

## II. Thin Hydrogel Film Fabrication

Hydrogel can form by mixing the proper pre-polymers and initiate the crosslinking. Wafer-scale thin hydrogel films fabrication have 4 differences compared to bulk piece fabrication. First, polymer needs to be added to the pre-polymer solution to enhance viscosity for spin coating. Second, wafer needs to be pre-treated to promote hydrogel adhesion. Third, photo-crosslinking is necessary for device alignment and pattern and thermal-crosslinking is only possible for blank fabrication on wafers. Fourth, oxygen diffusion should be prevented to increase free-radical polymerization efficiency. The general process is illustrated in Figure 1 at the end of the section.

The procedure listed here is just a starting point. I narrowed down the parameters to a range where the procedure can be “working”, but the parameters are not optimized yet for resolution or repeatability. The wet chemistry has a high run-to-run variation and it is recommended to always have a few test wafers.

### A. Mixing pre-polymers

The hydrogel pre-polymer solution consists of 3 key ingredients – monomers, initiators, and cross-linker. Initiators generates free radicals and elongates monomers into polymers, while cross-linkers binds nearby polymers into 3-D scaffolds. Many monomers come as liquids, but most initiators are powders. Therefore, we need to add all chemicals into certain common solvents, fully dissolve the powders, and thoroughly stir the chemicals. Once a pre-polymer solution is prepared, it is recommended to be used within a few days to prevent unwanted premature crosslinking. It is also recommended to add initiators only before final crosslinking.

Compared to bulk hydrogel, usually additional polymer needs to be added to increase solution viscosity for the spin coating process.

#### **Materials:**

HEMA (2-hydroxyethyl methacrylate; monomer; liquid)

DMAEMA (N,N-dimethylaminoethyl methacrylate; pH-responsive monomer; liquid)

TEGDA (tetraethylene diacrylate; cross-linker; liquid)

DMPA (dimethoxy-phenylacetophenone; photoinitiator; powder)

Poly-HEMA (poly 2-hydroxyethyl methacrylate; polymer; liquid)

Silane A174 (3-(Trimethoxysilyl)propyl methacrylate, a.k.a.  $\gamma$ -MPS; silane; liquid)

All materials should be approved by SNF staff member and come with yellow label. Listed ratios based on [1] can be adjusted based on your need.

#### **Lab space:**

exfab-wbsolve, wafer saw room laura-wb, NSIL fumehood 1.

#### **Equipment:**

weighing scale, weighing paper, 25ml graded glass cylinder x 2, 50 ml glass beaker, amber jar, pipette controller, matching pipette tips x several, waste container bag, waste disposal bottle, paraffin film. All materials should have a blue card to record safety information.

#### **At exfab-solve:**

1. Put a clean 25mL graded glass cylinder on the weighing scale, gradually pipette into 13.01g (0.1mol) of HEMA. Change pipette tip.
2. Pipette 3.93g (0.025mol) of DMAEMA and 0.567 g (0.001875 mol) of TEGDA into the same cylinder in 1. Measure the total volume by looking at the bottom

- curve of the liquid surface, mark the volume as V1. Change pipette tips in between.
3. Put another clean 25mL graded glass cylinder on the weighing scale, pipette 50% V1 of DI water.
  4. Mix the solutions from 2 and 3 in a 50mL glass beaker. Measure the total weight as W. The solutions will look cloudy at the beginning but should clear up after light shaking.
  5. Transfer the solution to an amber jar. Close the cap tightly and seal with paraffin film. Label the jar with chemical names and ratios.
  6. Rinse all glassware, collect all solid waste in a plastic waste container bag, collect waste chemicals in a waste disposal bottle and return to the waste disposal pickup shelf.

**At wafer saw room laura-wb:**

7. Transport the amber jar of hydrogel pre-polymer with a secondary container basket.
8. Fully cover all windows with aluminum foil. Turn on the yellow light at laura-wb. Leave a sign on the door and close the door. Turn off all white lighting.
9. Weigh 2% to 5% of W1 of poly-HEMA powder and add to the amber jar.
10. Weigh 2% of W1 of DMPA powder, directly add to the amber jar.
11. Clean up the waste and return the room to original condition.

