4. Standard Operating Procedures

4.1. Objectives

These standard operating procedures are meant as a guide for future SNF users who wish to do any or all of the following:

1. Use Nanoscribe with thick (>20µm) SPR 220-7 positive photoresist
2. Use Nanoscribe with opaque and/or reflective patterned substrates
3. Electroplate metal in templates made via two-photon lithography

Additionally, we hope that this will be a useful guide for understanding and solving common problems in these processes.

4.2. Materials and Equipment

Materials

- 1 inch square Nanoscribe DiLL Hi Res substrates
- SPR 220-7 resist
- MF26A developer
- Potentiostat (Gamry)
- Copper counter electrode (McMaster-Carr, Super-Conductive 101 Copper Sheets and Bars, with 99.99% copper contents, 1/8 Hard Temper Sheets)
- Reference electrode (BASI, Ag/AgCl reference electrode with 3M NaCl, product number MF-2052)
- Commercial electroplating solution (Sigma-Aldrich, High speed bright copper electroplating solution, semiconductor grade, product number 900569)

Equipment

- Evaporator (KJL, aja, etc.)
- Yes (2)
- Headway (3)
- Solvent bench (exfab)
- Developer bench (exfab)
- Nanoscribe
- optical microscope
- Keyence (snf optical and/or snsf confocal)
- SEM (Nova or Apreo)

4.3. Metal Patterning

Metal patterning process consists of a lithography (using Heidelberg) to define the pattern of the metal layer, a subsequent metal evaporation and liftoff.

4.3.1. Coat

1. Clean DiLL Hi Res 1 inch square wafers with acetone and IPA. Dry with a nitrogen gun.
2. Dehydrate and HMDS prime the wafers in the yes or yes2 oven.
3. Manually spin coat SPR 3612 resist at 2230 rpm for 60 seconds with a 500 rpm/s ramp rate. This should result in approximately 1.6µm resist thickness. Headway 2 or 3 can be used for coating.
4. Pre-bake on hotplate at 90°C for 90 seconds.

4.3.2. Exposure, develop and descum

1. Expose the desired mask file in heidelberg with a dose of 100 mJ/cm^2 and a defocus of –2.
2. Manually develop in a beaker with MF26A for 30 seconds. Agitate manually. Immediately immerse in DI water. Dry with a nitrogen gun.
3. Check for proper exposure and development with an optical microscope.
4. Post-bake at 115°C for 90 seconds.
5. Descum. We used technics with the standard recipe for 60 seconds.

4.3.3. Evaporate, and liftoff

1. Using aja (snf ex-fab), kjl (snsf), or any other standard evaporator, evaporate 5nm of titanium and 50nm of gold.
2. Place the wafers in a beaker with acetone and sonicate for at 10 minutes or until liftoff is complete. Do not let the acetone dry before liftoff is complete or metal particles may redeposit where they are not desired.
3. Rinse the substrate with acetone, IPA, and dry with a nitrogen gun.

4.4. Nanoscribe Writing

Nanoscribe writing consists of double coating thick SPR220-7 resist, exposure in Nanoscribe, and subsequent development of the photoresist.

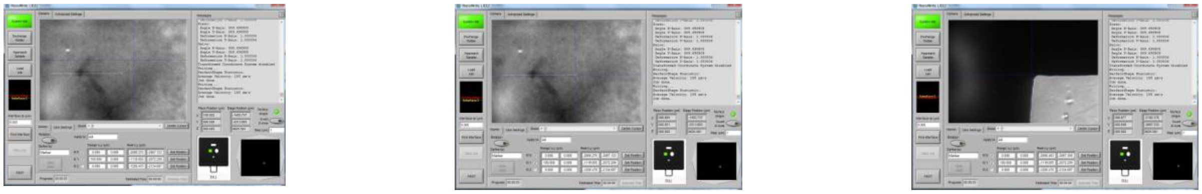
4.4.1. Coat

1. Clean the patterned substrate with acetone, IPA, and dry with nitrogen.
2. Dehydrate and HMDS prime the wafers in the yes or yes2 oven.
3. Manually coat the wafers with SPR220-7 in headway3 or headway2. The following two-coat procedure should give a resist thickness of 29 ± 3µm [4].
    a. Dispense 5mL SPR220-7 at the center of the wafer at 100 rpm for 10 seconds or until all resist is deposited on the wafer. Take care to minimize bubbles. A syringe may be preferable to a pipette.
    b. Cast the film at 1400 rpm for 20 seconds.
    c. Dry the film at 2200 rpm for 90 seconds.
    d. Bake the resist on a hotplate at 100°C for 2 minutes, minimum.
    e. Dispense 5mL SPR220-7 at the center of the wafer at 100 rpm for 10 seconds or until all resist is deposited on the wafer, avoiding bubbles.
    f. Cast the film at 1400 rpm for 20 seconds.
    g. Dry the film at 2200 rpm for 180 seconds.
    h. Bake the resist on a hotplate at 100°C for 5 minutes, minimum.

