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

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Research Report

Alisha Piazza and Qianying Wu

SNF Mentor: Swaroop Kommera
Industry Mentor: Tony Ricco
Faculty Advisors: Ken Goodson, Mehdi Asheghi, Jonathan Fan, Roger Howe

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1. Motivation

1.1. Vertically Aligned Laterally Close-Packed (VALCP) Metal 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).

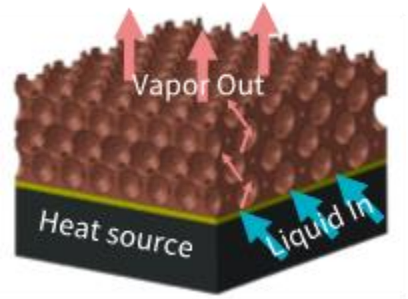


Fig. 1. Working principle of copper inverse opals for two-phase cooling

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 capillary 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 anisotropic structures will exhibit superior thermal performance to traditional FCC inverse opal metallic porous media. We use the Nanoscribe Professional Photonics GT in the Stanford Nanofabrication Facility (SNF) ex-fab to write these two-photon lithography sacrificial templates.

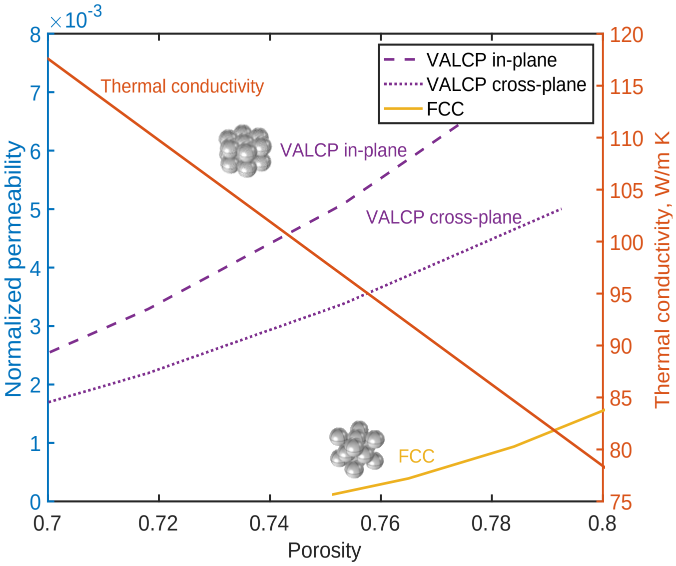


Fig. 2. Comparison of permeability, thermal conductivity, and porosity for inverse sphere packing structures

1.2. Benefit to Stanford Nanofabrication Facility

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

1. Develop an SOP for using Nanoscribe with patterned reflective (metallic) substrates and characterize how these surfaces affect writing parameters.
2. Develop an SOP for electrodeposition on small 3D negative resist templates and removal of these sacrificial templates.

2. Process Flow

An overview of the process is shown in Figure 3. First, the template is written in thick IP-dip photoresist using two-photon lithography (Nanoscribe). Then, metal is electroplated into the interstices of the template. Finally, the template is removed and the metallic VALCP inverse opals structure is revealed.

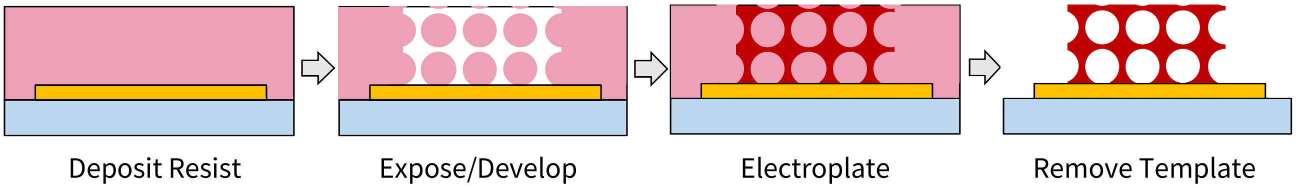


Fig. 3. Formation of VALCP metal structure via electrodeposition on a sacrificial two-photon lithography-generated template

3. 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 not explicitly controlled. it is primarily a function of laser power and write speed, but also depends on feature size, feature geometry, print size, substrate, and writing mode (top or bottom of wafer, dip-in, oil-immersion, through air, etc.).

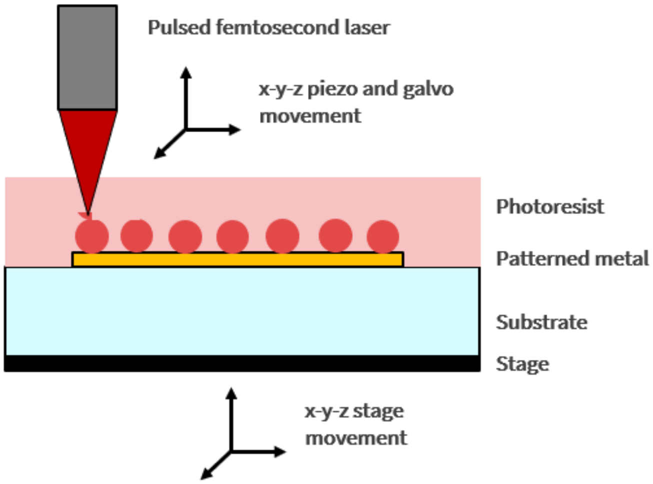


Fig. 4. Working principle of two-photon lithography

3.1. Nanoscribe

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 writing speeds. The piezo range is limited to 300μm x 300μm x 300μm [2], [3].

Suggestions:

1. If your final structure involves stage movement, we suggest writing at least one entire block for the parameter sweep, so that the optimal parameters found during the parameter sweep can be applied to the final structure.
2. It is better to write a for loop in DeScribe instead of using Nanoscribe arraying, moving, and parameter sweeps.

3.2. Photoresist selection

Both positive and negative photoresists were considered for templates printed using Nanoscribe. Positive photoresist was originally preferred, primarily because it is easier to remove than negative photoresist. Ultimately, it was determined that negative photoresist was more appropriate for this application.