**At NSIL fumehood 1:**

12. Stir with magnetic stirrer or shaker table in the fumehood for at least 4 hours, or use the vortex mixer for 10 min with smaller volumes. Powders should be fully dissolved.
13. Store the solution in the solvent fridge for up to 3 days. Because the solution is light sensitive now, it should be stored in amber jar or wrapped with aluminum foil.

**B. Wafer treatment (Silanization)**

Hydrogel needs to be adhered to wafer with chemical process, otherwise hydrogel delamination can occur over time. Adhesion can be improved with a silanization process [3]. However, silanization renders the wafer surface hydrophobic and makes hydrogel difficult to spin-coat on the wafer, the level of silanization needs to be controlled. There are 2 typically 2 methods of silanization, vapor based and solution based. Vapor based method is prohibited at SNF because it may damage the vacuum line. For vapor-based method, simply put a few drops of silane solutions and wafers in a dessicator and pump down to vacuum for 30 minutes to over-night. Talk to staff member if you are interested in this process or try other solvent-based silanization. Details on other methods can be found in "silanization FAQ".

**Lab space:**

Wbclean, exfab-wbsolve, thermoco-1

**Equipment:**

Beaker, disposal bag, disposal bottle, pipette.

**At wbclean:**

1. Perform standard RCA clean

**At thermoco-1:**

2. Grow desired thickness of thermal wet oxide on wafers.

**At wbclean:**

3. Soak in 2% HF for 5 minutes.

**At exfab-solve:**

4. Prepare a beaker. Add 200 mL of toluene.
5. Add 0.5ml (0.25%) of silane 174. Stir every 2 minute for 10 minutes.
6. Soak wafer for a few minutes. The soaking time varies from run to run as the silanization speed is exponential.
7. Dispose liquid waste in the disposal bottle. Dispose solid waste in a zip lock bag.

**At all-litho room:**

8. Bake at 100C in the blue oven to bake off unreacted silane.
9. Check wafer hydrophobicity using contact angle measurement. Desired angle is 15-25 degrees. When surface is fully covered with silane 174, the contact angle is around 55 degrees. This usually renders the surface too hydrophobic and difficult to spin coat hydrogel pre-polymers.

C. Cross-linking

Photo-patterning is needed for pattern alignment and thin film generation. As oxygen diffuses through thin films rapidly and prevents inhibits radical generation, it is necessary to operate using vacuum setting on the exposure tool [2-5].

See "FAQ on fabrication and characterization" for more information.

**Lab space:**

Exfab-headway3, Exfab-wbclean, Karlsuss

**Equipment:**

Beaker, disposal bag, disposal bottle, pipette.

**At headway-3:**

1. Dispense 5mL of pre-polymer onto wafer, the liquid is viscous so do not use syringe
2. Spread for 5 second up to 1000 rpm, spin for 30 seconds at 1000 rpm.
3. Put the wafer in a wafer container, close it well, and transport it to Karlsuss. Make sure you close the wafer container well because the pre-polymer is not baked and will vaporize odor.

**At Karlsuss**

4. Align your masks before doing spin coating.
5. Use vacuum exposure to expose for 40-60 second based on the desired thickness. I used an intermittent exposure with a duty cycle of around 1 second on and 7 second off. This intermittent exposure [12] is claimed to improve hydrogel shape regularity. Wet chemistry can have a high run-to-run variation. In addition, because Karlsuss lamp is changed regularly, the light intensity changes over time. It is recommended to always do a test run first. 40-60 seconds exposure generates film from 4.5um to 12um thickness. Again, these parameters have not been extensively optimized yet.

**At wbclean:**

6. Immediately soak in ethanol for 2 minutes.
7. Rinse thoroughly with IPA and blow dry with air gun.
8. Sonicate in DI water for 5 minutes. Rinse with water and then repeat.
9. Soak in water to store the hydrogel film.
10. Gather solid waste in a zip lock bag and liquid waste in a waste bottle. Transport to the waste disposal pick up area.

