2.3 Using positive photoresist (AZ4620 or SPR 220-7) on the Nanoscribe

Templating substrates are a promising method to create order colloidal self-assembly. This is crucial to initial nucleation and subsequent assembly of particles. In this case, the Nanoscribe is used in order to create templated substrate through the photosolubility of a positive resist (AZ4620 or SPR 220-7). This allows for the inverse structure to be fabricated using the same 2-photon lithography system, but in an oil immersion configuration. The method is chosen in order to have full flexibility in the templated structure (as opposed to lithography or etching, in which only certain geometries can be created).

2.3.1 Oil immersion configuration for Nanoscribe

Oil immersion is one configuration used with positive photoresist and is desired because it uses an index matching fluid between the objective and the bottom of the substrate (in this, we use ITO covered coverslip). In this configuration, the stack is the following (from the top to bottom): positive photoresist, substrate, oil, objective.

1.) Load the objective of choice into the objective turret
2.) Attach the substrate of choice on the sample holder, with the photoresist facing upward towards the ceiling (Top side) (this is the opposite of the standard Dip-in method)
3.) Add a droplet of Zeiss immersion oil on the substrate side without the photoresist (Bottom side)

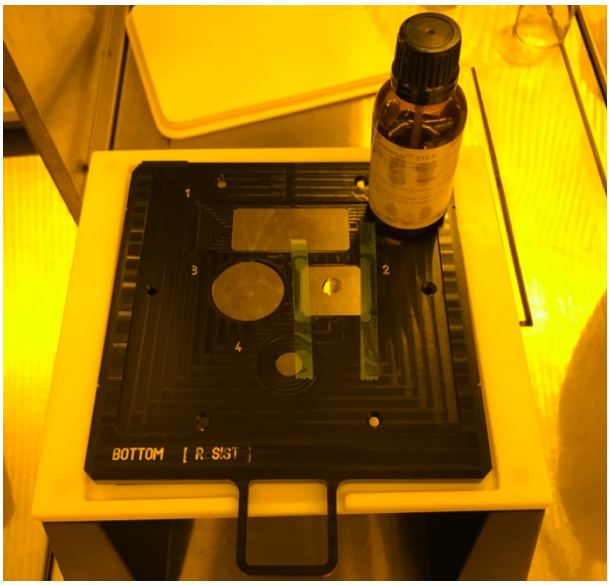

Figure 7: Deposition of immersion oil on the BOTTOM of the substrate

4.) Insert the sample holder so that the oil is facing the objective (top side up)

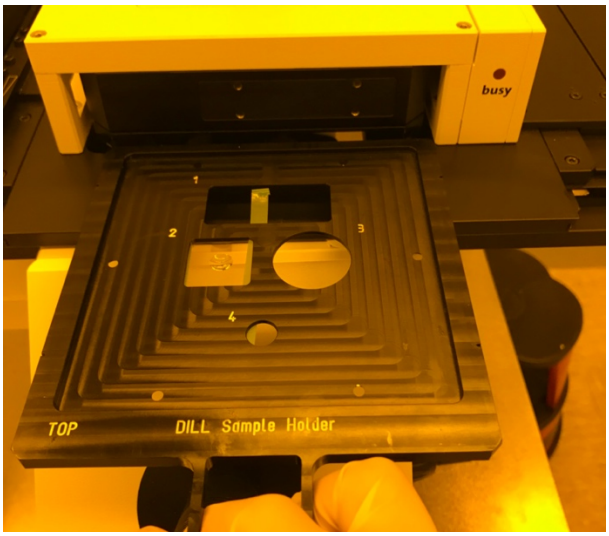

Figure 8: Inserting holder into the Nanoscribe with the oil facing towards the objective

2.3.2 Preparing and loading substrate with positive photoresist (AZ4620 or SPR 220-7)

1.) Prime the substrate using YES Oven standard recipe
2.) Using a syringe, deposit AZ4620 or SPR 220-7 onto the substrate while it is loaded on the spin coater but before starting the spin recipe (over saturating the sample is better than under saturating)

