Lab 9 – Gold Electrodeposition

Pre-Lab Reading:

Deposition is a fundamental process in nanofabrication, playing a crucial role in the creation of nanoscale structures and devices. Deposition techniques are employed to precisely add or grow thin layers of materials onto substrates, enabling the fabrication of intricate nanostructures and devices with enhanced functionalities.

There are various deposition methods used in nanofabrication, each with its specific advantages and applications. Some common deposition techniques include physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), and electrochemical deposition. In this study, we will explore the deposition of gold on the substrate through electrodeposition.

Objective:

The objective of this lab is for students to learn the process of electrodeposition. Thin gold films are electrically deposited on the surface of a clear tin oxide coated conductive glass. The color change of the thin film will be observed with increasing thickness of the film by the students. The optical properties can also be observed upon thermal oxidation of the deposited film.

Background:

Electrodeposition is a process in which an electrical current is passed through a solution to reduce cations to form a thin layer on the surface of a conductive material. It is a common technique used in electrochemistry, where oxidation-reduction reactions occur. **Oxidation** involves the loss of electrons, resulting in an increase in the oxidation state or oxidation number. **Reduction** involves the gain of electrons, leading to a decrease in the oxidation state or oxidation number. This concept can be remembered using the acronym **OIL RIG** (Oxidation Is Loss, Reduction Is Gain). The oxidation and reduction occur simultaneously where the electrons are transferred between redox species.

In electrochemistry, two main applications are the **Galvanic Cell** and the **Electrolytic Cell**. A **Galvanic Cell** uses a spontaneous chemical reaction to generate electric power. The batteries we use in everyday life are examples of galvanic cells. An **Electrolytic Cell** uses electrical power to drive a nonspontaneous reaction. Electrodeposition is essentially an application of an electrolytic cell. Like in a Galvanic cell, two electrodes are employed in an electrolytic cell. The **cathode** is where reduction occurs (remembered as "Red Cat"). The **anode** is where oxidation occurs (remembered as "An Ox"). The current runs from the anode to the cathode. Both nodes are completely immersed in an electrolyte solution, which allows for the flow of electricity through the circuit. *Figure 9.1* shows the setup of an electrolytic cell for electrodeposition.

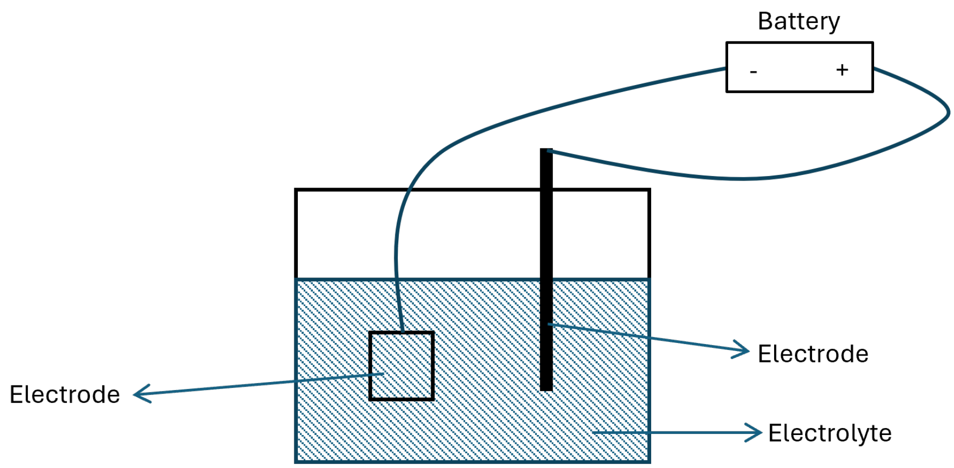


Figure 9.1: Setup of an electrolytic cell for electrodeposition.

Electrodeposition is an effective technique because it enables precise control over the surface composition of materials. In the manufacturing of microelectronics, a common approach involves applying a patterned "mask" to an object, which selectively blocks metal deposition, allowing it to occur only on the exposed areas. The process involves first applying the mask to the sample, then depositing the metal onto the exposed regions, and finally removing the mask with a solvent. The reverse of this process, known as electrochemical micromachining, involves etching metal from a precisely controlled area. This technique provides the ability to control the surface structure and composition at the micro- and nanometer scale.