3.2.1. Positive Photoresist

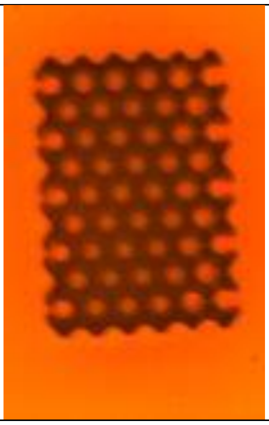
Originally, we wanted to use positive photoresist, especially because it is easy to dissolve with solvents which made it ideal for sacrificial templates. Additional pros and cons of positive photoresists are shown in Table 1. We experimented with AZ4620, a positive photoresist used in literature [4] and SPR 220-7, the most common thick photoresist used in SNF. Ultimately, the process window for these resists was limited and writing trials were highly variable. We deemed positive photoresist a poor choice for our small, thick, tortuous, 3D structures. However, we hope that our experiences can help other users with positive photoresist in Nanoscribe.

Table 1. Pros and cons of positive photoresist

Pros	Cons
Easy to dissolve with solvents	Not tuned for two-photon lithography
Covers all areas not intended to be electroplated	Not well-characterized in literature
Contributes a new process to SNF	Small process window for exposure dose, development time, and/or resist coating and baking
For the VALCP structure, less volume needed to be written	Dose is highly dependent on feature size, geometry, and total print area
	Tortuous features are difficult to develop
	Generally requires slower write speeds
	Coating procedure is more complex than drop-casting and may require multiple coats to achieve desired thickness
	Can be challenging to descum the substrate surface with 3D features

Comparison of the two positive photoresists that we experimented with are shown in Table 2.

Table 2. Comparison of two positive photoresists

	SPR220-7	AZ4620
Coating Method	Spin coat, double coat	Spin coat, single coat
Nominal thickness	29µm	17µm
Developer	MF-26A	AZ400K:DI water = 1:4
Develop Time	2.5 minutes	5 minutes
Advantages	Very thick resists are achievable, preferred resist for applications requiring thick resists in SNF	Previously used in literature and by other SNF users
Disadvantages	Uncharacterized in Nanoscribe in SNF (to the best of our knowledge)	SNF prefers to discontinue use of this resist due to health hazards
Representative Optical Microscope Image for structures with 5µm pores		

Additionally, we found it necessary to take cross-sectional scanning electron microscope images to confirm the exposure and development of the positive photoresists. Due to the 3D nature of the structure, it is hard to determine if the photoresist is exposed and developed to the desired geometry by optical and top-view imaging, as shown in figure 5. We printed a structure that is large enough (1000µm long) for hand cleaving across the structure, mounted the structure on a vertical SEM mount, coated the sample with Pd/Au to reduce charging, before taking the sample to SEM.

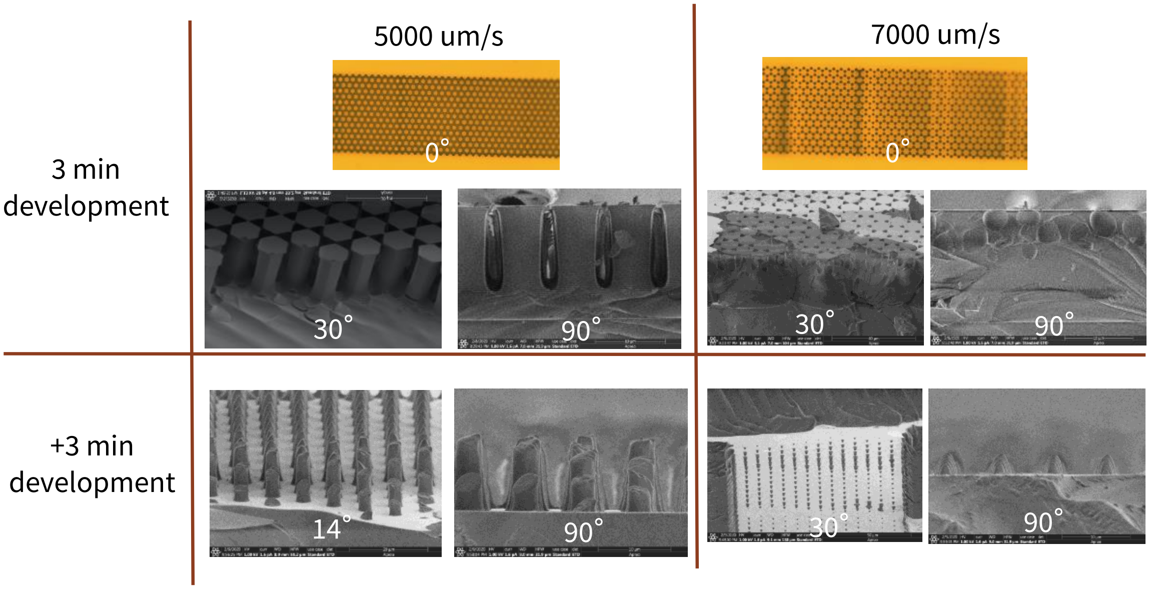


Fig. 5. Optical imaging and SEM imaging of VALCP templates patterned with AZ4620 resist with laser scanning speed of 5000µm/s and 7000µm/s respectively.

We found that after development, the top layers did not appear to be spherical as we expected, and the bottom layers were undeveloped, as shown in figure 6.