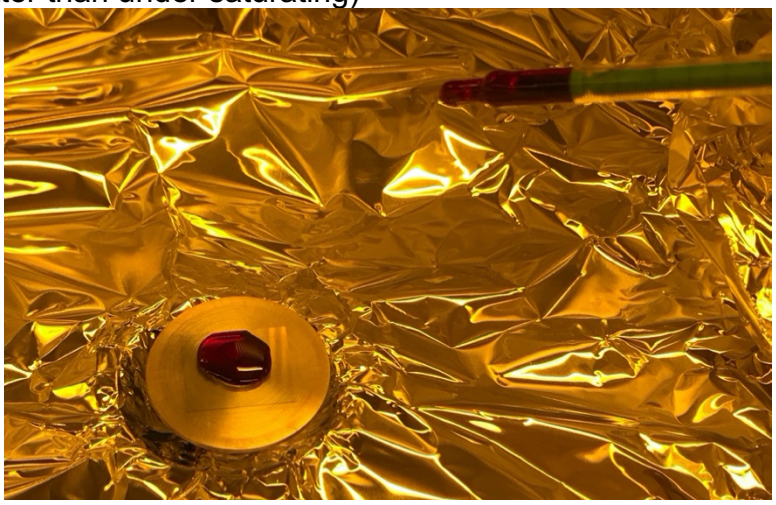

Figure 9: Deposition of SPR 220-7 onto a substrate with a syringe

3.) Ramp control spin coating to 3500 RPM at 250 rpm/s for 2 minutes
4.) Ramp control spin coating to 0 RPM at 500 rpm/s
    a. This should give you ~7 um coating for both AZ4620 and SPR 220-7
5.) Visually inspect to ensure that the substrate is fully coated
6.) Prebake the substrate on a hotplate at [**AZ:** 90C for 90s or **SPR:** 115C for 90 seconds]
7.) Remove and load the substrate into the Nanoscribe using the oil immersion configuration (from 2.3.1 procedure)

8.) Use standard operating procedures to find the interface, making sure that the correct interface is detected (in this case, there are many interfaces: air-oil, oil-substrate, **substrate-photoresist**, and photoresist-air)

2.3.3 Programming a dosing matrix

1.) Open Describe and File >> Advanced STL Processing
2.) Click the tab with “Parameter Sweep”

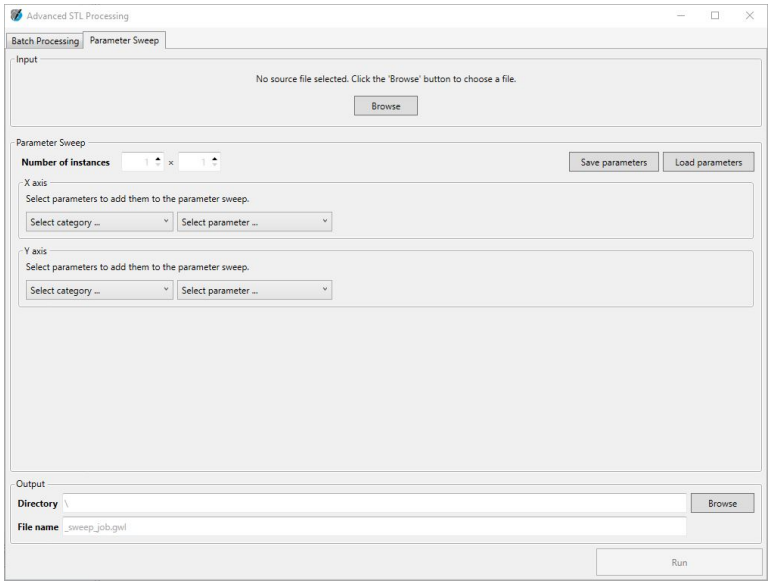

Figure 10: Parameter Sweep tab in the Advanced STL Processing menu

3.) Input a STL of a shape to be printed by “Browse” (usually a smaller, representative geometry of the final print)
4.) Change the “X axis” by “Select category …” and “Select parameter …”
    a. Category: Exposure, Parameter: BaseLaserPower
5.) Change the “Y axis” by “Select category …” and “Select parameter…”
    a. Category: Exposure, Parameter: BaseScanSpeed
6.) Change the number of columns or rows by changing “Number of instances”, which is found at the top of the “Parameter Sweep” box.
7.) Change the initial and end values, with how to interpret those values, by further expanding the option with the arrow next to your selected category and parameter

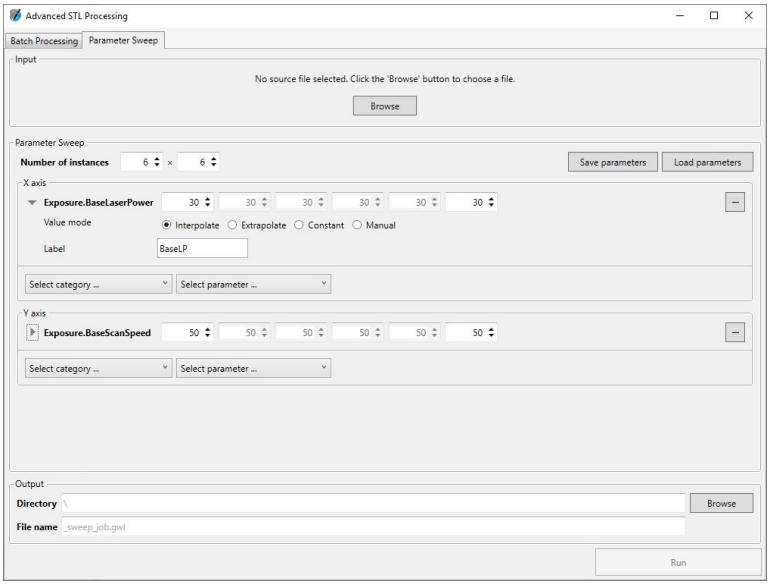

Figure 11: Paramter Sweep tab with the Exposure.BaseLaserPower and Exposure.BaseScanSpeed as the variables in 2 directions (X,Y)

