

Figure 4: Scanning electron x-ray spectroscopy micrograph showing the location of (a) Au, (b) Cu, and (c) O on a patterned Cu_2O electrode made using localized photodoping process. Brightly colored areas correspond to higher density of the element analyzed. Au was electrodeposited under illumination of red light. Image (d) is the SEM scan of the electrode.

Almost all the applications for microfabricated gold surfaces previously discussed would not work with the gold pattern on a Cu_2O electrode, as the substrate's conductivity would be an interference for the Au pattern's functionality. The questions remaining from this previous work therefore have to do with the improving the applicability of this electrochemical noble metal patterning method: can we rework the above process in such a way that the Au features can ultimately be decoupled from the Cu substrate they are currently stuck to? Are there chemical reagents that can isolate Au from all Cu-containing compounds in the substrate? How can we keep the Au features intact while chemically isolating them so that they can be moved to more useful surfaces? Answering these questions would lend the above techniques the scalability and generalizability that would allow them to be useful to the discussed applications.

Generalized Au Electrodeposition and Pattern Transfer

To address the challenges discussed above, I propose a method to selectively electrodeposit controllable, larger-scale features of Au onto Cu_2O and to remove the Au features from the growth electrode while maintaining its structure and transfer it to a more helpful substrate, such as a silicon wafer. This method employs the use nail polish as a Au electrodeposition mask and a hydrogel "stamp" that serves as a medium for an etchant solution which selectively dissolves Cu-containing species, but not Au. We hypothesize that when this swollen hydrogel is placed on the Au-Cu/Cu_2O composite, the hydrogel acts like a "solid etchant" while the Cu/Cu_2O becomes a sacrificial release layer that is intentionally dissolved away, leaving the Au feature with the polymer surface. This process requires fundamental investigations of the mechanical interactions at the Au-hydrogel interface and at the Au-Cu/Cu_2O

interface on the electrode. We want to answer questions such as: what are the physical and chemical interactions happening at the Au-Cu/Cu_2O and Au-hydrogel interfaces? Which interactions are stronger? How can we manipulate those interactions to isolate the Au pattern?

I. Au Electrodeposition with Nail Polish Mask

When developing a more generalized benchtop method of Au electrodeposition, we first experimented with an adhesive called electroplating tape. Electroplating tape is a vinyl tape that is resistant to most chemicals used in the electrodeposition process and is able to withstand rugged conditions, such as high temperatures. It is used in current experiments to mark off areas of the working electrode where deposition is to take place, because it can remain adhered to FTO-coated glass slides even in the 60°C solutions used. For this reason, electroplating tape was used to mark off a small square on a Cu_2O electrode with the intent of Au only depositing in the square. However, it was found that the tape did not adhere well to the Cu_2O substrate while submerged in 60°C Au electrodeposition solution. Solution leaked under the edges of the taped-out square and resulted in blotchy, non-uniform films, and occasionally the entire tape mask slipped off during the experiment. Alternatively, it was found that nail polish acts as an excellent Au electrodeposition mask and remains stably coated to the Cu_2O substrate throughout the entire experiment.

The major component of nail polish is a polymer called nitrocellulose, a common ingredient in paints, adhesives, and coatings. Nitrocellulose is a nitrated ester of cellulose with various nitrogen and cellulose content, depending on how it is prepared.[14] Its notable durability, toughness, and adhesion to natural nails make it an ideal film former for cosmetic coating products like nail polish. For the purposes of these experiments, nail polish is not a conductive material, does not dissolve in the Au electrodeposition solution, and shows excellent adhesion to

Cu_2O films in the experimental conditions. Additionally, it can be easily removed in acetone. For these reasons, nail polish was used to paint around a 0.5 cm x 0.5 cm square on a Cu_2O electrode so that only the small square would be exposed to electrodeposition conditions. The nail polish was found to completely block any deposition from occurring on the painted Cu_2O substrate. Hence, a fast, easy, and cost-effective method of electrodepositing controllable features of Au was developed.

II. Swollen Hydrogel Stamp

To develop a method of isolating and transferring the Au features, we experimented with using hydrogels as a “stamp” that could hold onto the Au while serving as a medium for a Cu_2O etchant. Hydrogels are hydrophilic polymerous networks that can absorb and hold onto water and aqueous solutions while maintaining structural integrity due to the crosslinking of their polymer chains. Hydrogels have recently gained significant attention in their applicability to many fields, including tissue engineering, biomedicine, and environmental science.[15] Their swelling properties and structural stability make them excellent candidates to serve as a stamp and medium for the Cu_2O etchant solution. The etchant solution chosen consists of sodium sulfite, sodium thiosulfate, and sodium phosphate. Previously, this mixture (with the inclusion of an Au salt) was tested as a solution to electrodeposit Au onto Cu_2O, but the null solution was found to etch Cu_2O away before Au could properly deposit onto the substrate surface. While inconvenient for depositing Au, this makes it an ideal etchant for the purposes of this project. The idea was to allow the hydrogel to swell with etchant and place it on top of the Au-Cu/Cu_2O composite. This would allow the etchant easy access to the Cu_2O substrate and the Cu directly underneath the Au features (Figure 5).