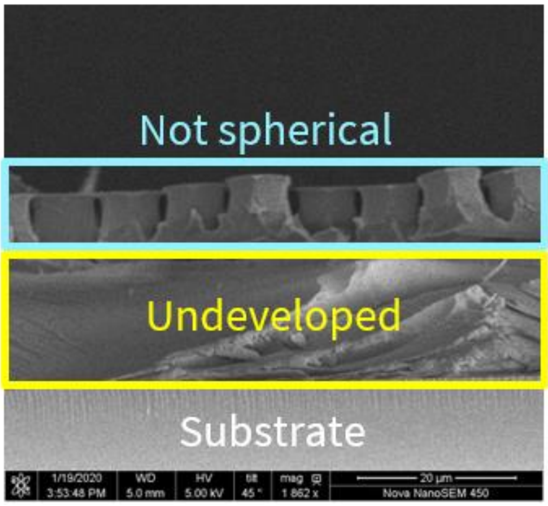
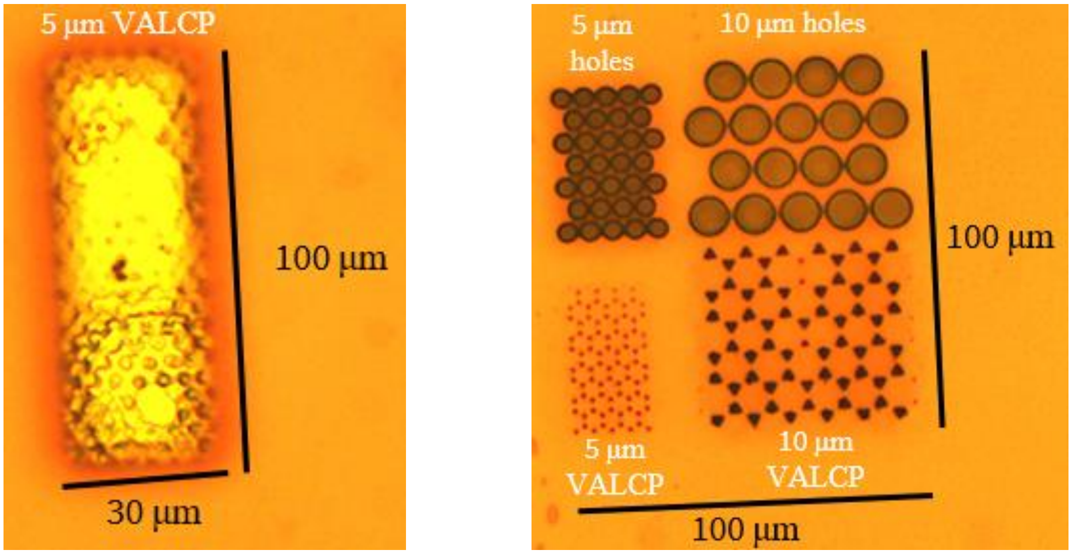


Fig. 6. Not desirable exposure and development process of AZ4620

Another characteristic of the positive photoresist is that the process window for the laser dose is relatively small comparing to negative resists. Since Nanoscribe does not allow users to the specify the dose explicitly, but use the laser power, and scanning speed to indirectly appoint a dose, this might lead to the exposure to be highly sensitive to the geometry and the total footprint of the structure. Figure 7 shows that for the same laser power and scanning speed, one might get different exposure depending on (a) if the structure is printed alone or inside a larger array, (b) the geometry of the structure.

Therefore, if your final structure involves any stage movement, we suggest writing at least one entire block for the parameter sweep, so that the optimal parameters found during the parameter sweep can be applied to the final structure. And if your structure does not involve a stage movement, we suggest using your exact final structure for the parameter sweep.



(a) 5µm VALCP structure printed alone

(b) 5µm VALCP structure printed together with other structures

Fig. 7. Inconsistent exposure of AZ4620

3.2.2. Negative Photoresist

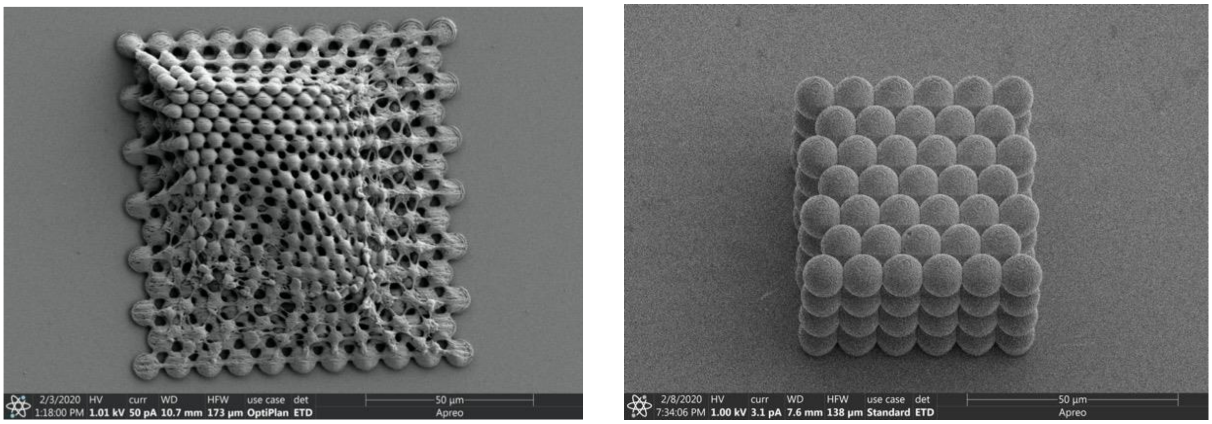
IP-Dip [5] is chosen as our choice of negative photoresist for this project because it is most suitable for structures with small feature sizes among the various negative photoresists provided in SNF, for example IP-S, etc. It has a larger process window for laser dose comparing to positive resist like AZ4620, so it is more likely to get repeatable and consistent results in different runs. Additional pros and cons of negative photoresists are shown in Table 3.

Table 3. Pros and cons of negative photoresist

Pros	**Cons**
Tuned for two-photon lithography and supported by Nanoscribe	Difficult to remove
Drop-casting is simple and capable of creating thick resist	Must protect areas outside intended structure from electrolyte
Generally writes faster than positive photoresist	
Developer cleans the substrate surface, so there is generally no need to descum after development	

It is also possible to engineer the roughness or texture of the template by tuning the writing parameters in DeScribe software. For example, decreasing the slicing thickness and contouring can improve the smoothness of the print. For our application as a wicking structure for capillary-fed boiling, we found it preferable to have rough surfaces for bubble nucleation.

Figure 8 shows a structural collapsing effect during the development and drying process. The cause of the structural collapsing is due to the capillary force of the solvent during its drying process after development of the photoresist [6]. Lower doses result in lower tensile strength of the structure, and lead to more severe collapsing. The collapsing effect can be mitigated by increasing the exposure dose, using a low surface tension solvent such as HFE7100 to replace isopropanol after developing in SU-8, and to allowing the solvent to evaporate in air instead of using a nitrogen gun to blow dry the structure.



Collapsed structure after development Improved structure after development

Fig. 8. Structural collapsing and its mitigation

We also experienced poor attachment of the IP-Dip to the substrate, and figure 9 shows that the structure was lifted off before or during electroplating. And this can be mitigated by the substrate pretreatment process before patterning IP-Dip. We determined that acetone sonication, isopropanol rinse, plasma cleaning, followed by salinization in “yes” oven provides a better surface for the adhesion of the IP-Dip photoresist on our Au patterned substrate.