8.) Click “Run” after finalizing
9.) For oil immersion mode, change InvertZAxis 1 to InvertZAxis 0
10.) Change “% Text parameters”
    a. TextScanSpeed 1000 to TextScanSpeed 10000
    b. TextLaserPower 55 to TextLaserPower 40

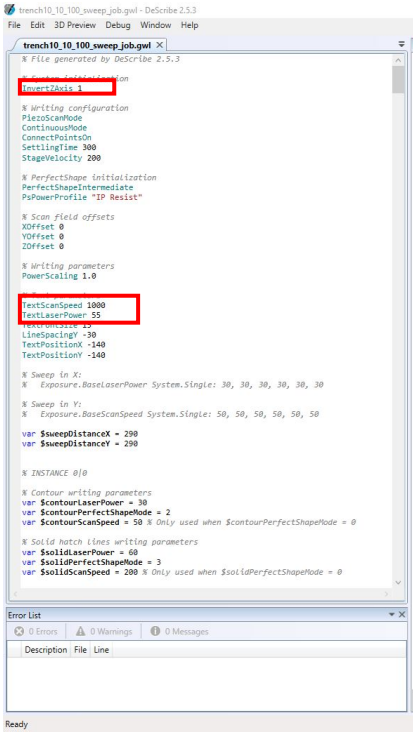

Figure 12: .GWL file generation after STL processing showing regions of code that need to be changed per Step 10

11.) Save the file and load/run the program in Nanowrite

2.3.3 Post processing positive photoresist

1.) Develop the substrate in [**AZ:** AZ400K Developer:water = 1:4 dilution or **SPR:** MF-26A] for 120 seconds with slow agitation
2.) Wait 30 minutes
3.) Post bake at [**AZ:** 125C for 30 minutes or **SPR:** 115C for 30 minutes]

References

1. Baggethun, Paul. ImageJ radial distribution file: https://imagej.nih.gov/ij/plugins/radial-profile.html. Based on a guide: https://imagejdocu.tudor.lu/macro/radial_distribution_function
2. Zhang, Xiaoran, and G. J. Blanchard. "Polymer Sol–Gel Composite Inverse Opal Structures." *ACS applied materials & interfaces* 7.11 (2015): 6054-6061.

Dosing Matrix for AZ4260

Laser Power (%) \ Scan Speed x 10^2 (µm/s)	10	57.5	105	152	200
20	+	+	–	–	–
40	x	+	+	+	+
60	x	x	+	+	+
80	x	x	x	x	x
100	x	x	x	x	x

Table 1: Dosing matrix for AZ4260 showing under exposed (-), well exposed (+), or over exposed resist (x).

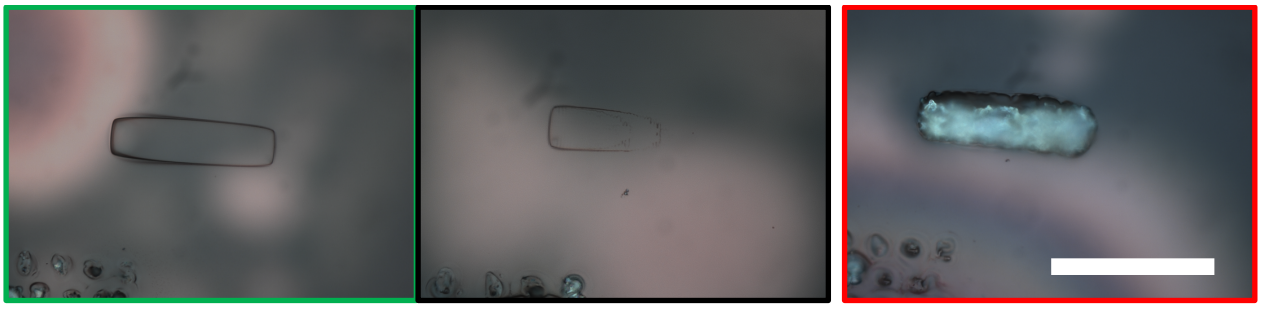

Figure 19: All images are of AZ4620. (left) Optical image of well exposed condition. (middle) Optical image of under exposed condition. (right) Optical image of over exposed condition. Scale bar is 100 um.

Dosing Matrix for SPR220-7

Laser Power (%) \ Scan Speed x 10^2 (µm/s)	50	70	90	110	130
36	+	+	–	–	–
42	+	+	+	+	–
48	x	+	+	+	+
54	x	x	+	+	+
60	x	x	x	+	+

Table 2: Dosing matrix for SPR 220-7 showing under exposed (-), well exposed (+), or over exposed resist (x).