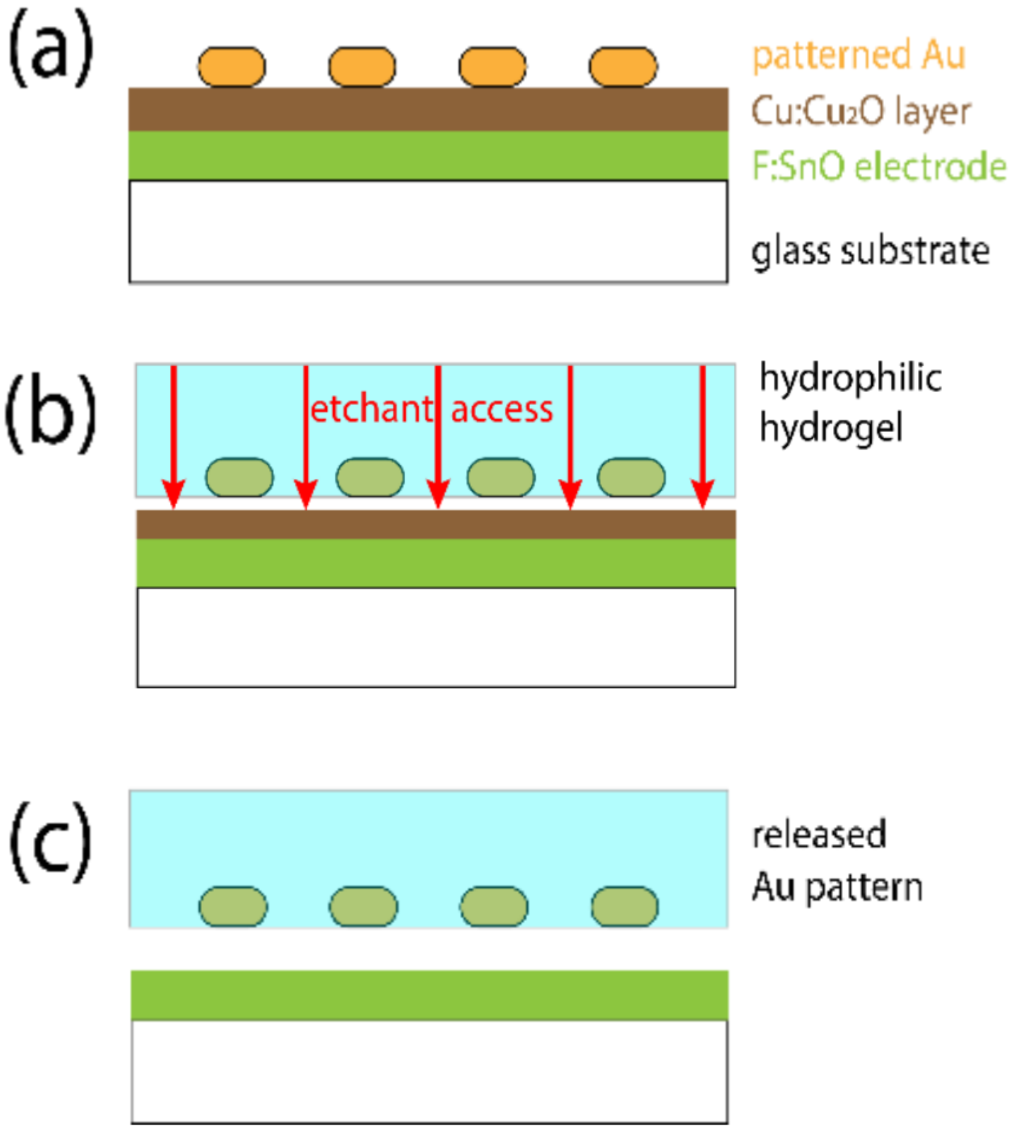

Figure 5: Schematic of the hydrogel etching process, beginning with (a) an electrodeposited Au pattern on top layer of Cu_2O that was electrodeposited on a FTO-coated glass slide. (b) Then a hydrogel soaked in etchant solution is placed on top of the electrode, allowing the etchant access to Cu_2O and Cu from the top. (c) The Cu_2O and Cu are etched away as a sacrificial release layer, leaving the Au pattern.

After experimenting with several hydrogel preparations and procedures, the hydrogel chosen for this experiment is a prefabricated bandage called Spenco 2nd Skin Moist Burn Pads.[16] These bandages are hydrogels soaked in a saline solution intended to protect and soothe burn wounds. If they dry out while in contact with the skin, they can be rehydrated with more water, suggesting they have good swelling properties. By allowing an electrode-sized piece of hydrogel to soak in etchant solution, the hydrogel swells up with the etchant while remaining in one structurally-sound piece. By measuring the mass of hydrogel pieces every five minutes of swelling in etchant solution, it was found that the hydrogel continues to significantly uptake etchant at least up to the 20 minutes that soaking was allowed, making them ideal mediums for the etchant solution. The swollen hydrogels can then be placed on the Au-Cu/Cu_2O composite.

Materials & Methods

Cu_2O Electrodeposition

Fluorine-doped tin oxide (FTO) coated glass slides are cut into 2 cm x 2.5 cm pieces for use as deposition substrates. These slides are rinsed sequentially with acetone, methanol, isopropanol, and HPLC-grade water. The pieces are labeled on the top of the nonconductive side of the slides. A thin strip of electroplating tape is wrapped around the electrode 1.5 cm from the bottom of the long side. This gives a 1.5 cm x 2 cm area of electrode with the intention of giving plenty of room for a small area of Au to be deposited in the center in later steps.