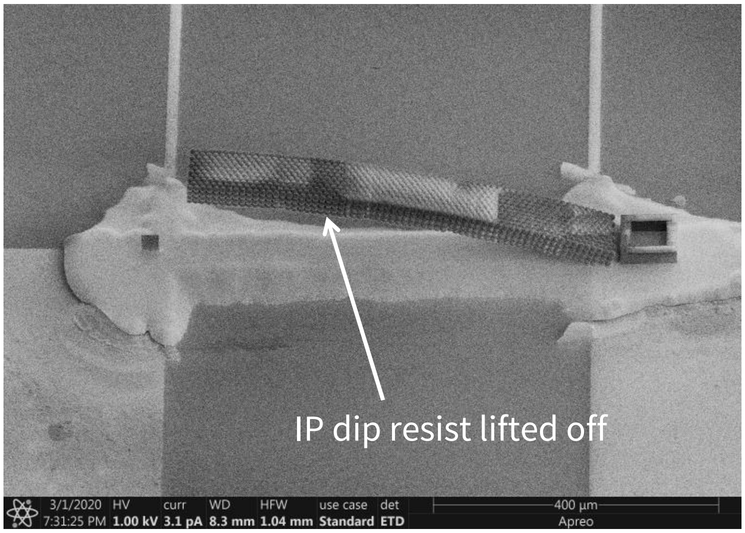


Fig. 9. Poor adhesion of IP-Dip photoresist to the substrate

To better control the electrodeposition process described in the next session, we introduced some “overplate barrier” at the edge of the structure to prevent overplating, and a control structure next to the structure for thickness monitoring. As shown in Figure 10, the structure is also aligned well to the patterned substrate for a four-point probe measurement.

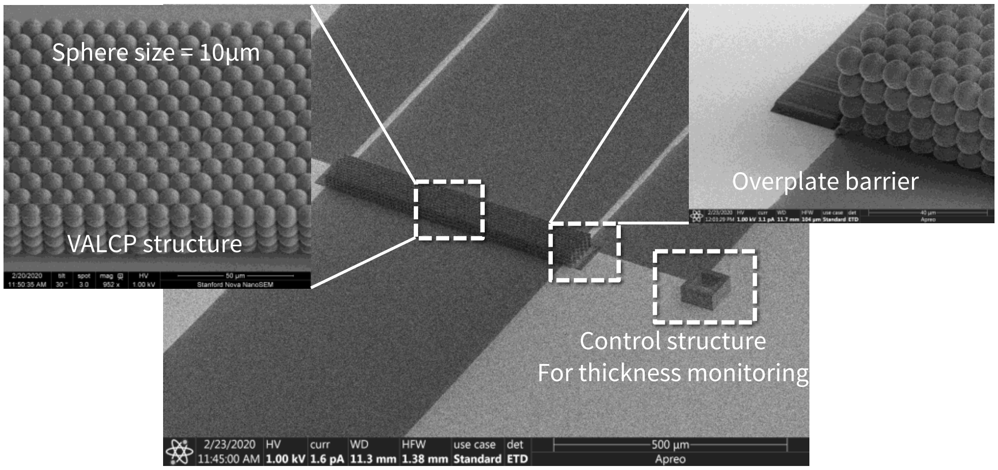
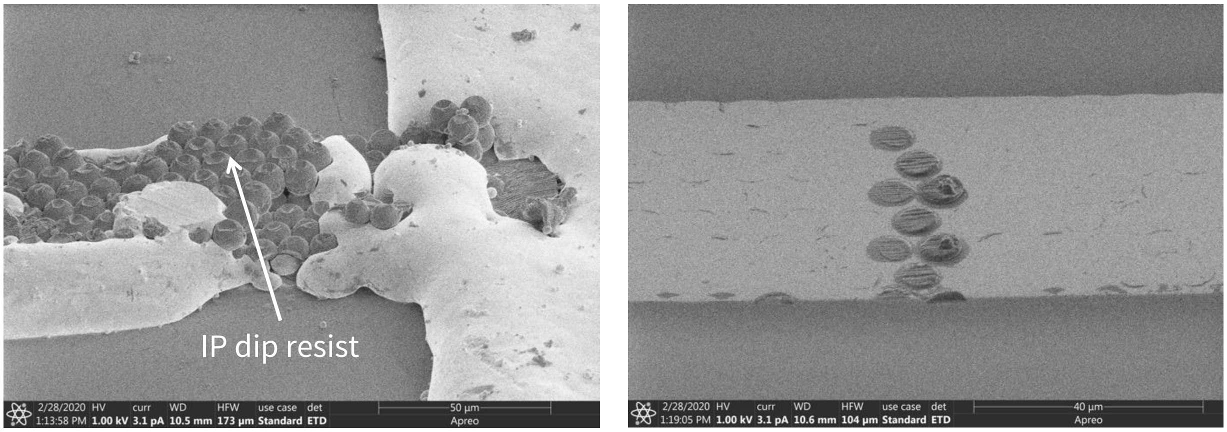


Fig. 10. 10µm sphere size VALCP template with "overplate barriers" and control structure

4. Resist removal

While the positive photoresists (AZ4620 and SPR220-7) can be dissolved in acetone, the removal of negative photoresist IP-Dip is not trivial. After exposure and development, IP-Dip photoresist becomes highly cross-linked and difficult to remove with many solvents. Experiments show that acetone, isopropanol, methylene chloride, and/or Methyl isobutyl ketone (MIBK) failed to effectively remove IP-Dip, and the only wet etching method that is proved to be effective is fresh piranha solution, with sulfuric acid : hydrogen peroxide = 3:1, for 20 min at 60-70ºC, or 24 hours at room temperature. For structures with torturous pathways, one should expect the diffusion effect to elongate the photoresist removal process, compared to low aspect ratio and straight features.

Since the removal of IP-Dip involves piranha solution, which attacks copper, we switched to electroplating gold in order to preserve the electroplated metal.



(a) 24 hours methylene chloride + 24 hours MIBK (b) 24 hours piranha, room temperature

Fig. 11. Removal of IP-Dip photoresist

An alternative approach is to dry etch IP-Dip in oxygen plasma, although this would take a significant amount of time (~24h at 500W at the maximum oxygen flow with non-directional setting) [7].

5. Electroplating

Electroplating is a process that utilizes the electric current supply to reduce metal cations on the electrode. A conductive seed layer is necessary to close the electric circuit, and a patterned seed layer can be used to define the area where we want to have metal deposition.

