

Copper Plating

Standard Operating Procedure

Faculty Supervisor: Prof. Robert White, Mechanical Engineering (x72210)

Safety Office: Peter Nowak x73246 (Just dial this directly on any campus phone.)

(617)627-3246 (From off-campus or from a cell phone)

Tufts Emergency Medical Services are at x66911.

For more information on Copper plating see:

W.H. LI, J.H. YE and S.F.Y. LI. "Electrochemical deposition of Copper on patterned Cu/Ta(N)/SiO₂ surfaces for super filling of sub-micron features", Journal of Applied Electrochemistry 31: 1395–1397, 2001.

Revised: September 21, 2012

Warning: Both copper sulfate and sulfuric acid cause eye and skin irritation and burns. Causes digestive and respiratory tract irritation with burns. Very dangerous if swallowed.

1. Material Requirements:

1.1 Equipment: Two 1000 mL glass beakers, 2 4L rectangular glass tanks, , stainless steel tweezers, plating bath (polypropylene), 10" by 10" hotplate, FloKing filtration pumping system, small probe thermometer, DC power supply, two 16" long banana to alligator clip wires, two binder clips, threaded Teflon rod, 6" long

1.2 Chemicals: Copper sulfate, sulfuric acid

"Technic Copper FB Bath Ready to Use" contains copper sulfate (5-10%), sulfuric acid (15-20%), chloride ions, and brightener

"Technic Copper FB Brightener" contains proprietary materials but is not considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

1.2.1 Hazards associated with chemicals (copper sulfate, sulfuric acid):

1.2.1.1 Exposure to particulates or solution may cause conjunctivitis, ulceration, and corneal abnormalities. Causes eye irritation and possible burns.

1.2.1.2 Causes skin irritation and possible burns.

1.2.1.3 May cause ulceration and perforation of the nasal septum if inhaled in excessive quantities. Causes respiratory tract irritation with possible burns.

1.2.1.4 May cause severe gastrointestinal tract irritation with nausea, vomiting and possible burns. Ingestion of large amounts of copper salts may cause bloody stools and vomit, low blood pressure, jaundice and coma. Ingestion of copper compounds may produce

systemic toxic effects to the kidney and liver and central nervous excitation followed by depression.

1.2.1.5 May cause liver and kidney damage. May cause anemia and other blood cell abnormalities. Individuals with Wilson's disease are unable to metabolize copper. Thus, copper accumulates in various tissues and may result in liver, kidney, and brain damage. Adverse reproductive effects have been reported in animals. Laboratory experiments have resulted in mutagenic effects. Chronic copper poisoning in man is recognized in the form of Wilson's disease.

1.3 Engineering Controls: Store bottles of chemicals (sealed tightly) in cabinets with secondary containment. Work area should contain an eye wash and safety shower. All chemical processing should occur in the chemistry fume hood.

1.4 Personal Protective Equipment: Trionic gloves on top of nitrile gloves, goggles.

2.0 Procedure:

Complete all processes in the fume hood

2.1 Seed Layer Deposition

2.1.1 Deposit (using sputtering or evaporation) a “seed layer” consisting of 20 nm of Ti and 100 nm of Cu onto your wafer. Other metals may work as a seed layer. 50/300 nm Cr/Au also works fine.

2.1.1.1 The copper will plate only onto the seed layer, so if you pattern the seed layer before plating you will end up with patterned thick copper.

2.1.1.2 *Note that there must be a continuous electrical connection between the seed layer and the cathode during plating, so if you leave any unconnected “islands” of Ti/Cu on your wafer they will not plate at the same rate as the rest of the wafer.*

2.2 Option # 1 : Use the Technic “Ready to Use” copper plating solution

(Note: this is truly “ready to use” ... it has all the necessary components, including chloride ions and brightener, and has already been balanced by the manufacturer.)

2.2.1 It is likely that there is already a 4L rectangular tank with Copper Plating solution in it, in the acid hood, labeled as Copper Plating Solution. Use this if it is already there.

2.2.1.1 Do NOT fill the tank to the fill line yet. The tank should be filled to the fill line only AFTER the filtration pump is in place (this will be discussed below).