The 0.04 $CuSO_4$ / 3 M lactic acid electrodeposition is prepared using copper (II) sulfate hydrate (98%, Sigma-Aldrich), lactic acid solution (85%, reagent grade, ≥85%, Sigma-Aldrich), and HPLC-grade water. The solution is adjusted to pH=10 with sodium hydroxide solution to create stable Cu_2O films. The lactic acid is used to form copper (II) lactate, which prevents precipitation of copper (II) hydroxide in the alkaline solution and stabilizes the copper ions.

Electrodeposition of Cu_2O thin films is performed with an Admiral Instruments Squidstat Solo potentiostat. A 100 mL beaker is clamped onto a ring stand and placed in a water bath kept at 60°C on a hot plate. Then, 40 mL of 0.04 $CuSO_4$ / 3 M lactic acid solution at pH=10 is added to the beaker and allowed to reach 60°C. The prepared FTO-coated glass slide (working electrode) is placed into the solution up to the taped mark. A copper metal counter electrode and Ag/AgCl reference electrode are placed in solution, with the reference electrode placed closer in proximity to the working electrode than the counter electrode to minimize the contribution of uncompensated solution resistance. After connecting all electrodes to the potentiostat leads, a chronoamperometry program is run with a working potential of -0.4 V vs. Ag/AgCl and a maximum charge pass of 0.3 mAh.

For photoelectrodeposition, the same procedure as above is used with minor adjustments. The beaker is placed flush with the side of the glass dish holding the water bath. Then the working electrode's conductive surface is placed directly against the beaker glass on this same side. A 455 nm LED lamp with collimating lens is placed 16 cm from the working electrode and set to full intensity. The path of illumination is directed to the center of the working electrode. Then electrodeposition can begin as described above.

Au Electrodeposition

A 0.5 cm x 0.5 cm square is scribed in the center of the nonconductive side of a Cu_2O electrode prepared as above. This is used as a guide for where to paint the nail polish. Nail polish is used to paint around the square on the conductive side, leaving an empty square in the center of the electrode. The nail polish is allowed to dry completely before the experiment begins.

A 0.015 M $NaAuCl_4$/ 0.1 M tri-ammonium citrate/ 0.13 M Na_2SO_3 solution is prepared using sodium tetrachloroaurate (III) dihydrate (99%; Sigma-Aldrich), citric acid, tri-ammonium salt (97+% pure; ACROS ORGANICS) and sodium sulfite (≥98%; Sigma-Aldrich). This electrodeposition solution allows the formation of stable Au (III) complexes via a fulminating gold reaction with the ammonia and chlorine ions in solution. The solution is adjusted to pH=10 with sodium hydroxide to create stable metallic Au films. About 15 mL of solution is placed into a small beaker hooked to a ring clamp in a water bath and allowed to reach 60°C. A platinum mesh counter electrode and Ag/AgCl reference electrode are placed into the solution and hooked up to the potentiostat. A chronoamperometry program is set to -0.5 V vs. Ag/AgCl with no maximum charge pass. Once the program is completely ready to run and the nail polish on the Cu_2O electrode has completely dried, the working electrode is placed in solution and the program is started. After the electrodeposition has finished, the working electrode is placed in a beaker of acetone for about 5 minutes or until all of the nail polish is removed.

Hydrogel Preparation and Cu_2O Etching

A 0.42 M Na_2SO_3/ 0.42 M $Na_2S_2O_4$/ 0.3 M Na_2HPO_4 solution is prepared using sodium thiosulfate pentahydrate (ACS grade, ≥99.5%; Sigma-Aldrich), sodium sulfite (≥98%; Sigma-Aldrich), sodium phosphate dibasic (ACS grade, ≥99.0%; Sigma-Aldrich) and adjusted to pH=10 using NaOH. Spenco 2nd Skin Burn Bandages are cut into 2 cm x 1.5 cm pieces to fit the entirety of the Cu_2O substrate. The blue film is peeled off the hydrogel pieces and they are submerged into the etchant solution and allowed to swell for 20 minutes. The swelled hydrogels are placed face up in a glass petri dish and excess etchant is poured around the hydrogel to continue hydrating. The Au-Cu/Cu_2O electrode is placed face-down onto the hydrogel. After Cu_2O has been completely etched, the leftover glass slide is peeled off the hydrogel, leaving the Au square on the hydrogel.

Results

Cu_2O Substrate Electrodeposition

Figures 6 and 7 below show representative chronoamperometric curves of a regular Cu_2O electrodeposition and a Cu_2O photoelectrodeposition, respectively. In both figures, it can be observed that the experiments begin with a large spike in negative current. This can be attributed to the initial abundance of nucleation sites for deposition at the start of the process, and the large amount of resulting reduction happening at the working electrode surface. In Figure 6 for the regular Cu_2O electrodeposition, the decrease in negative current immediately following the initial increase corresponds to the depletion of Cu^{2+} ions near the working electrode surface after the initial jump in reduction, signifying the formation of a diffusion layer. Then, the current levels off as an equilibrium is reached and deposition continues. In contrast, in Figure 7 of the illuminated electrodeposition it is observed that the current density stays highly negative for the rest of the experiment. This is because the photons hitting the surface of the working electrode continue to excite electrons as Cu^{2+} and Cu^{1+} are reduced to Cu^0, contributing to the negative current density. The result is a black area in the middle of the electrode seen in the figure, where the illumination was centered. In agreement with Figure 3, the intensity of black color is highest in the very center of the electrode, where the illumination intensity was highest. The black color fades around the edges of illumination.