5.1. Electroplating setup

In this work, we used a two-electrode setup to electrodeposit gold on a gold seed layer covered by lithography-generated templates. Figure 12 shows the relative positions of the platinum anode, and the target sample cathode.

Commercially available gold plating solution Elevate Gold 7990 [8] was used, and the electroplating was done at an elevated temperature of 55°C with a hotplate. Note that this is the temperature of the solution. The set temperature of the hotplate must be higher. It is preferable to have a sample holder that can keep the working electrode parallel to the counter electrode at a fixed distance. To mitigate the evaporation of the solution, we covered the glass beaker with parafilm. We used a Gamry Reference 600 potentiostat to supply the designated waveform and to monitor the current/voltage along the electroplating process.

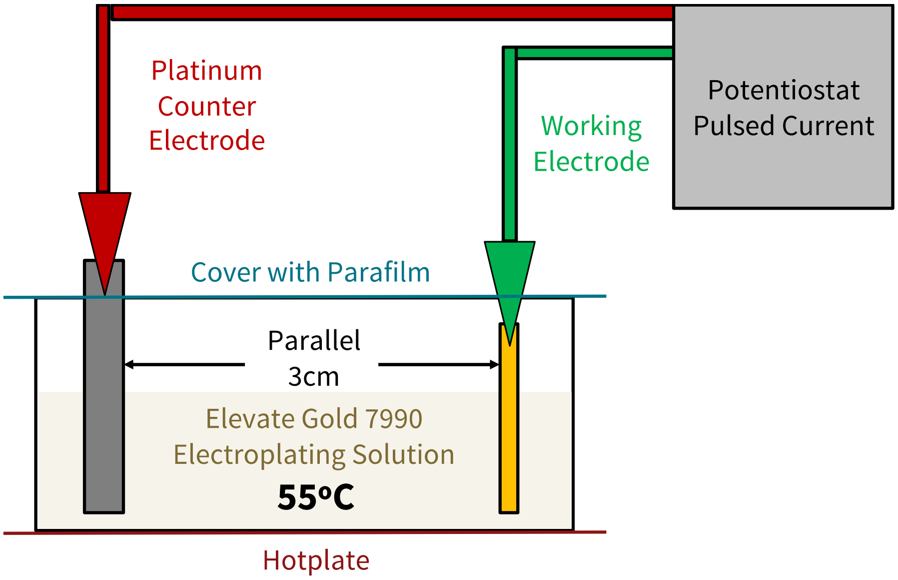
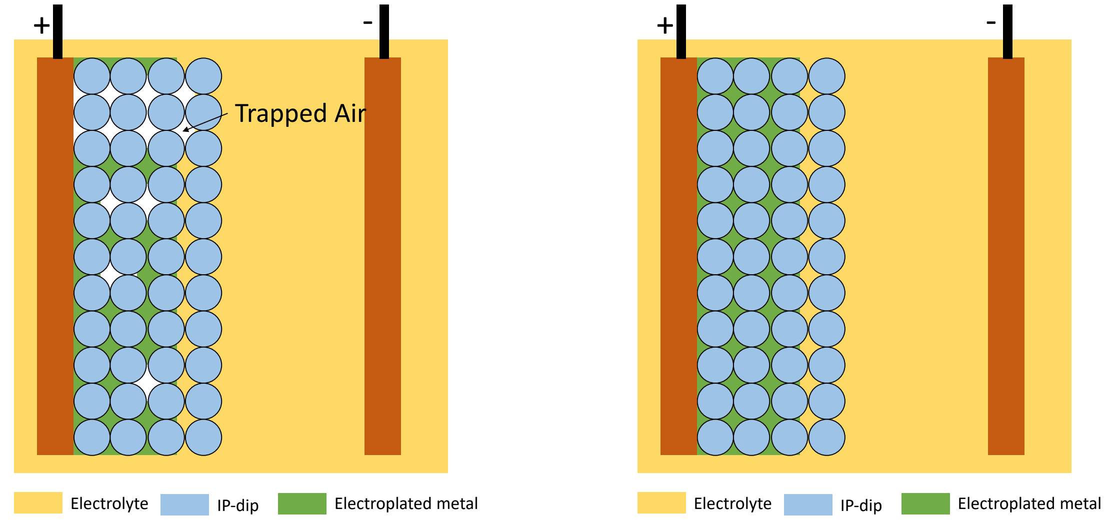


Fig. 12. Two-electrode electrodeposition setup for Au electroplating

5.2. Wetting

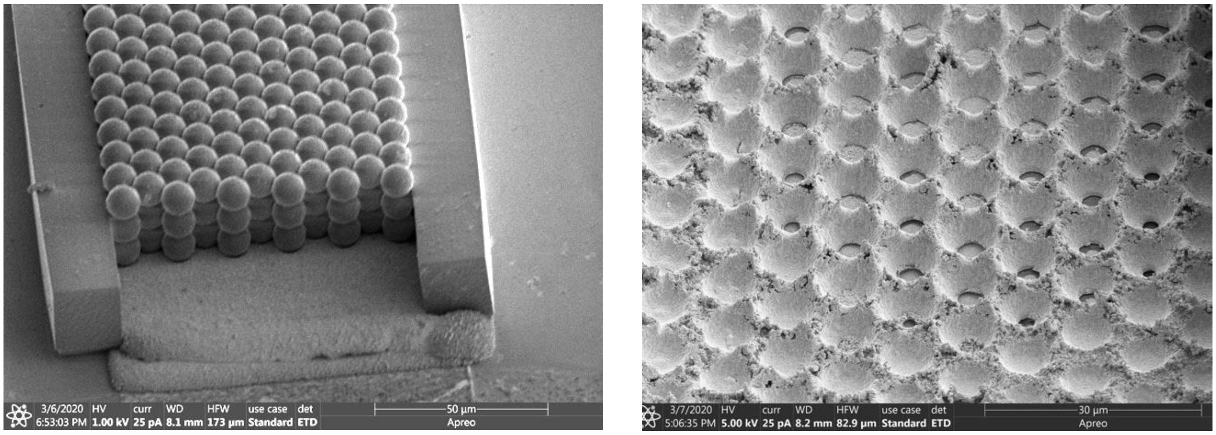
Wetting is important for high aspect ratio structures or structures with a torturous pathway. Without appropriate wetting, air trapped inside the structure may result in undesired voids in the electrodeposited metal matrix. Figure 13 illustrates the effect of proper wetting before electroplating. Commercial electroplating solutions often contain surfactants to help with wetting. Additional steps can be taken to improve wetting before electroplating.



