Electroplated, Porous, 3D Metallic Structures using Sacrificial Two-Photon Lithography Templates

ENGR241
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Research Report

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Contents

1. Motivation

1.1. Vertically Aligned Laterally Close-Packed (VALCP) Copper Inverse Opals

Porous metallic structures can be used for high heat flux, two-phase (liquid-vapor), passive hot spot cooling of electronics [1]. Liquid is fed from the sides and the porous structures wicks liquid across the hotspot. The liquid boils, taking advantage of latent heat of the coolant, and vapor is guided up and out through the porous structure (Figure 1).

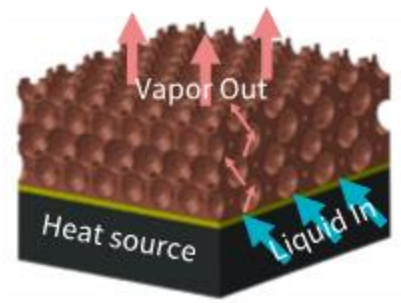


Fig. 1. Working principle of copper inverse opals for two-phase cooling

Previous studies have been conducted on copper inverse opal porous structures made via electrodeposition on self-assembled sintered polystyrene sphere sacrificial templates. Self-assembly is limited to close-packed face-centered cubic (FCC) structures. This is advantageous for wicking in the lateral direction, but limits vapor removal in the vertical direction. A simple cubic (SC) structure would aid in vapor removal. In this work, we aim to use two-photon lithography to create a hybrid SC/FCC vertically aligned, laterally close-packed structure (VALCP) not possible via self-assembly. We hypothesize that these novel structures will exhibit superior thermal performance to traditional FCC inverse opal metallic porous media. We will use the Nanoscribe Professional Photonics GT in the Stanford Nanofabrication Facility (SNF) ex-fab to write these two-photon lithography sacrificial templates.

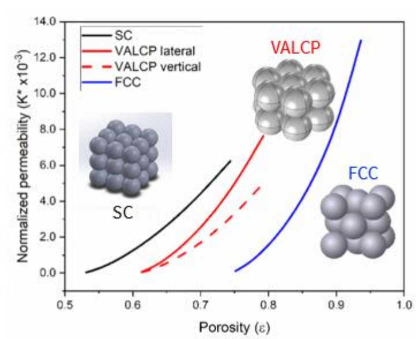


Fig. 2. Comparison of permeability and porosity for sphere packing structures

1.2. Benefit to Stanford Nanofabrication Facility

This work has three main deliverables that will benefit the SNF community:

1. Develop a Standard Operating Procedure (SOP) for writing three dimensional structures in thick positive photoresist in Nanoscribe.
2. Develop an SOP for using Nanoscribe with patterned reflective (metallic) substrates and characterize how these surfaces affect writing parameters.

3. Develop an SOP for electrodeposition on lithography-generated templates and removal of these sacrificial templates.

2. Methods and Preliminary Results

2.1. Process Flow

An overview of the process is shown in Figure 3. First, the template is written in thick positive photoresist (SPR 220-7) using two-photon lithography (Nanoscribe). Then, copper is electroplated into the interstices of the template. Finally, the template is removed.

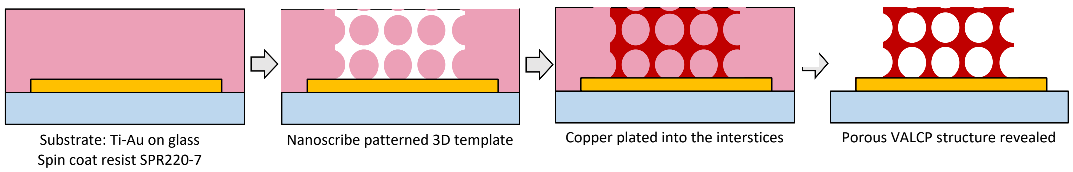


Fig. 3. Formation of VALCP copper structure via electrodeposition on a sacrificial two-photon lithography generated template

2.2. Direct Laser Writing Two-Photon Lithography

Two-photon lithography is a method of writing three dimensional structures with sub-micron resolution. A high-power pulsed femtosecond laser rasters in the lateral and vertical directions to write the desired structure in photoresist (Figure 4). Only at the focal volume of the laser is the laser intense enough to result in two-photon absorption, exposing the voxel (3D pixel). The exposure dose in two-photon lithography is primarily a function of laser power and write speed.