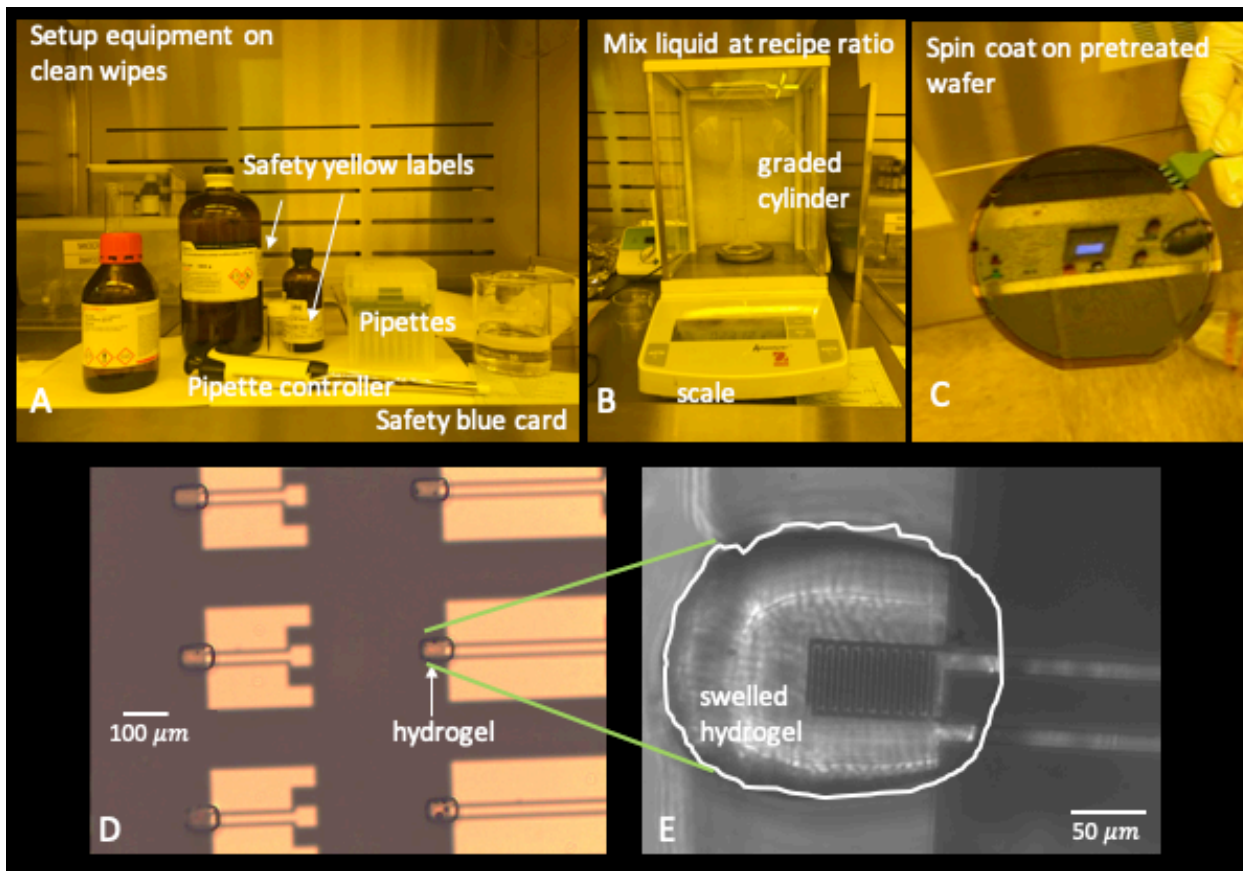


Figure 1. Thin film hydrogel fabrication process. A and B, set up equipment and weight out liquid chemicals at exfab-wbsolvent. Note powders are not allowed in SNF and should be added elsewhere. C, spin coat hydrogel pre-polymer on wafer pretreated with silane A-174. D, hydrogel after exposure and development. E, hydrogel swells up in analyte.