In this study, fluorine doped tin oxide (FTO) coated conductive glass is used as the cathode. FTO is a thin uniform clear film coating which allows the observation of color change during the deposition process. If optical properties are not the main focus of the lab, any conductive substrate such as penny will demonstrate the process of electrodeposition. The cathode is also referred to as the working electrode. A graphite electrode is used as the anode and is also referred as the counter electrode. The two electrodes are immersed in a 1.0 mM hydrogen tetrachloroaurate $HAuCl_4$ solution. When the power is applied, the current is passed through the circuit. $AuCl_4^-$ is reduced to Au^0 and deposited on the FTO surface. *Figures 3 and 4* show the setup for the electrodeposition. A 1.5V AA battery can be used to provide the power that drives the deposition to occur. By varying the deposition time, the thickness of the gold film can be controlled. As the thickness of the gold film changes, interesting optical properties can be observed. Eventually, the surface on the glass appears to be gold.

Experiment:

SAFETY DISCLOSURE: This lab contains the use of hydrogen tetrchloroaurate solution which is corrosive to skin and can cause severe eye damage. It is recommended that the instructor prepares the solution for students to use. For students' safety and protection, personal protective equipment (PPE) is required for this lab. PPE should include gloves, chemical splash goggles, and aprons. It is recommended the lab is conducted under the fume hood.

Required Materials:

1. Graphite electrode
   a. Link can be replaced with pencil lead.
2. Florine Doped Tin Oxide Coated Glass Electrode
   a. Link The conductive glass electrode works well for optical observation and measurement. For deposition purpose only, any conducting substance such as pennies will work.
3. 1.0 mM hydrogen tetrachloroaurate
   a. Link The solid is hygroscopic so purchase $HAuCl_4{:}3H_2O$ (Aldrich 244597 or 520918) in 1.0 g quantities and use the entire bottle. Dissolve 1.0 g $HAuCl_4{:}3H_2O$ in 250 mL distilled water to make a 10.0 mM stock solution of gold(III) ions that can be kept for years if stored in a brown bottle. Dilute 25 mL of stock to 250 mL to make the 1.0 mM concentration for this experiment.
4. Brown bottle for storage gold solution
   a. Link
5. 25mL graduated cylinder
   a. Link
6. 250ml Volumetric flask
   a. Link
7. 50mL beaker
   a. Link
8. Multimeter and test leads
   a. Link
9. 1.5 V AA battery
   a. Link
10. Single AA battery holder with lead wires
    a. Link
11. Alligator clips set
    a. Link
12. 1.0M KCl solution

a. Solution can be ordered through the link or prepared using solid KCl (Aldrich P3911 link). Dissolve 18.64g of solid KCl in 100 mL water, then dilute the solution to 250mL using volumetric flask.

13. Sharpie for marking the conductive side of the FTO glass

Step 1: Identify the conducting side of the conductive glass.

Identify the conducting side of a tin oxide-coated piece of glass by using a multimeter to measure resistance. Set the multimeter to measure resistance. Place testing leads on the surface of the glass without leads touching each other but touching the glass and measure the resistance. The conducting side will have a resistance of 20-30 ohms. Use a sharpie to mark on the corner on the conducting side such as a letter or a symbol to recognize the conducting side. The FTO glass will serve as the cathode where the $AuCl_4^-$ will be reduced and deposited on its surface.

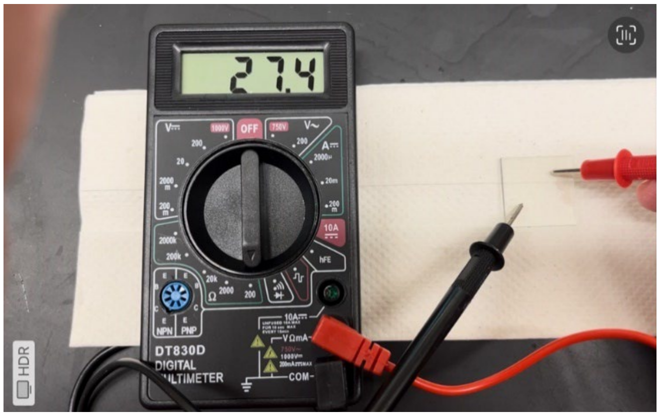


Figure 9.2: Resistance measurement for the conductive side of FTO coated glass.


Figure 9.3: Assembly of the 1.5 V power source

Step 2: Assemble Power Source

Place a single 1.5 V AA battery into the battery holder. Clip the red alligator to the lead wire of the positive end and clip the black alligator to the lead wire of the negative end.

Step 3: Set up electrolytic cell for deposition

Transfer 30 mL of 1 mM $HAuCl_4$ solution into a 50 mL beaker. Connect the black alligator clip from the power source to the FTO glass electrode and suspend it in the gold solution making sure the clip is not in the solution. Connect the red alligator clip to the graphite electrode and place the graphite electrode in the gold solution. Orient the conducting side of the glass facing towards the graphite electrode.