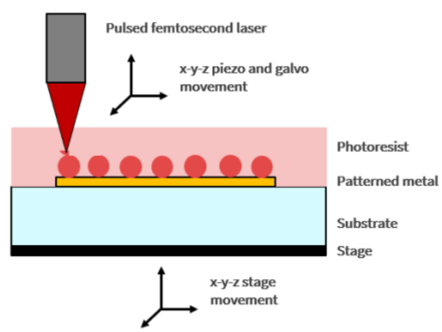


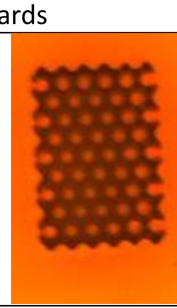
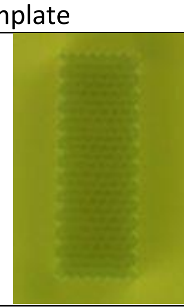
Fig. 4. Working principle of two-photon lithography

The two-photon lithography tool in SNF is the Nanoscribe Photonics GT Professional in the ExFab. The Nanoscribe has a minimum lateral feature size of 200nm and a lateral resolution of 500nm. Additionally, the Nanoscribe laser can move in a piezo or galvo mode. The piezo mode has faster write speeds. The piezo range is limited to 300μm x 300μm x 300μm [3].

Template formation involves three main steps common to all lithography processes: (1) photoresist coating, (2) exposure, (3) development.

Three photoresists were considered for template formation. These resists are compared in Table 1. SPR 220-7 was selected as the best resist for this application. Positive photoresist allowed writing of the template in a form that required less written volume than negative photoresist, with less stringent alignment requirements and less risk of overplating when electroplating. Additionally, developed positive photoresist is easier to remove than developed negative photoresist, making it preferable as a sacrificial template. The two main drawbacks of positive photoresist are that they are less well characterized in the Nanoscribe user community than negative photoresists and they require higher power to expose, which generally corresponds to slower write times. SPR 220-7 was selected over AZ4620 because AZ4620 was inconsistent in exposure, expired, and undesirable to restock due to health hazards.

Table 1. Photoresist comparison

	SPR220-7	AZ4620	IP-dip
Tone	Positive	Positive	Negative
Coating Method	Spin coat, double coat	Spin coat, single coat	Drop cast
Nominal thickness	29µm	17µm	N/A
Laser Power	100%	100%	30%
Power Scaling	1.2	1.2	1
Scan Speed	3000-10000µm/s	3000-10000µm/s	20000µm/s
Developer	MF-26A	AZ400K	SU-8 + IPA
Develop Time	2.5 minutes	5 minutes	25 minutes
Advantages	Consistent exposure, very thick resists are achievable, preferred resist for applications requiring thick resists in SNF	Previously used in literature and by other SNF users	Relatively low power and fast write speeds, simple drop casting
Disadvantages	Uncharacterized in Nanoscribe in SNF (to the best of our knowledge)	Inconsistent exposure, current stock is expired, SNF prefers to discontinue use of this resist due to health hazards	Unfavorable for templating an electroplated structure, difficult to remove as a sacrificial template
Representative Optical Microscope Image for structures with 5µm pores			

A conductive seed layer is necessary for electroplating. For our purposes, a patterned conductive substrate is necessary. Most previous Nanoscribe users who required conductive substrates used transparent indium tin oxide (ITO), with which oil immersion mode can be used in Nanoscribe. However, ITO is challenging to pattern compared to most metal evaporation and it is difficult to align structures with a transparent patterned substrate. We chose gold as our seed layer because we have used it in self-assembly template electrodeposition. Opaque and reflective substrates introduce several unique features to writing in Nanoscribe. (1) Writing must be done from the top of the substrate through air. (2) Nanoscribe can experience difficulty finding the resist-substrate interface. This is mitigated if the point at which Nanoscribe starts looking for the interface is close to the actual interface. We recommend finding the interface on a non-patterned (glass) section of the wafer and then moving the laser to the patterned region. (3) Aligning the written structure with the seed layer pattern is easier because the seed layer pattern can be clearly seen on Nanoscribe real-time camera. (4) Reflection of the laser by the seed layer, particularly for planes close to the resist-substrate interface, increases the intensity of the laser exposure. Figure 5 shows that doses that provide good exposure on glass lead to overexposure (boiling) on gold and good doses for gold result in underexposure on glass. We have not yet characterized if the reflectivity of the substrate affects the entire template, or just the layers closest to the interface.