4.4.2. Exposure

1. Wait a minimum of 8 hours and a maximum of 1 week before exposure in Nanoscribe. This is particularly important for thick resists.
2. Convert a desired CAD file to an stl file. Using the Describe software, slice the stl file and prepare for exposure. We used the default parameters. If the structure is large, it may be written in multiple segments which may overlap. Overexposure may occur at overlaps. The overlap distance can be changed manually at this point. Change the desired power and write speed in the output gwl file. 100% base laser power with 1.2 power scaling is the maximum possible power.

3. Preheat the laser in Nanoscribe for at least 30 minutes before writing by enabling the tool and opening the NanoWrite software.
4. Install the 63x lens.
5. Tape the substrate face-down in the DiLL Hi Res holder and load the holder into the tool.
6. Click “approach sample.”
7. In the Axio Vision software “properties” toolbox, adjust the exposure time, contrast, and brightness to improve visuals.
8. Find the interface. The automatic “find interface” command is more successful on transparent substrates and on reflective substrates when it starts at a position close to the actual interface. For a patterned substrate, is recommended to find the interface first on a glass area of the wafer and then on a reflective area.
9. Align the Nanoscribe to start writing at the desired point on the patterned substrate. Take care to note the orientation of the substrate (inverting the z-axis may be helpful) and the point of the file at which the structure will begin writing. Close the AxioVision software to view the camera in NanoWrite. Follow the steps in Figure 14 to align the laser with the patterned substrate.



1. Turn on camera, manually write a line to track the laser

2. Align blue hairline to laser spot using mouse

3. Move stage to the 1st position on the axis, click “get position”

5. Click “Rotate” to transform coordinates

6. Move to the start point, then start!

Fig. 14. Nanoscribe alignment procedures

10. Load the desired gwl file.
11. Click “start job”

4.4.3. Develop

1. Wait a minimum of 2 hours and a maximum of 36 hours after exposure before developing for nitrogen to diffuse out of the resist and for water to diffuse in. This is particularly important for thick resists.
2. Develop the wafer manually by submerging in a beaker in MF26A for 3 minutes with agitation. Initial observations indicate that underdevelopment is more likely than overdevelopment.
3. Immediately immerse in DI water to stop the development. Dry with a nitrogen gun.
4. Check for proper exposure and development using an optical microscope. Do not use the optical or confocal Keyence microscopes. They may further expose the resist.

4.5. Electrodeposition

4.5.1. Preparing Substrate

1. A clean seed conductive seed layer is vital to the electrodeposition process. Descum the developed template soon after development and optionally again before electroplating, if the wafers have been sitting for a while since development. The matrix plasma asher is expected to be the most appropriate tool.
2. Rinse with DI water immediately before electroplating.

4.5.2. Electroplating Setup

1. Fill a beaker with copper electroplating solution.
2. Attach the sample to a glass slide.
3. Rinse the counter electrode and reference electrode with DI water.
4. Attach the proper wires to the potentiostat, working, counter, and reference electrodes and orient the working and counter electrodes such that they are parallel and the sample is facing the counter electrode (Figure Previous). The reference electrode is not necessary to the setup. While we encountered difficulty when not using the reference electrode, others may encounter the opposite and choose not to use it.

4.5.3. Electroplating Parameters

1. Conduct a linear sweep of voltage to determine an appropriate voltage for electrodeposition. This voltage should give a current that is in the appropriate range for electrodeposition. There may be a large process window of appropriate voltages. For our preliminary structures, we found that 155mV worked well.
2. Collect current data during deposition. The absolute value of current should increase smoothly over time.

4.6. Removal of the Sacrificial Template

1. Submerge the substrate in a beaker filled with acetone and sonicate for 30 minutes or until all resist is removed. Rinse with DI water and dry with nitrogen. Do not use O_2 plasma, O_3, etc. As they will corrode the copper.
2. Characterize the final structures physically using a confocal microscope (SNSF Keyence) or an SEM. Uniformity, pore size, neck diameter, and structure height are the primary features of interest.