Experiment #4  Dip-pen Nanolithography on Responsive Materials

Sample Preparation

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1. Initial Piranha Cleaning

2. PFPA-Silane Bonding

3. Poly(4-vinylpyridine) Spin Coating

4. UV Cross Linking

5. Final Cleaning of Excess Polymer
1. Initial Piranha Cleaning

- Cut Silicon wafers of desired size
- Wash all organic material (ex. pen markings) off samples with acetone followed by water
- Air dry each piece to insure there is no organic solvent on the samples

**IMPORTANT:** Any organic solvent remaining on the samples with react violently with the piranha solution

- Prepare piranha solution in a 3:7 ratio of H₂O₂ (30-31%) to H₂SO₄ (96-98%)
  - Pour 3 parts H₂O₂ into crystallization dish (beaker)
  - Then SLOWLY pour in 7 parts H₂SO₄ into dish making sure not to boil the solution
- Once mixed heat solution to 80-90 degrees Celsius
- Place samples in heated solution and mix for 1 hour
- After 1 hour remove from heat and remove samples, rinsing each with water and place into hot water at 80-90 degrees Celsius
- Mix in hot water for 30 minutes
- After 30 minutes remove samples and rinse each with water and place them in a new water bath at the same temperature for 30 minutes
- Repeat the previous step for a total of three washes in hot water for 30 minutes each
- Air dry each sample again

  - Piranha cleaning adds –OH groups to the SiO₂ surface which are used to bond with PFPA Silane
2. PFPA-Silane Bonding

- PFPA-Silane bonding must occur immediately after the piranha cleaning because the surface will oxidize.
- Solution of PFPA-Silane is prepared in a four step synthesis by Dr. Mingdi Yan’s lab (see link) and the solvent is toluene:
- In a jar covered in aluminum foil (for darkness) place samples and enough solution to submerge the samples.
- Place in a cabinet of drawer (dark place) for 4 hours (not 3 or 5).
- After 4 hours remove each sample, rinse with toluene, and place in a crystallization dish with toluene.
- Stir for 20 minutes in toluene.
- Remove each sample, rinse in toluene, and place in a new toluene bath for 20 minutes.
- Repeat for a third 20 minute toluene wash.
- Place samples in to Petri dish covered in aluminum foil.
  - You can now stop for the day as the samples can last several months in their current stage, but the samples must dry for at least 24 hours.
3. Poly(4-vinylpyridine) Spin Coating

- Before the spin coating you need to measure the thickness of the PFPA-Silane layer using ellipsometry
  - Silicon optical constants: \( n_{\text{Si}} = 3.87 \) and \( k_{\text{Si}} = 0.018 \)
  - \( \text{SiO}_2 \) layer: \( n = 1.465 \) and thickness=30 A
  - PFPA-Silane (top) layer: \( n = 1.503 \) and thickness=0 (the unknown to solve for)
    - Roughly 23-24 A thick

- Turn on vacuum

- Wash stage with acetone

- Place sample on stage and put several drops of P4VP solution on the top (enough to cover the surface)

- Turn on at 2000 rpm for 60 seconds

- Gently remove sample from stage with back of tweezers (sample will stick)

- Sample is now ready for cross linking
4. UV Cross-Linking

- Place in box with UV lamp for approximately 5 minutes to cross-link polymer
  - 450 W medium pressure mercury lamp
  - 280 nm low pass filter
  - Intensity approx. 3.5 mV/cm² at 18 cm with 2.5 min warm-up
  - UV radiation and sample thickness is highly variable and not easy to predict
5. Cleaning Excess Polymer

- Place samples in dish with 2-propanol (isopropanol)
- Place in ultrasound cleaner for 2-3 minutes
- Repeat this process in a new dish of 2-propanol
- Put in a new dish of 2-propanol and place on mixer and stir gently for 12 hours (overnight)
- The following day remove samples and rinse with water and air dry
  - And you’re done. The P4VP thickness can be measured by ellipsometry.