2.2.2 If a new tank is needed, fill the tank with “Ready to Use” Technic Copper Plating Solution .

2.2.3 Replenishing the brightener: After every 20 Ampere-Hours of plating, add 2.5 mL of Brightener. **Make sure to fill in the copper plating log book so we know how much total Amp-Hours of plating has been done. Make sure to note in the log book when you add brightener.**

The “photoresist” pipettes have a bulb volume of 4.6 mL... so add one half pipette of brightener after 20 Ampere-Hours of plating. One Ampere-Hour of plating is running at 1 Amp for 1 hour (or 100 mA for 10 hours, etc).

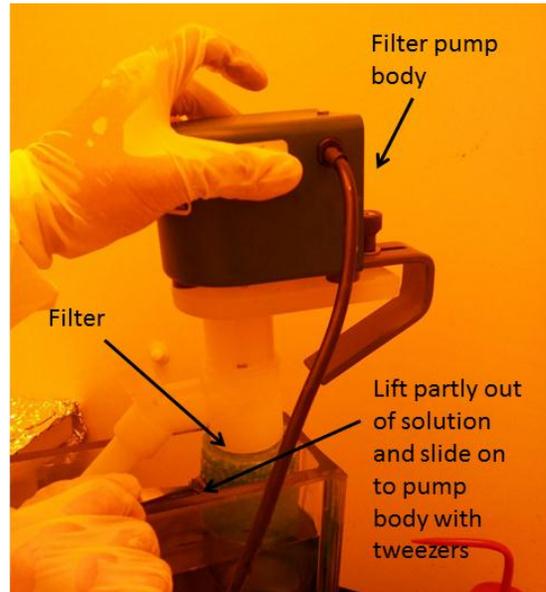
2.3 Option # 2 : Make your own Plating Solution

Perform these steps in the Chemistry Fume Hood.

- 2.3.1 A 1250mL solution will almost cover an entire wafer in a wafer holder. The small exposed section above the solution is a good place to make electrical contact. Other size containers can be used for smaller wafers
- 2.3.2 Fill a 2000mL beaker with deionized water to less than 700mL.
- 2.3.3 Put 150g copper sulfate anhydrous (or 240g copper sulfate pentahydrate) in the beaker using a scale.
- 2.3.4 Add 100mL sulfuric acid to the beaker.
- 2.3.5 Bring the total volume up to 1250ml by adding DI water.
- 2.3.6 Stir this 1250mL solution (0.78 M CuSO_4 + 1.5 M H_2SO_4) to dissolve the copper sulfate.
- 2.3.7 For smaller samples, this solution can be scaled down accordingly.

2.4 Setting up the Filtration Pump

- 2.4.1 Remove the FloKing filtration pump body from the water soak where it is stored. It should not yet have a filter on it.
- 2.4.2 You should see the filter cylinder floating in the copper plating tank (it is stored in there so it is always soaked with copper plating solution). Lift the filter gently part way up and at an angle with your tweezers, so that you can slide the filter pump down into the center of the filter. Note that one side of the filter is closed with a plug, only one side will be open, make sure it is the right way around.
- 2.4.3 Hang the filter pump body on the back of the tank using the clamp.
- 2.4.4 Once the filter is in place, check the level of the copper plating solution. It should come up to the line marked on the side of the tank, so it is below the motor portion of the pump, but above the branch for the Y shaped tube. If necessary, add some copper plating solution from the “ready to use” bottle to bring the solution level up to the marked fill line.