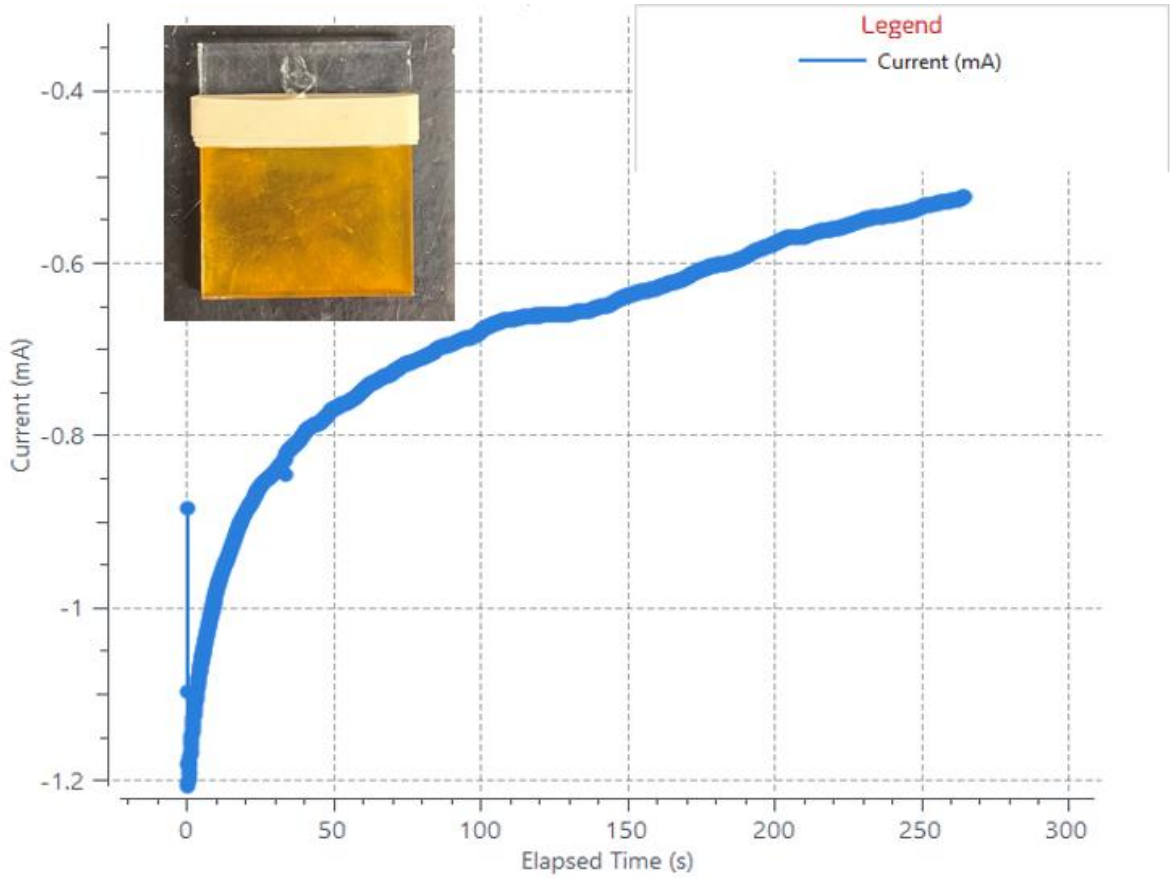

Figure 6: Chronoamperometric scan from the regular (not illuminated) electrodeposition of Cu_2O onto FTO-coated glass slide and the resulting yellow-orange electrode.