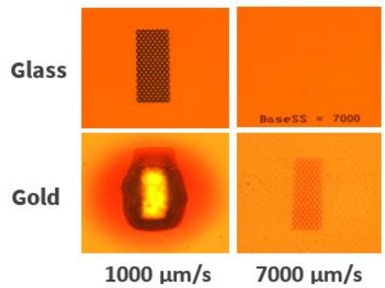


Fig. 5. Exposure dose comparison for glass and gold substrates

Figure 6 shows the results of a parameter sweep with maximum power for different write speeds on gold for 29µm thick SPR 220-7 resist. As shown in Figure 7, the top view of the exposure might not only depend on the does, but also depend on what height of the spheres is written at the top surface of the resist, making it difficult to identify the optimal write speed. We will conduct another parameter sweep with a different structure that will eliminate this issue before winter quarter.

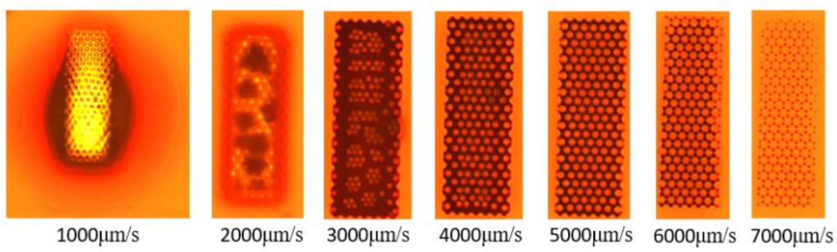


Fig. 6. Write speed parameter sweep for 29µm thick SPR 220-7 resist on gold with 100% base laser power and 1.2x power scaling with 63x objective

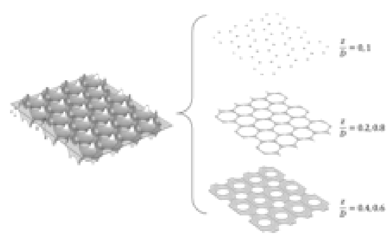


Fig. 7. Comparison of top views of different planes of inverse opal structures. Underexposure with the top surface of the structure at z/D=0.4 might look similar to the optimal exposure dose with the top surface of the structure at z/D=0.

After exposure, the resist must be left in the litho area long enough for nitrogen to diffuse out of the resist and for water to diffuse in. This is particularly important for thick resists. A minimum wait time of 2 hours and a maximum wait time of 36 hours is recommended. When developing, underdevelopment was observed to be more sensitive than overdevelopment, although care should be taken not to overdevelop the structures. An optical microscope inspection is recommended for characterizing exposure and development. The optical Keyence is not recommended as it has been observed to boil resist (Figure 8). This may be mitigated or eliminated by baking the resist, but baking may also make the template more difficult to remove after electroplating.

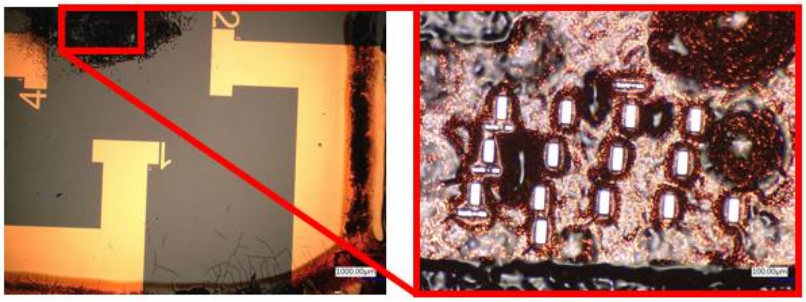


Fig. 8. Keyence optical microscope boils developed resist

2.3. Template-Assisted Electrodeposition

In this work, we used a three-electrode setup to electrodeposit copper on a gold seed layer covered by lithography-generated templates. Figure 9 shows the relative positions of the sacrificial copper anode, the target sample cathode, and the reference electrode, as well as the flow of current and copper ions.