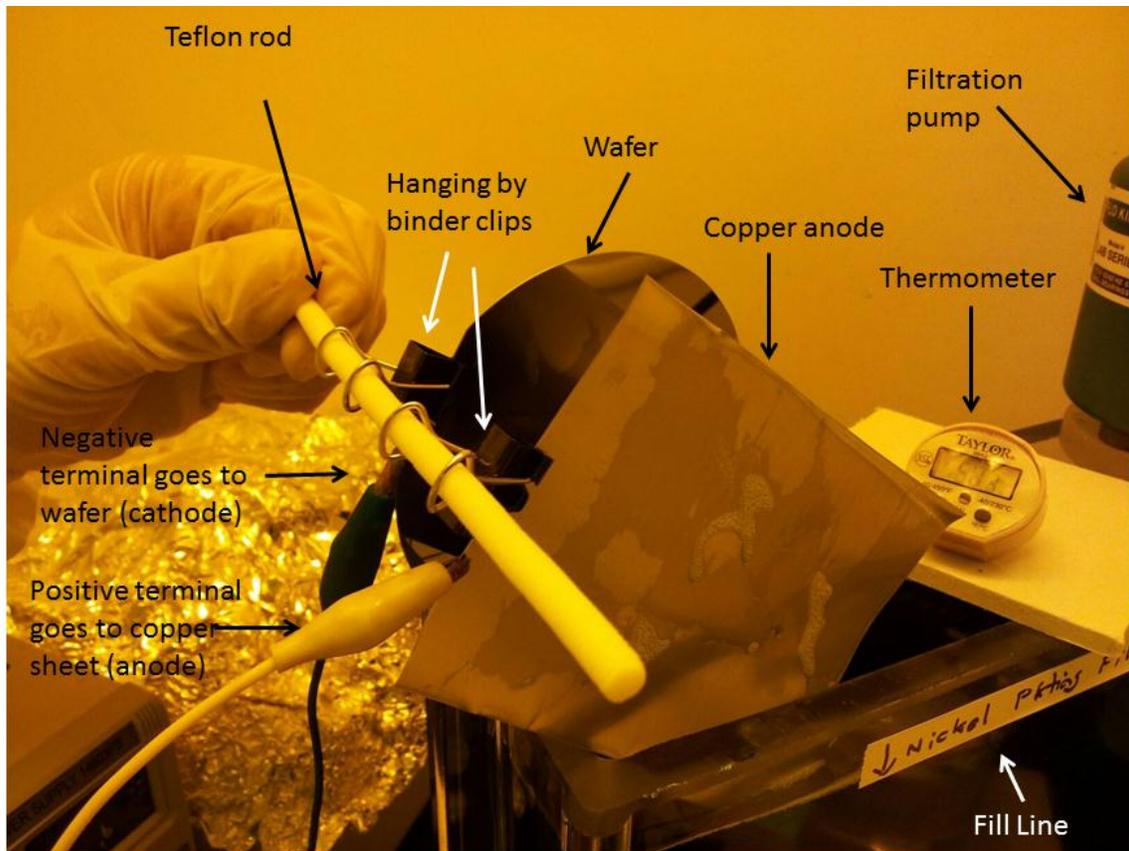


- 2.4.5 Plug in the filter. You should see gentle recirculation of the solution. It is being mixed and actively filtered. This is critical to achieve a smooth and particle-free film.