(a) Without proper wetting (b) With complete wetting

Fig. 13. Effect of proper wetting on the electrodeposited metal

For our highly tortuous samples, we combined various wetting methods to ensure a better wetting. First, we did air plasma treatment in Harrick Plasma PDC-32G for 1 minute to create a hydrophilic surface. Then, we immediately put a droplet of ethanol on the side of the sample and let it wick into the voids of the structure and submerge the sample into the electrolyte before the ethanol evaporates. After that, we further put the beaker with the sample soaked in electrolyte into a vacuum chamber and pulled a vacuum of 29 inHg to allow for the removal of trapped air. Although sudden bubbling of the electrolyte was seen during the vacuum degassing process is normal, we kept the vacuum pumping to be slow and gentle to prevent splashing of the electrolyte into the vacuum chamber. Figure 14 shows the complete wetting of the sample before and after the removal of the template. The bottom layer is continuous with no large voids.



(a) Before template removal (b) After template removal

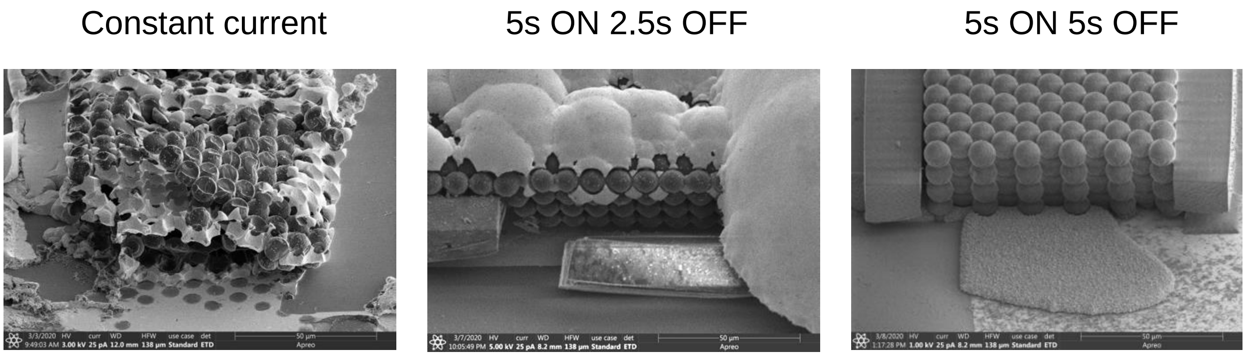
Fig. 14. Complete wetting of the sample and the resulting continuous deposited metal

In literature, people also tried replacing air in the voids with carbon dioxide gas before submerging the structure into the electrolyte to achieve better wetting. [9]

5.3. Electroplating conditions

We found that the current density or voltage, waveform (pulsed or constant), and agitation may influence the quality and characteristics of the electroplated metal, although more work needs to be carried out to derive the causal relationships of each factor on the electrodeposition.

Pulsed electrodeposition has an advantage of allowing diffusion time for the depleted gold cations to replenish from the solution. Different waveform is compared in figure 15. We used first order calculation of Fick’s law to calculate the time scale for the ion diffusion and chose on time to be 5 seconds, and off time to be 5 seconds for our electroplating, with a control current of -8µA during the on periods.



Voids not completely filling

Au deposition from top
(not enough penetration)

More uniform electroplating
from bottom to top

Fig. 15. Comparison of different waveform on the electrodeposited metal

We made sure to keep the two electrodes parallel to each other and keep the distance of the two electrodes to be constant. We did not use a stir bar to agitate the electrolyte because it gave us a rougher surface finish.

As shown in figure 16, we also noticed discontinuity and boundaries if we electroplate the structure in multiple sessions, between which we took the sample out of the electrolyte, characterized and resumed electrodeposition after the same wetting process. To get the optimal quality of the electroplated metal, it is recommended to complete the electrodeposition in one session.

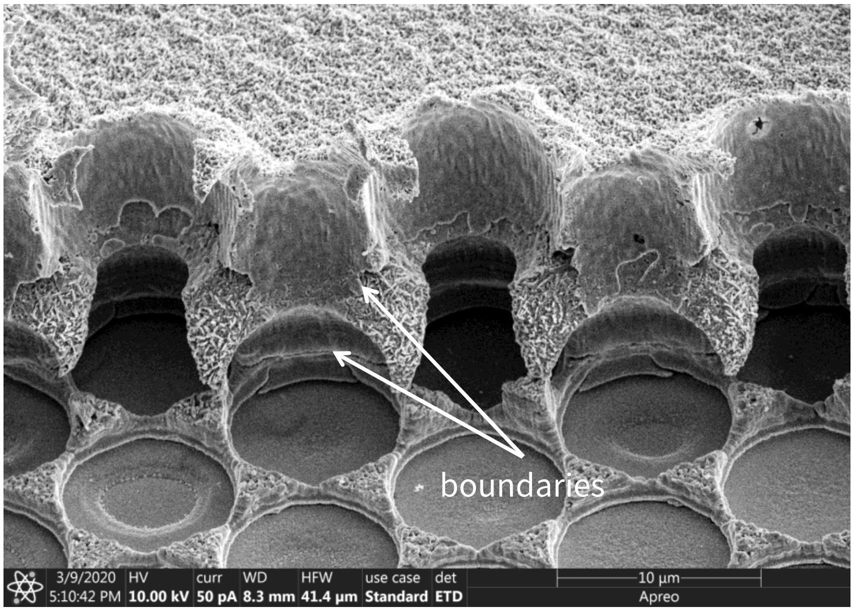
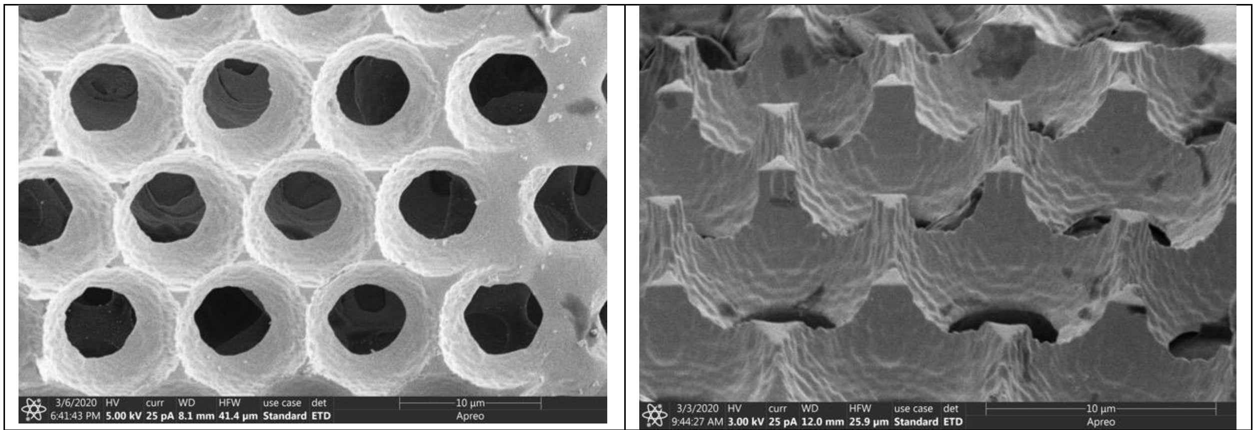