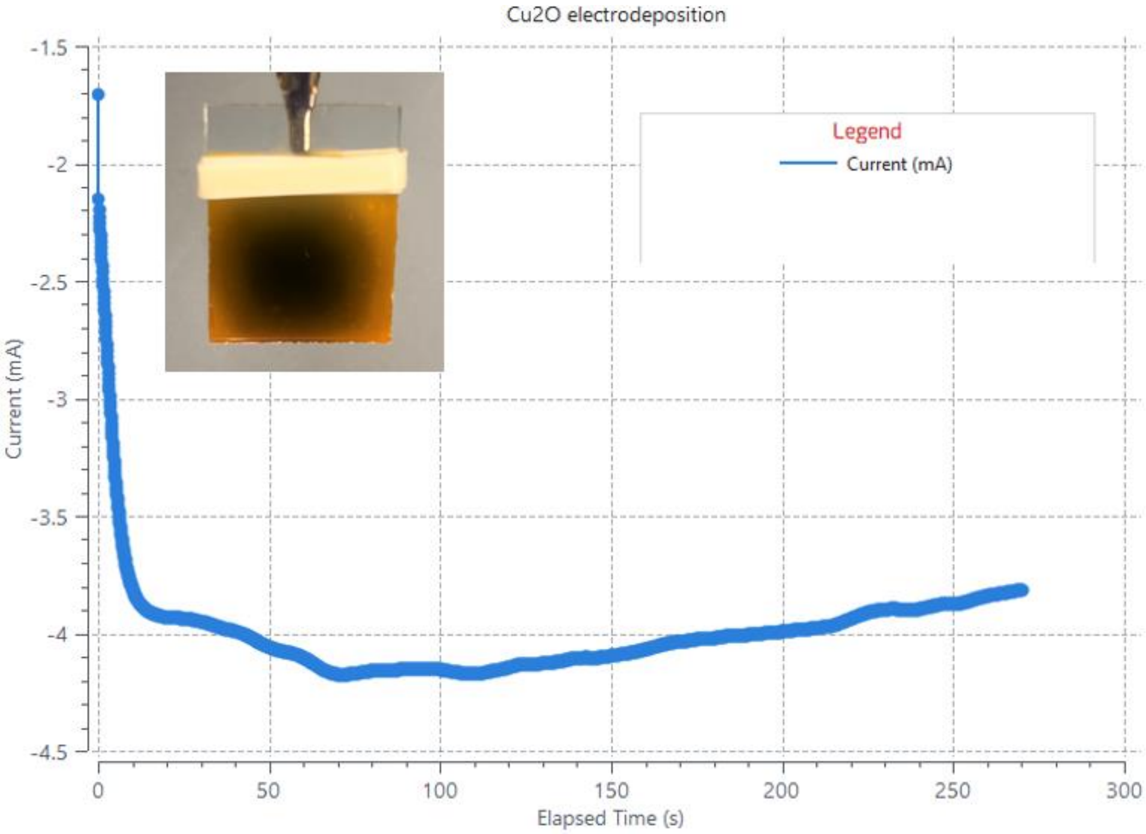

Figure 7: Chronoamperometric scan of photoelectrodeposition (under illumination) of Cu_2O onto FTO-coated glass slide and resulting orange electrode with a black area concentrated in the center, where illumination was aimed.

Au Feature Electrodeposition

After making the Cu_2O substrates, the electrodes are painted with nail polish to prepare for Au electrodeposition. Figure 8.a shows a regular Cu_2O electrode painted with nail polish, leaving a 0.5 cm x 0.5 cm square of Cu_2O in the center for Au to deposit on. Figure 8.b shows the electrode after deposition with the Au square deposited in the center, and no Au deposited on the nail polish areas. Finally, the electrode is soaked in acetone for 5 minutes. The acetone removed the nail polish layer while leaving the Au and Cu_2O untouched (Figure 8.c), and it is confirmed that no Au deposited onto the formerly painted Cu_2O.

Figure 9 shows a representative chronoamperometric curve from a corresponding Au electrodeposition. There is an initial peak in negative current at the beginning of the experiment, which can be attributed to the complete reduction of Cu^{1+} in Cu_2O to Cu^0 to allow for Au deposition. This is followed by a decrease in negative current as the diffusion layer forms, then an equilibrium is reached as Au continues to deposit for the rest of the experiment, which was set for 20 minutes. The resulting film has an Au feature in the center of the electrode, surrounded by Cu_2O substrate that was protected from deposition by the nail polish mask.

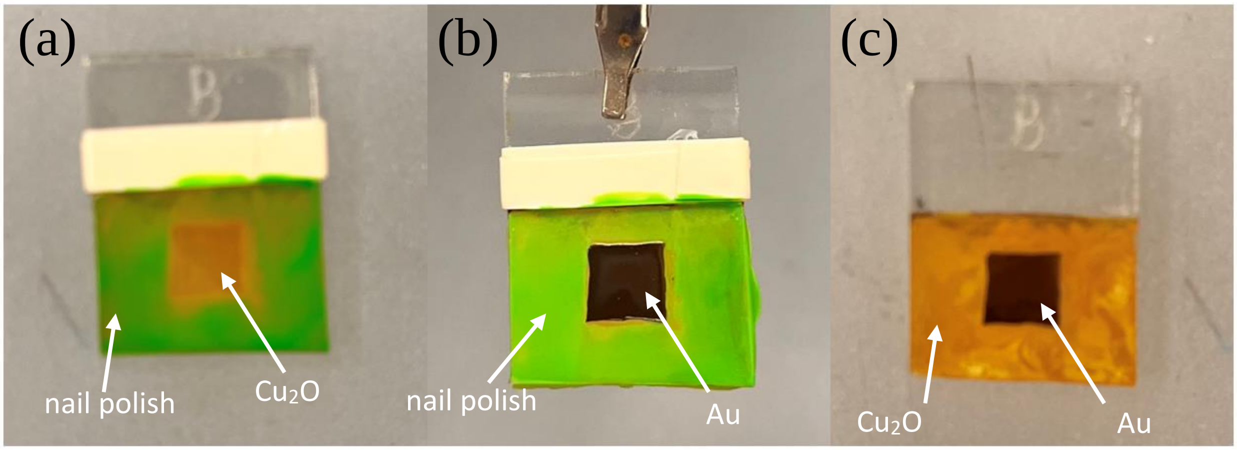

Figure 8: (a) Cu_2O substrate painted with nail polish (green layer) before Au electrodeposition and (b) after Au electrodeposition. A square in the center of the electrode was left unpainted, leaving a defined area of Cu_2O exposed to the electrodeposition solution. (c) Au-Cu/Cu_2O electrode after removal of nail polish mask with acetone.