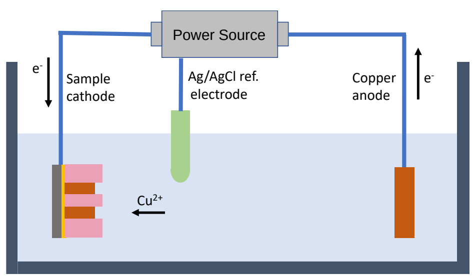


Fig. 9. Electrodeposition setup

Preliminary electrodeposition was conducted on flat gold samples and 2D inverse pin fin templates with 2μm features made using the Heidelberg maskless aligner. Several parameters were determined from these tests. First, the cleanliness of the seed layer is vital to proper deposition. For two dimensional structures, this was achieved by cleaning with DI water and descumming. However, descumming for three dimensional structures may prove more challenging. Second, the cathode and anode should be vertical and facing each other for best deposition. Third, spinning has the potential to better diffuse copper ions, but the lowest possible spin speed (60RPM) still resulted in highly non-uniform electrodeposition (Figure 10) and should be avoided. Fourth, controlled current electrodeposition is preferable for controlling the height of a deposition, but controlled voltage resulted in more uniform deposition without voltage spikes (Figure 11) and chaotic deposition during initialization. -155 mV worked well for the 2D inverse pin fin structures and is thus chosen as a starting point for 3D structures. Fifth, the Faraday efficiency was observed to be relatively constant between depositions (Table 2). This presents a simple method of estimating the height of electroplated samples during deposition.

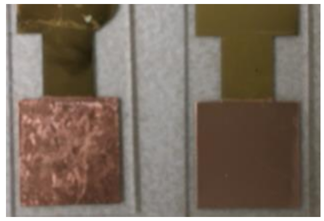


Fig. 10. Electrodeposition on an unpatterned gold seed layer (a) with 60rpm stirring and (b) without stirring, and smooth copper surface is achieved.

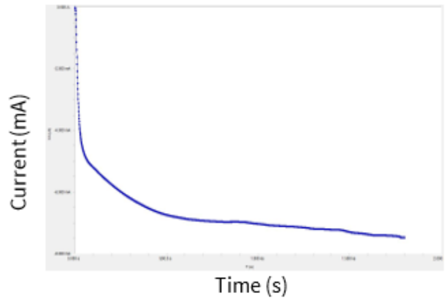


Fig. 11. Current versus time for electrodeposition on a patterned substrate with constant -155mV

Table 2. Supplied electric charge, thickness, and effective Faraday efficiency for two electroplated inverse pin fin samples with 10μm pores with -155mV constant applied voltage

Electric charge supplied	**Measured thickness**	**Effective Faraday efficiency**
36 mC	17.7 μm	49.2%
15 mC	7.7 μm	51.3%

After electrodeposition, the template is best removed by sonication in an acetone bath.

2.4. Characterization

The first level of characterization that should be done is physical characterization of both the two-photon lithography templates and the electroplated structure. There are four primary tools that can be used to characterize the templates. These are compared in Figure 12. (1) The in situ Nanoscribe camera shows if the photoresist is severely overexposed (boiling) or underexposed (not visible), but does not provide good images of the relative quality of intermediate exposures. (2) Optical microscopes are simple and can provide clear images of the top layer, and possibly top two layers, of resist, but may have limited magnification and capture capabilities. (3) The optical and confocal Keyence microscopes can provide higher quality images, but expose or boil the resist if it is not baked, which is preferably avoided to aid in later template removal. (4) SEM requires coating the template with metal to eliminate charging issue, but the coating also makes it unsuitable for further electroplating, and provides no additional information about the top layer of the structure. However, if the structure is large enough to take a cross section, SEM may be able to provide additional information on the exposure quality on different planes of the photoresist. Arguably, the same could be achieved by mounting a cross section on a 90° stage under an optical microscope.

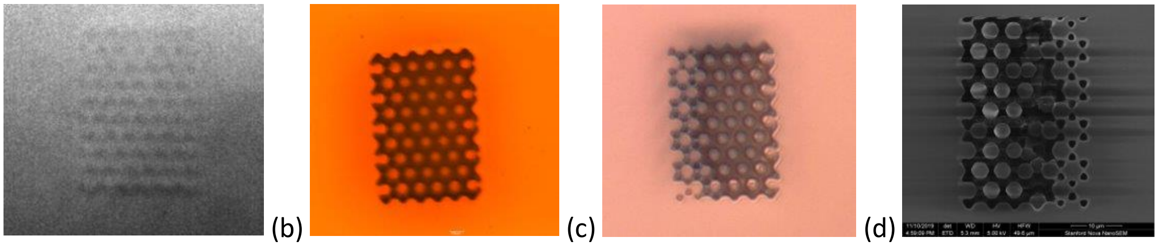
(a) (b) (c) (d)


Fig. 12. Comparison of template characterization methods for a 10μm inverse opal structure with 100% base laser power, 1.2x power scaling, 3000μm/s scanning speed in AZ4620 photoresist. (a) Real time Nanoscribe camera during exposure, (b) optical microscope after 5 minutes development, (c) optical Keyence microscope after 13 minutes development, (d) SEM after 13 minutes development

The same tools are considered for the physical characterization of the electroplated structure. However, neither Keyence nor the SEM damage the final structure. The confocal Keyence provided the best images of the electroplated structure in initial tests (Figure 13).