Fig. 16. Boundaries on the electrodeposited metal when electrodeposited in multiple sessions

6. Characterization

We mainly used scanning electron microscope (SEM) to characterize the IP-Dip template and the electrodeposited metal. IP-Dip photoresist is not conductive and there might be potential charging issue when imaging under SEM. However, it is not recommended to sputter Pd/Au on IP-Dip to make it conductive just for characterization since a metal coating will make the template unsuitable for further electroplating. The best way to characterize the IP-Dip structure is to image the IP-Dip with a low power setting, for example 1kV and 25pA.

Figure 17 shows a portion of our final structure after the removal of the photoresist. It is clear that we achieved the VALCP structure - the spheres in the next layer is aligned with the top layer.



(a) Top view of VALCP structure

(b) VALCP structure in 54º angle

Fig. 17. Scanning electron microscopy of the VALCP structure after removal of the IP-Dip template

7. Future Work

In the future, optimization of electroplating waveform/current density should be studied for better filling, smoothness and uniformity of the electroplated metal. It is also of interest to study better ways to remove IP-Dip photoresist to be compatible with the electroplated copper structures.

After the material fabrication, capillary-fed boiling experiment can be carried out on the VALCP structures, and further parametric study of the pore sizes and necks of VALCP structures on fluid permeability, capillarity, and capillary-fed boiling performance is of interest to better understand the mechanisms of capillary-fed boiling and the decoupling of fluid delivery and vapor removal effect.

8. Standard Operating Procedures

8.1. 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 opaque and/or reflective patterned substrates
2. Use Nanoscribe to print three-dimensional features on the order of 1-10μm in IP-Dip negative photoresist
3. Electroplate gold in templates made via two-photon lithography
4. Remove exposed IP-Dip

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

8.2. Materials and Equipment

Materials

- 1 inch square Nanoscribe DiLL Hi Res substrates (or other desired substrates)
- IP-Dip negative photoresist
- SU-8 developer
- SPR 3612 positive photoresist
- MF-26A developer
- Novec HFE 7100 (IPA may also be appropriate, see details in section 8.4.3)
- Platinum anode ("Purity 99.99% Platinum Plate Electrode Coated with PTFE Insoluble Anode" from Amazon or similar or platinum-coated SiO_2-coated Si)
- Commercial electroplating solution (Elevate Gold 7990 or similar cyanide-free gold plating solution)

SNF Equipment

- Evaporator (aja, KJL, etc.)
- HMDS prime oven (yes or yes2)
- Spin coater (headway2 or headway3)
- Solvent bench (wbexfab-solv)
- Developer bench (wbexfab-dev)
- Plasma cleaner (technics)

- Maskless aligner (Heidelberg)
- Nanoscribe
- Optical microscope
- SEM (Apreo, Nova, etc.)

Additional Lab Equipment
- Air plasma cleaner (optional)
- Desiccator or vacuum (optional)
- Potentiostat (Gamry Reference 600 or any other)

8.3. Metal Patterning

Metal patterning process consists of lithography (using Heidelberg) to define the pattern of the metal layer, metal evaporation, and liftoff. We did not use LOL for our substrates. However, improved metal patterning can be achieved by following standard SNF recommendations for LOL.

8.3.1. Coat

1. Clean DiLL Hi Res 1 inch square wafers with acetone and IPA. Dry with a nitrogen gun. Additional cleaning with 1-2 minutes in technics using the default recipe is recommended if the wafers are new because they come in a sticky package or if the wafers have been sitting for a long time.
2. Dehydrate and HMDS prime the wafers in the yes or yes2 oven. This salinization process promotes the adhesion of photoresist and the substrate by functionalizing the surface to be hydrophobic.
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.

8.3.2. Expose, 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 in technics with the standard recipe for 60 seconds.

8.3.3. 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.
3. Rinse the substrate with acetone, IPA, and dry with a nitrogen gun.

8.4. Nanoscribe Writing

Nanoscribe writing consists of drop casting IP-Dip, exposure in Nanoscribe, and development of the photoresist.

8.4.1. Drop Cast

1. Clean the patterned substrate with acetone, IPA, and dry with nitrogen. Additional cleaning with oxygen plasma in technics 1-2 minutes is recommended.
2. Dehydrate and HMDS prime the wafers in the yes or yes2 oven to improve adhesion of IP-Dip to the substrate.
3. Place the substrate in the DiLL Hi Res sample holder and tape in place.
4. Deposit a small drop of IP-Dip on the desired exposed area.