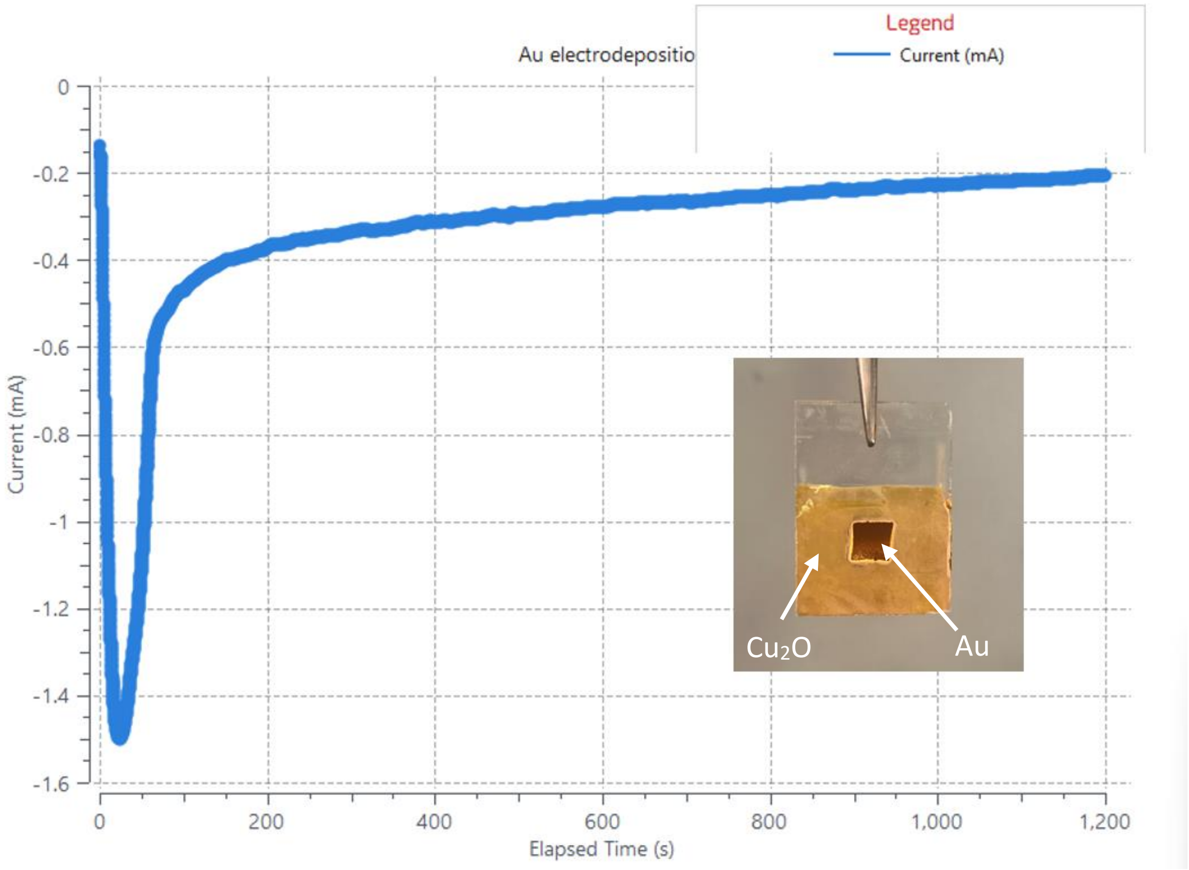

Figure 9: Representative chronoamperometry scan of Au electrodeposition onto a Cu_2O electrode that was painted with nail polish around a square in the center. In the resulting electrode, the feature in the center is Au, while the surrounding yellow-orange areas are Cu_2O that were protected by nail polish.

Hydrogel Etching

After experimenting with the setup used in Figure 5, it was found that the hydrogels dry out from air circulation during the etching process. While etching is still able to complete before the hydrogel dried out, a dried-out hydrogel does not adhere well with the Au surface. To account for this, we instead used an “upside-down” etching approach. First the soaked hydrogel was placed face-up in a glass Petri dish. To drive the equilibrium of the reaction to favor etching, more etchant was poured around the hydrogel in the dish, as an “etchant pool”. This continually replenished the hydrogel to prevent drying. Then the Au-Cu/Cu_2O electrode was placed face-down on top of the hydrogel so that the Au-Cu/Cu_2O surface was in contact with the soaked hydrogel, as seen in Figure 10.b. Finally, the Petri dish lid was placed on top of the dish to protect the reaction from the air circulation in the lab. This setup kept hydrogels hydrated for days at a time. After 48 hours, peeling back the empty glass slide successfully reveals an intact Au feature on the hydrogel (Figure 10.c).

After working with Au squares that had undergone 10-, 15-, and 20-minute electrodepositions, it was found that robust features were needed for the Au to remain in one piece during the etching portion of the experiment. This indicates that the etchant does not reach all areas of Cu metal equally; as the outer edges of the square are exposed to the etchant first, agitating the system causes those areas to break off the rest of the feature, under which the Cu metal has not been completely etched. For this reason, the Au squares that had been electrodeposited for 20 min. were used so that the features would be thick enough to remain in one piece as the substrate is etched. The resulting features are foil-like in appearance (Figure 10.c) but are structurally sound and attached to the hydrogel.