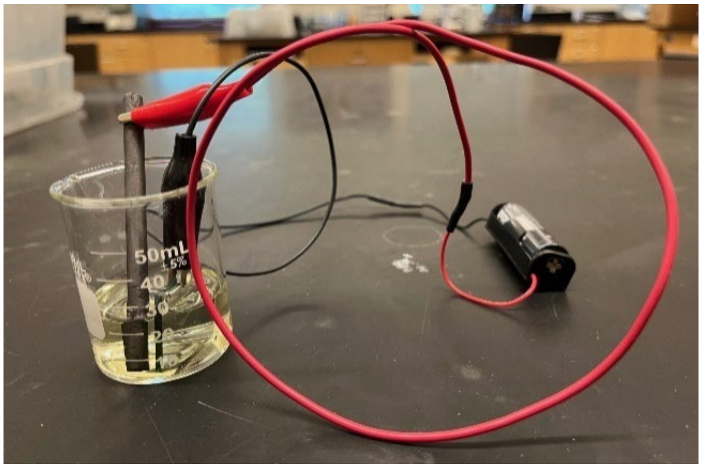
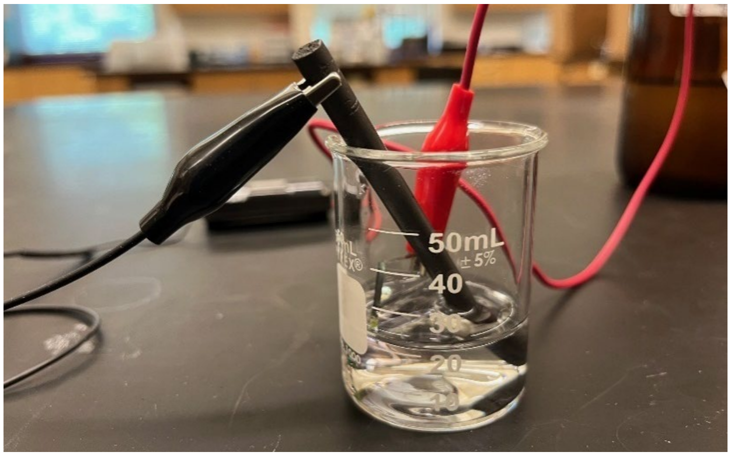


Figure 9.4: Setup of electrodeposition cell.

Step 4: Deposition

Once the circuit is complete, the deposition will start immediately. Use a timer to track the deposition time. The deposition for the first glass electrode is 10 minutes (0.2~0.3mA current).



After deposition, the electrode is rinsed with distilled water. Repeat step 1 and step 2 two more times with a new piece of glass electrode each time. The deposition time for second piece is 10 minutes and the third piece is about one hour. Record the color of the gold film.

Figure 9.5: Setup of electrical oxidation cell.

Table 9.1: Data from step 4

Glass electrode deposition time	**10 min (1st)**	**10 min (2nd)**	**1 hr**
Gold Film Color			

Step 5: Oxidation of the Au film

The first gold film covered electrode (10 min deposition) is electrically oxidized in 1.0 M KCl solution. The electrical cell set up is similar to the setup in electrical deposition. The electrolyte in this experiment is 30 mL 1.0 M KCl solution and the positive lead of a voltage source will connect to the glass electrode and the negative lead will connect to the graphite electrode. The second (10 min deposition) and third gold film (1 hr deposition) covered electrode are thermally oxidized. Place the glass electrodes on the hotplate and oxidize the gold film with medium heat. Record the color of the gold film after oxidation.

Table 9.2: Data from step 5

Glass electrode deposition time	**10 min (1st)**	**10 min (2nd)**	**1 hr**
Oxidized gold film color			

Questions:

1. Why is the color of the gold film not golden after 10 minutes of deposition?
2. What are the purposes of the cathode and anode?
3. What are some other materials that can be electrodeposited? Research and cite a source.
4. How is electrodeposition used in industry and research? Research and cite a source.
5. What are some of the advantages and disadvantages of electrodeposition over other methods of deposition?
6. Explain the process of electrodeposition in your own words.
7. What are some of the limits of electrodeposition?
8. If you pay close attention to the color change of the 3rd FTO glass electrode, at about what time do you observe the surface appears to be golden?
9. Explain the color change of the gold film (10 min deposition) after being electrically oxidized in the 1M KCl solution?
10. Explain the color change of gold film (10 min deposition) after being heated on a hot plate?