8.4.2. Exposure

1. Expose immediately after drop casting.
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 following parameters:
    a. In the open stl/import step:
        i. Default parameters for the IP-Dip 63x Fused Silica
        ii. Increased the "base slice count" to 20 slices (This is to have around 7µm of base layer for which we would like to have a different laser power/writing speed from the main body, to prevent boiling near the reflective interface)
        iii. Used "none" as the splitting mode. Structures must be smaller than 150µm in the x and y directions to avoid splitting (Otherwise the structures will be written in different "blocks" between which there is a stage movement)
    b. In the main job file
        i. Set $interfacePos = 1.0. This ensures that the structure writes on and adheres to the substrate by starting from a plane below the interface.
        ii. Set $baseLaserPower = 35%, $baseScanSpeed = 25000. The base (near the substrate surface) dose should be lower than the solid (main body) because reflective substrates increase the effective dose. Perform a power and scan speed test with a unit cell of your final geometry to determine the appropriate dose. If your final structure involves several blocks, this "unit cell" should be at least one block in size to make sure the dosing matrix gives transferable result to your final structure.
        iii. Set $solidLaserPower = 70%, $solidScanSpeed = 50000. Larger scan speed is preferred for a saving of writing time which is linear to the usage cost of the tool.
        iv. Manually code stage movement and for loops to write multiple blocks to write larger blocks, if needed.
        v. Open the included gwl files and disable the find interface command for individual files. This step is meant to prevent difficulties in interface finding when the stage moves to a field of view with coexisting glass and gold, which have very different reflective index. This is optional depending on your substrate.
3. Preheat the laser in Nanoscribe for at least 30 minutes before writing by enabling the tool and opening the NanoWrite software. Follow prompts to calibrate the stage. Preheating is helpful to achieve a more stable laser power and consistant exposure result.
4. Install the 63x objective lens in position 3.
5. Click "approach sample."
6. Turn on the light source and adjust the intensity on NanoWrite software. For transparent substrate, choose transmission, otherwise choose reflection light source.

7. Open the Axio Vision software. In the “properties” toolbox, adjust the exposure time, contrast, and brightness to improve visuals. If you see strips of vertical lines, it is an indication of over exposure.
8. Find the interface. The automatic “find interface” command was generally successful on both transparent and reflective substrates with IP-Dip. If you encounter difficulties, try finding the interface on a glass region of the patterned substrate first and then move to a reflective region where you can do finding interface command again. Finding the interface is more successful when it starts at a z-position close to the actual interface.
9. Align the Nanoscribe in order 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 according to the animation in DeScribe software. Close the AxioVision software to view the camera in NanoWrite. You cannot have both open at the same time.
    a. Manually write a line to find the laser by typing the following line in the command window in NanoWrite. This will result in writing a 100µm line in x-axis.

    ```
    0 0 0
    100 0 0
    write
    ```

    b. Align the horizontal and vertical hairlines to meet at the point where the laser stopped writing. This is the laser position.
    c. Identify three points for alignment. Enter their values, move to these points and click “get position” for each.
    d. Transform coordinates.
    e. Turn off the camera and re-open the AxioVision software.
10. Load the desired gwl file.
11. Click “start job.”
12. When the job is done, unload the substrate.
13. Remove the objective and clean with SU-8 developer and IPA.

8.4.3. Develop

1. Submerge the wafer in SU-8 developer for 20 minutes.
2. Immediately transfer to Novec HFE 7100 for 5 minutes. HFE 7100 is a refrigerant with low surface tension and was selected to address issues with structures collapsing. IPA is the standard solvent recommended for this step and can be used if collapsing is not observed.
3. Allow the wafer to air dry. This is recommended to prevent structures from collapsing.
4. Post baking and additional UV exposure (regular white light is fine) are not recommended if you eventually want to remove the IP-Dip structure because it will increase cross-linking.

8.5. Electrodeposition

8.5.1. Preparing Substrate

1. A clean seed conductive seed layer is vital to the electrodeposition process. Clean with acetone and IPA. Oxygen plasma is not recommended as it can attack IP-Dip if treated for a long time.
2. Attach a wire to the conductive part of the substrate with silver paint for electrical connection and epoxy for mechanical connection and protection from liquid electrolyte.

3. Coat all areas that will be electrically connected and submerged in solution, but that you don't want electroplated with nail polish.
4. If your features are small (<10μm) or have a high aspect ratio, we used and recommend the following wetting enhancements:
    a. Expose to air plasma for 60 seconds.
    b. Wet with ethyl alcohol. This should not attack nail polish. Immediately submerge in plating solution.
    c. Desiccate the sample in plating solution for about 60 seconds at a pressure of -29inHg.

8.5.2. Electroplating Setup

1. Fill a glass beaker with gold electroplating solution. We used Elevate Gold 7990. Any similar cyanide-free electroplating solution is appropriate. You should be able to reuse the same solution for many trials, depending on the solution, volume, and amount of plating.
2. Submerge the sample in the plating solution after air plasma and ethanol treatment, and before desiccation, if applicable.
3. Heat solution on a hot plate. For Elevate 7990, a solution temperature of 45°C to 65°C is recommended and we used 55°C. The hot plate will need to be set at a higher temperature than the desired solution temperature.
4. Rinse the platinum anode with DI water and place in the solution parallel to the working electrode.
5. Attach appropriate wires to the working electrode (sample) and counter/reference electrode (platinum anode). An Ag/AgCl reference electrode is not necessary for this two-electrode setup.
6. Cover the beaker with parafilm to prevent the solution from evaporating. Note that this may increase the temperature of the solution and adjust the hot plate setting as needed.

8.5.3. Electroplating Parameters

1. A current density of -0.5 mA/cm^2 is recommended for Elevate 7990. We used a higher current density, -8 μA instead of the approximately -0.2 μA estimated for our theoretical exposed area. Regions that were not completely covered by nail polish, imperfect connections, and other plating conditions can affect the deposition rate. To experience less sensitivity and have better control with small samples, you can simultaneously electroplate on a larger (mm^2 scale) sample, although this will deplete ions in your solution.
2. Pulsing the plating is recommended to allow for ion diffusion. We used 5 seconds on and 5 seconds off.
3. Monitor the current and voltage during plating. Adjust plating parameters as needed. Use an optical microscope, profilometer, and/or SEM to determine your plating rate and quality. If gold is rough, try decreasing the current to slow down plating. If your sample is lifting off the substrate, try increasing the current to increase the plating rate. If your gold quality is poor and the solution looks more yellow, replace the solution.

8.6. Removal of the Sacrificial Template

1. Submerge the substrate in 3:1 sulfuric acid: hydrogen peroxide (piranha) for 30 minutes to 24 hours. Fresh piranha is best. Heat will increase the rate of template removal. Piranha should not attack gold or glass in the short term, but it may attack Ti or other metals used as an adhesion layer. Monitor the piranha to ensure that your metal is not being attacked.
2. Submerge in DI water and dry.

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11. Expenses

Total expenses for this two-quarter project is $8359.20. A pie chart visualizes the breakdown of the expenses. The major expense for this project is Nanoscribe.