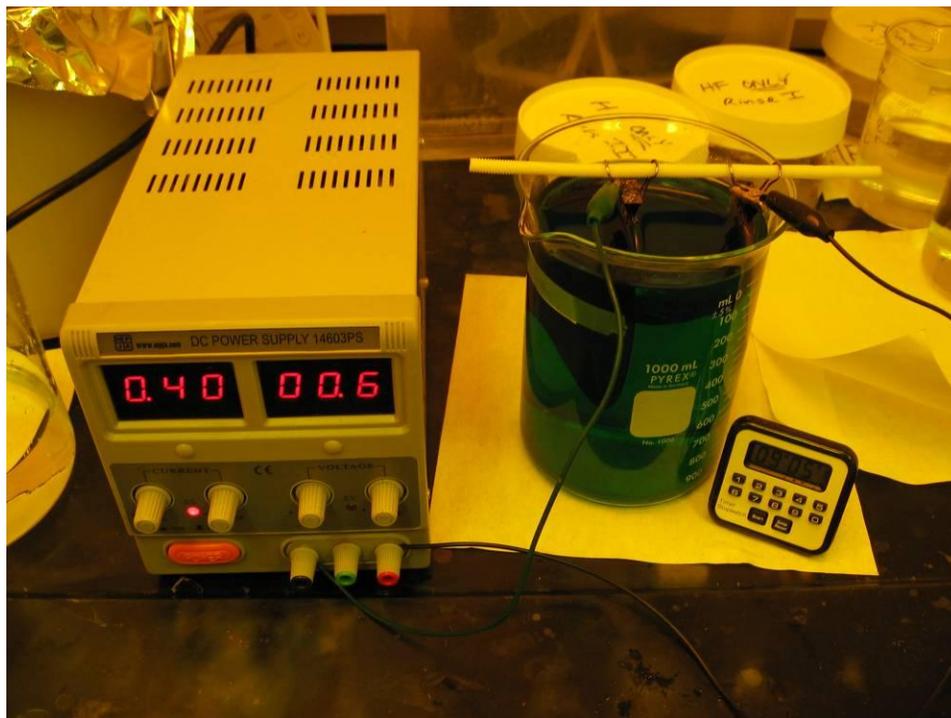
2.5 Copper Plating

Perform these steps in the Chemistry Fume Hood.

- 2.5.1 Get two water rinse beakers which will fit your samples (1000 mL beakers for a 4" diameter wafer). **Do this first.** If something goes wrong, you want the water available to quench the reaction. Fill the 1000 mL beakers with deionized water such that the water level will cover the entire sample.
- 2.5.2 A piece of pure copper sheet or foil works well as an anode. You should use an anode approximately the same size as the sample. A 3" x 5" strip works well for a 4" diameter wafer.
- 2.5.3 A binder clip works well to hold the wafer. Attach the binder clip to the wafer so that the wafer hangs down from the binder clip.
- 2.5.4 Attach the second binder clip to the copper anode.
- 2.5.5 Hang the wafer and the copper anode from the Teflon threaded rod, with the surface to be plated facing the copper anode. Hang the two so they are approximately 1 inch apart, and parallel.
- 2.5.6 Immerse the cathode and anode in the solution. The top edge of the wafer and top edge of the copper should poke out above the surface a little bit.
- 2.5.7 Attach the alligator clips to the anode and cathode. Note that it is critical that there is a place for the alligator clip to attach to the wafer that is not coated with photoresist! You need a good contact region to make connection to the seed layer. This should be designed in as part of your mask, otherwise you may be forced to try to use acetone on a swab to open up a little region at the edge of the wafer to make contact.
- 2.5.8 **Make sure the electrical connection to the power supply is the right way around!!! Negative terminal (cathode): wafer, Positive terminal (anode): copper plate.**
- 2.5.9 The completed set up should look similar to the picture below.



Or maybe like this if you want to mix your own solution and work in a small beaker:



2.5.10 Compute your current based on the area of your seed layer... a current density of $<20 \text{ mA/cm}^2$ or less is recommended for a shiny film. (5mA/cm^2 is recommended). A higher plating current density will increase deposition rate but will probably increase roughness, and may affect other variables such as film stress. It is a good idea to set up this current value on the power supply beforehand, so that the correct current value will be attained immediately after turning on the power supply. Turn on the power supply and adjust to the correct current value if necessary.

2.5.10.1 You should see the voltage drop slowly while the current remains constant.

2.5.10.2 If the voltage starts to rise, it is most likely due to corrosion around the electrical connection to the wafer. Turn off the power supply, rotate the binder clip connection to another location on the edge of the wafer and then restart the power supply.

2.5.10.3 If the voltage rises very suddenly, the problem is most likely a connection coming loose. It could also be anode polarization (see above).

Note: Make sure to turn off the power supply before you remove your sample or the anode!

2.5.11 Calculate the plating time for your sample. You need to know the thickness of your copper layer. **At 25°C and 5mA/cm^2 , the copper will be deposited at a rate of approximately 200 nm/min .** This may not be exact! Testing it for yourself is a good idea. For best results, limit the plating current density to less than 20mA/cm^2

2.5.11.1 Higher temperatures (up to 50°C) allow for higher current densities, but the deposition will be less uniform and bright. Also at higher temperatures the copper can be oxidized. Put the plating solution on a hot plate, and monitor the solution temperature with the probe thermometer.

2.5.12 After the plating time is complete, turn down the current and turn off the power supply.

2.6 DI Water rinse

Perform these steps in the Chemistry Fume Hood.