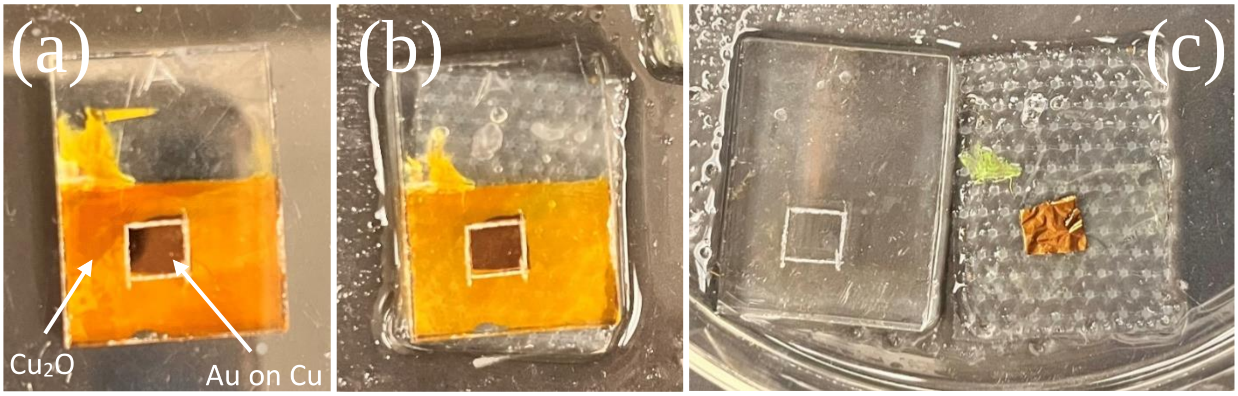

Figure 10: (a) Backside of a Au-Cu/Cu_2O electrode after nail polish mask removal. The metallic square in the center of the electrode from this view is Cu metal, because the Cu_2O is reduced to Cu when Au electrodeposition takes place. The Au square is on top of this Cu metal. The surrounding orange areas protected by nail polish are Cu_2O. (b) Au-Cu/Cu_2O electrode placed face-down on top of a hydrogel swelled with etchant. (c) 48 hours after etching process began, the remaining glass slide is peeled off the hydrogel, leaving the isolated Au feature on the hydrogel.

Figure 11 shows screenshots from a two-hour time-lapse video of the etching process. The first frame has a square surrounded by yellow areas, indicating the presence of Cu_2O at the very beginning of etching (Figure 11.a). One hour into etching, there are still some small areas of Cu_2O remaining (Figure 11.b). Most of the Cu_2O dissolves in the two-hour time frame (Figure 11.c), and all of the Cu_2O immediately surrounding the Au square is gone. However, when the electrode is peeled back after two hours, the Au square comes off in pieces, some of which are still stuck to the electrode. This indicates the Cu metal directly underneath the Au features is either more resistant to the etchant, or that the Cu is not as accessible to the etchant solution and takes longer to completely dissolve. In either case, if the setup is left unagitated for two days, the electrode can be peeled off to successfully leave an Au square completely intact on the hydrogel, as seen in Figure 10.c. The Au feature, rather than simply sitting on top of the hydrogel, seems to be stuck to the hydrogel. This suggests that there are mechanical interactions happening at the Au-hydrogel interface that drive Au to favor the hydrogel over the electrode surface after the substrate is dissolved.