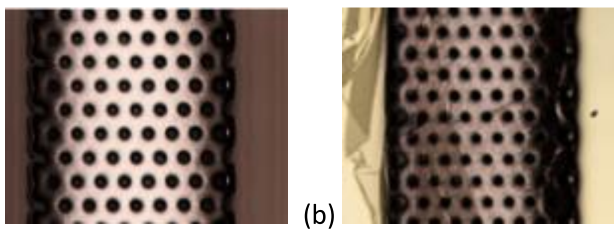
(a) (b)


Fig. 13. Confocal Keyence image of electroplated structures (a) before template removal, (b) after template removal

In winter quarter, we will further characterize the electrical resistance and the wicking performance of the final structures using an H-bridge setup similar to that used previously for self-assembled structures.

3. Future Work

Fall quarter was used to determine the preliminary Nanoscribe writing and electrodeposition parameters for the desired final porous structures.

We plan to determine the final writing parameters for SPR 220-7 resist using pin fin structures and prepare sufficient patterned samples.
After that, we will start by writing small footprint versions of our final design. We will clean these structures with DI water, the matrix descum tool, and see if electroplating is successful. We anticipate that cleaning this surface of resist residue is vital and may be challenging. Detergents or alternative plasma etching tools may be attempted if our first strategy is insufficient. Once electroplating is demonstrated, we will find a proper electroplating condition (voltage and time), and the time required to remove the template via acetone and sonication. We will then finalize the characterization techniques desired for our final structure. In parallel, we will build and test the setup for future measurements. Next, we will write the final structure templates and repeat the electroplating and physical characterization procedure. Finally, we will conduct electrical and wicking experiments. Time permitting, we may repeat the process with nickel. In the final application, nickel is advantageous because it does not corrode, but it is not as conductive as copper.

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.

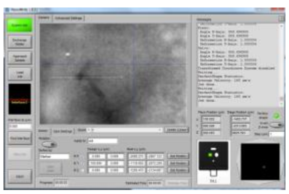
4.4.1. Coat

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.

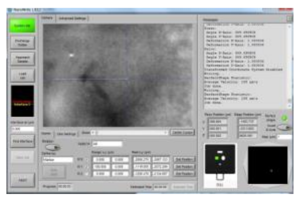
4.4.2. Exposure

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.

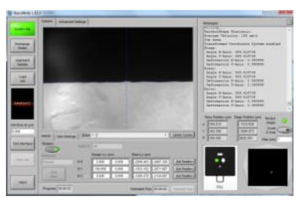


1. Turn on camera, manually write a line to track the laser



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.

5. References

[1] C. Zhang, et al., "Enhanced Capillary-Fed Boiling in Copper Inverse Opals via Template Sintering," *Advanced Functional Materials*, DOI: 10.1002/adfm.201803689, 2018.
[2] T. Huang, et al. “Two-photon lithography for dielectric structures and electroplating molds for retinal prostheses,” *Stanford SNF ENGR241 Final Report*, 2018.
[3] “Nanoscribe Photonic Professional GT User Manual,” July 2015.
[4] “MEGAPOSIT™ SPR™220 SERIES PHOTORESISTS Data Sheet,” July 2004.

6. Acknowledgements

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7. Expenses

Fall quarter project expenses were $3305.97 out of a maximum budget of $5000.00. A breakdown of expense categories is given in Figure 15.

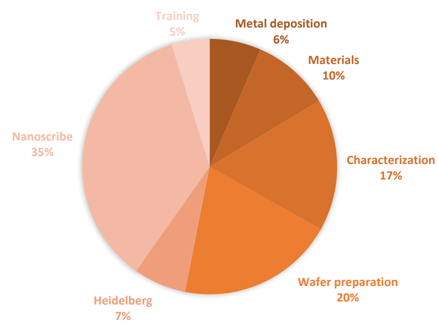

Fig. 15. Fall quarter expense categories