2.6.1 Disconnect the wires from the sample.

2.6.2 Transfer the sample carefully to the first DI water rinse beaker.

2.6.3 If you used tweezers to move the sample, make sure you rinse them as well.

2.6.4 Let the sample and tools soak in DI water for 3mins.

2.6.5 Transfer the sample to the second DI rinse beaker, and rinse for another 3 mins.

2.6.6 Do the same for the copper anode. As long as it has not corroded or oxidized too extensively, it may be reused.

2.7 Sample dry:

2.7.1 After the water rinse is finished, remove your samples and the anode and blow them dry with the air gun

2.7.2 Inspect wafer for the thickness of the copper. If more plating time is required, place wafer back into the plating tank with the solution. Repeat plating, rinse and drying procedure.

2.8 Clean-up:

Perform these steps in the Chemistry Fume Hood.

2.8.1 Unplug the filter pump.

2.8.2 With your tweezers, carefully slide the filter off the filter pump body so it stays in the copper tank and continues to soak.

2.8.2.1 If the filter becomes too dirty, leave it on the pump and pump water through it for 5 minutes. Then leave it to drip dry into the water rinse tank (4L rectangular tank labeled as water rinse). When it is dry discard it in the acid/base solid waste trash can.

2.8.2.2 If you discard an old filter, then get a new one and leave it to soak in the copper plating solution for at least 2 hours before being used.

2.8.2.3 If you replace the filter **note it in the log book.**

2.8.3 Move the filter pump body over to the water rinse tank (without the filter on it, unless the filter is being discarded as described above). Hang it on the side just like you did in the copper plating tank and plug it in. Let it recirculate rinse water for 5 minutes, then unplug it and leave it hanging in the water rinse tank.

2.8.4 The copper plating solution may be used many times before it needs to be replaced. Make sure to enter your deposition information in the log book so we know how old the solution is. The solution should be discarded after 80 Amp-Hours of plating, or 6 months, whichever comes first (These criteria are arbitrary as of the writing of this SOP, and may need to be refined based on experience).

2.8.4.1 In most cases, the copper solution will be re-used. Cover the tank carefully with parafilm and the glass cover, then with two layers of aluminum foil. We don't want evaporation. Move it off the hotplate and back into the corner of the hood. Make sure it is clearly labeled.

2.8.4.2 If the solution is too old and needs to be replaced, pump it (using the peristaltic waste pump) into the copper plating waste bottle (HDPE bottle) which is labeled "copper sulfate, sulfuric acid" with

the red hazardous waste tag. Keep the bottle in the satellite accumulation area (under the hood). If a waste bottle already exists, use that one, otherwise start a new one. You may need two waste bottles for a full 4L tank.

2.8.4.3 If you change the copper solution **note it in the log book.**

- 2.8.5** Dump the first DI rinse beaker and into the copper plating waste bottle (HDPE bottle).
- 2.8.6** Dump the second DI rinse beaker into the 5 gallon HDPE “Dilute Acid Waste” container.
- 2.8.7** Rinse both containers a second time with DI water. This time, dump them into the 5 gallon HDPE “Dilute Acid Waste” container.
- 2.8.8** Return all lab ware to its proper location.
- 2.8.9** Wipe up any drips in the area with chemical wipes and dispose in the acid trash.

3.0 Storage:

3.1 Chemical one: Copper sulfate

- 3.1.1** Store copper sulfate in a tightly closed container. Store in a cool, dry, well-ventilated area away from incompatible substances. Store protected from moisture.

3.2 Chemical two : Sulfuric Acid

- 3.2.1** If stored in non-reactive container, keep container tightly closed. Metal and, specifically carbon steel, storage tanks must be vented due to hydrogen release as noted above.

3.3 Technic FB Acid Copper Plating Solution “Ready to Use”

- 3.3.1** Store in a tightly closed container. Store in the acid cabinet. Keep cool, dry, and separated from incompatible materials.

3.4 Technic FB Brightener

- 3.4.1** Store in a tightly closed container. Store in the acid cabinet. Keep cool, dry, and separated from incompatible materials.