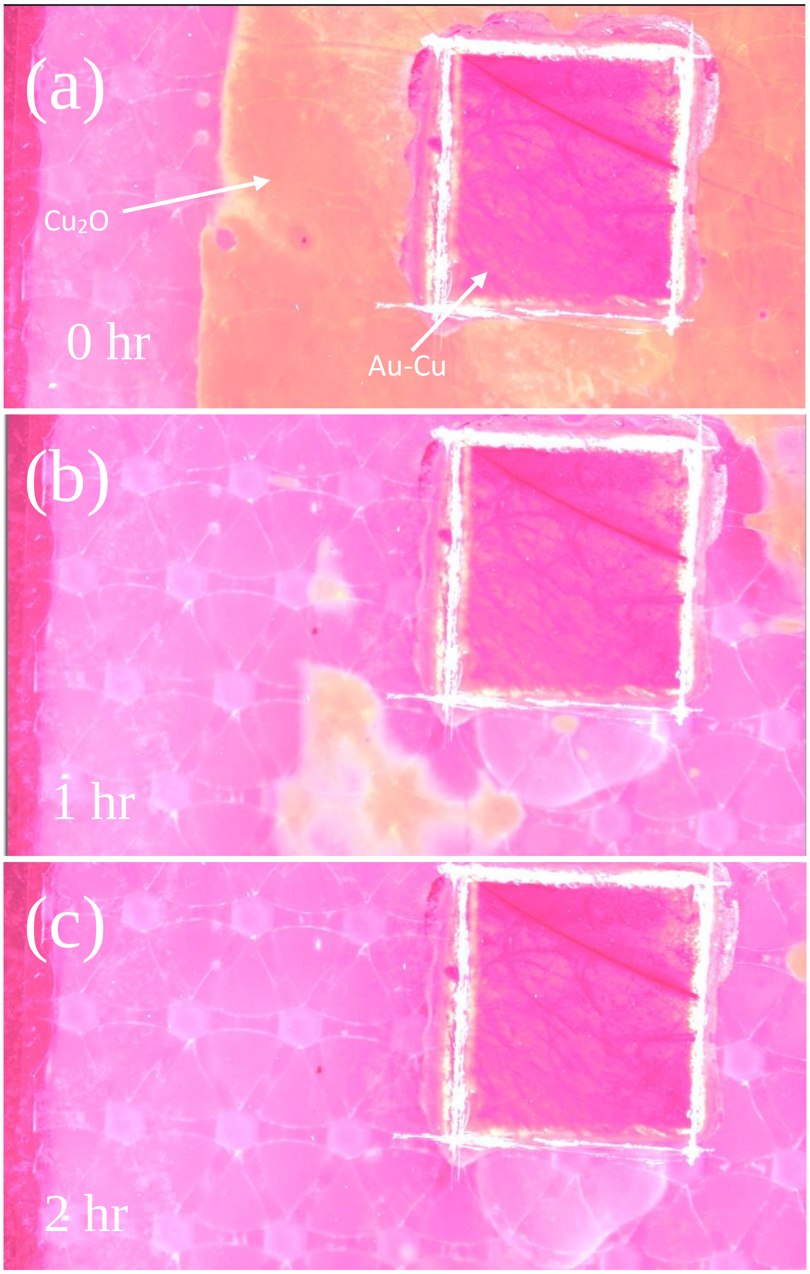

Figure 11: Screenshots from a timelapse of upside-down etching of Au-Cu/Cu_2O with soaked hydrogel. (a) at the beginning of etching, (b) 1 hour into etching, and (c) 2 hours into etching. As time passes, more Cu_2O (yellow areas) is etched.

Conclusions

The goal of this project was to generalize an electrochemical method of patterning Au and to develop a procedure of isolating the Au features from the conductive substrate. Au was electrodeposited onto Cu_2O thin films. It was found that nail polish can serve as a mask for this process, allowing selective electrodeposition of Au to unpainted areas. Then, we learned that hydrogel overlayers act as mediums for a solution that completely etches the Cu/Cu_2O substrates while leaving the Au untouched. The hydrogels additionally form mechanical interactions with the Au during the etching process, allowing for the Au features to remain intact to be later transferred to a more helpful substrate, such as a silicon wafer. The result is a cost and energy-efficient method of electrochemically fabricating large-scale Au features in a way that can be performed on the benchtop.

While the main goal of this project was successfully completed, there are still areas for improvement. The main hinderance of the current method is the fragility of the Au features during the etching process. At this point, waiting 48 hours results in the successful removal of the electrode to leave intact Au stuck to the hydrogel, while agitating the system after the Cu_2O appears to be completely dissolved (about 2 hours) tears the Au feature. This strain might not present an issue for smaller patterns; the currently larger surface area of the deposited features makes them more sensitive to applied stress through bending and grooves in the surface. One option is to deposit even thicker layers of Au, however noble metal resources are an important cost factor for this method. Another alternative would be to speed up the etching process by increasing the concentration of the etchant solution. In general, increasing the concentration of reactants of a rection increases the frequency of their collisions, thus increasing opportunities for reactions to occur.[17] Mathematically, this is expressed with a differential rate law. For a general reaction of Equation 2,

$$aA + bB \rightarrow cC + dD \qquad (2)$$

the differential rate law is expressed by Equation 3

$$\text{rate} = k[A]^m[B]^n \qquad (3)$$

where k is called the rate constant, which is specific to each reaction and set of conditions, and m and n indicate the positive reaction order, or the degree to which the rate depends on the concentrations of the reactants. While the rate constant and order of the etching reaction are not known, it can be seen from Equation 2 that regardless of the degree to which the rate depends on concentration, increasing the concentration does increase the rate of the reaction. We can use this fact to increase the chemical kinetics of the etching process by increasing the concentrations of the reactants in the etching solution. Raising the temperature of the reaction similarly speeds of the rate by increasing collisions frequency, and thus increasing opportunities for reactions. Heating the etchant solution might therefore speed up the etching process as well.

This process could also benefit from a deeper investigation on the chemical mechanisms that allow this method to work. For example, it is currently not known how the thiosulfate/sulfite solution selectively etches the Cu-containing compounds on the electrodes while leaving Au. A clue to this process is in the mechanism suggested by Fang et al.:

$$Cu_2O + xS_2O_3^{2-} + H_2O \rightarrow [Cu(S_2O_3^{2-})_x]^{2-2x} + 2OH^- \qquad (4)$$

in which thiosulfate ions react with Cu_2O and water to form soluble Cu-thiosulfate complexes and hydroxide ions.[18] However, more research is required to be certain of the exact mechanisms.

In addition, more study needs to be done on the interactions happening at the Au-hydrogel interface. As the Au features are currently stuck on the hydrogel while it remains hydrated, this suggests that the etching process drives a spontaneous arrangement of interactions between the hydrogel and Au. Learning more about this process could allow us to manipulate those interactions to our benefit, especially if we were to further this research to the transferring step.

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