4.0 Waste Disposal:

4.1 Chemical: Copper sulfate, sulfuric acid, Technic FB Acid Copper Plating Solution “Ready to Use”, Technic FB Brightener

- 4.1.1** Solid waste for chemicals and corroded anodes should go in the acid waste bin.
- 4.1.2** Liquid waste for chemicals should go in the copper plating waste bottle. Label “Copper Sulfate” and “Sulfuric Acid”.

5.0 Accident Procedures:

5.1 Contact: Read MSDS prior to working with any chemical to familiarize yourself with the symptoms of exposure and recommendations for treatment.

5.1.1 Chemical one: Copper sulfate

- 5.1.1.1** Skin contact: Get medical aid. Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse.

- 5.1.1.2 Eye contact: Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid.
- 5.1.1.3 Ingestion: Do not induce vomiting. If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.
- 5.1.1.4 Inhalation: Remove from exposure and move to fresh air immediately. If breathing is difficult, give oxygen. Get medical aid. Do NOT use mouth-to-mouth resuscitation. If breathing has ceased apply artificial respiration using oxygen and a suitable mechanical device such as a bag and a mask.
- 5.1.2 Chemical two: Sulfuric acid
 - 5.1.2.1 Skin contact: Immediately flush skin with running water for a **minimum** of 20 minutes. Start flushing while removing contaminated clothing. If irritation persists, repeat flushing. Obtain medical attention IMMEDIATELY. Do not transport victim unless the recommended flushing period is completed or flushing can be continued during transport.
 - 5.1.2.2 Eye contact: Immediately flush eyes with running water for a **minimum** of 20 minutes. Hold eyelids open during flushing. If irritation persists, repeat flushing. Obtain medical attention IMMEDIATELY. Do not transport victim until the recommended flushing period is completed unless flushing can be continued during transport.
 - 5.1.2.3 Ingestion: DO NOT INDUCE VOMITING. If victim is alert and not convulsing, rinse mouth and give ½ to 1 glass of water to dilute material. If spontaneous vomiting occurs, have victim lean forward with head down to avoid breathing in of vomitus, rinse mouth and administer more water. IMMEDIATELY contact local poison control center. Vomiting may need to be induced but should be directed by a physician or a poison control centre. IMMEDIATELY transport victim to an emergency facility.
 - 5.1.2.4 Inhalation: Move victim to fresh air. Give artificial respiration ONLY if breathing has stopped. Do not use mouth-to-mouth method if victim ingested or inhaled the substance: induce artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device. Give Cardiopulmonary Resuscitation (CPR) if there is no pulse AND no breathing. Obtain medical attention IMMEDIATELY.
- 5.1.3 Technic FB Acid Copper Plating Solution “Ready to Use”
 - 5.1.3.1 EYE CONTACT: Flush with water, including under lids, for fifteen minutes. Obtain immediate medical attention.
 - 5.1.3.2 SKIN CONTACT: Remove contaminated clothing and wash affected area thoroughly with soap and water. Launder clothing before wearing it again. Seek medical attention for prolonged skin irritation.

5.1.3.3 INHALED: Remove patient to fresh air. Support breathing if required. Obtain medical treatment for dizziness, unconsciousness or irritation or difficulty in breathing.

5.1.3.4 SWALLOWED: If patient is conscious, rinse mouth and drink at least two large glasses of water. DO NOT induce vomiting. Never give anything by mouth to an unconscious person. Obtain immediate medical attention.

5.2 Spill:

5.2.1 If a small, contained spill occurs, such as inside the hood, wipe it up with chemical wipes and dispose of in the appropriate trash container.

5.2.2 If a large spill occurs that you are not comfortable cleaning up:

5.2.2.1 If it is a **chemical one or two** spill, do this. Notify the Tufts emergency services (x66911) immediately. Also notify the faculty advisor.

If at any time you feel a situation is dangerous, do not hesitate to call the safety office (x73246, Peter Nowak) or the faculty supervisor (x72210, Robert White).

Report all accidents (injuries, major spills, fires) to the safety office at x73246 (Peter Nowak) and the faculty supervisor at x72210 (Robert White). For emergencies, call Tufts Emergency Services at x66911.