UC San Diego MRSEC
MATERIALS RESEARCH SCIENCE AND ENGINEERING CENTER

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MRSEC Educational Outreach

Hydrophilicity, Hydrophobicity, and Contact Angle

Guidance for Phenomena-based Lesson Development
for Middle and High School
Supported with Hands-on Activities

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MRSEC
Materials Research Science and Engineering Centers

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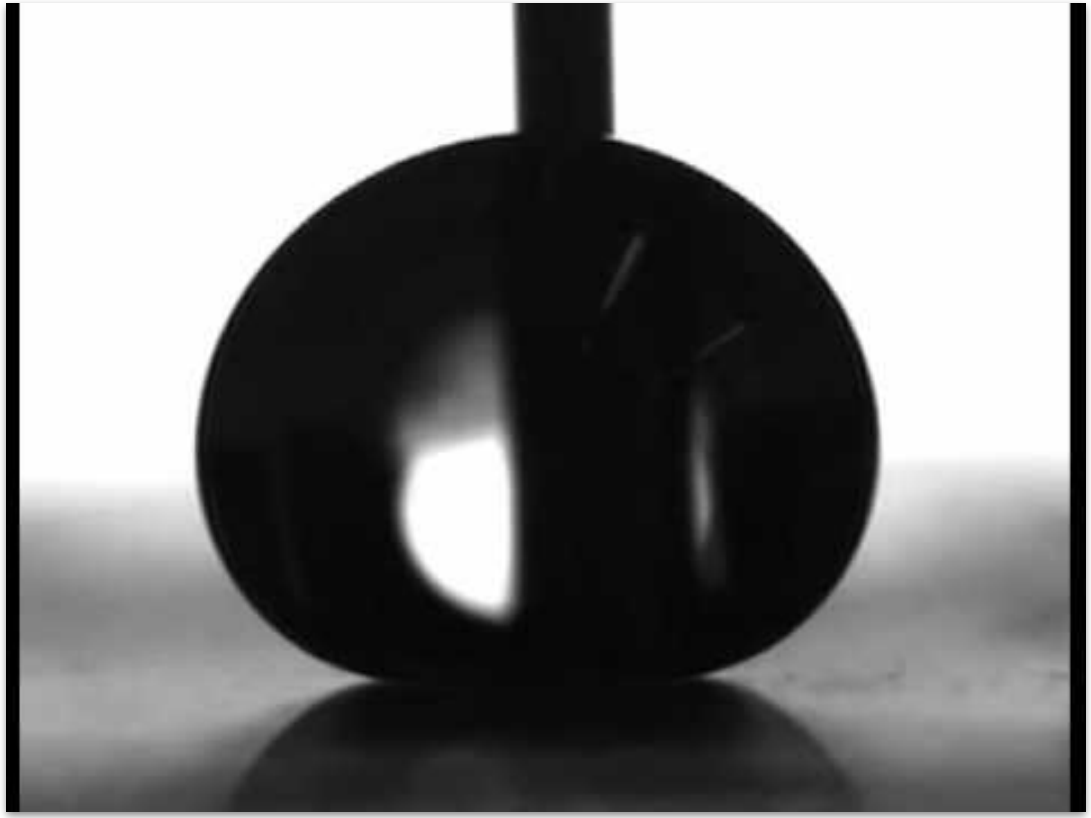
To begin, a cool video

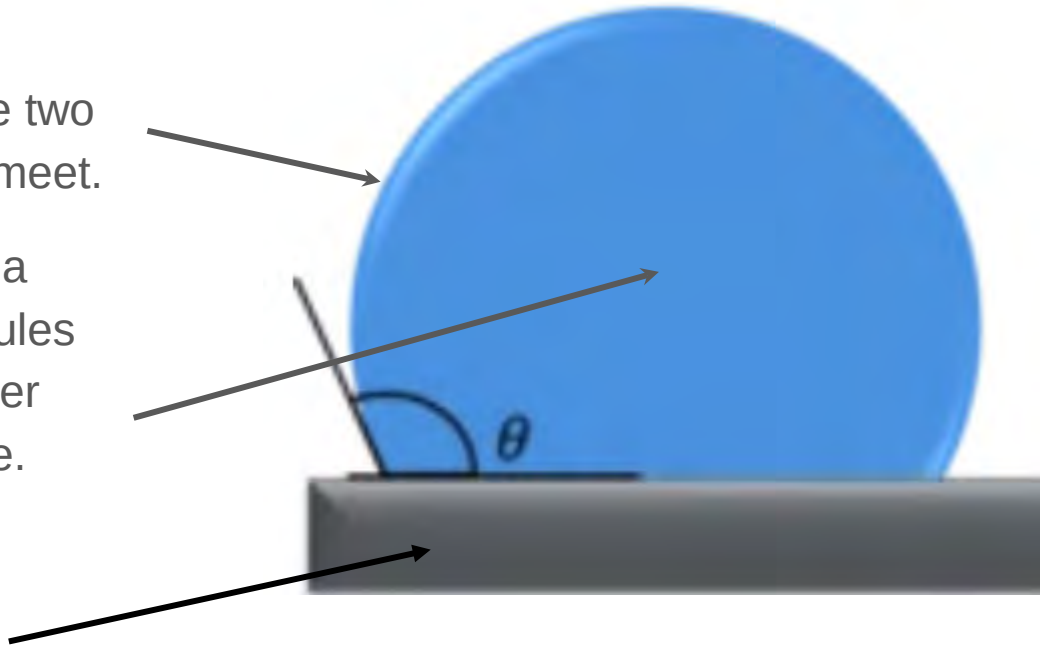


Surface and Bulk

A surface is a region where two different phases of matter meet.

The bulk is the “interior” of a substance, in which molecules are only in contact with other molecules of the same type.

The substrate is the solid surface that the liquid is dropped onto.



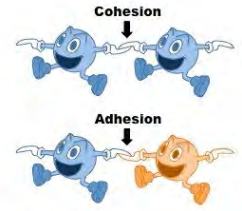
Source: https://www.ossila.com/pages/a-guide-to-surface-energy

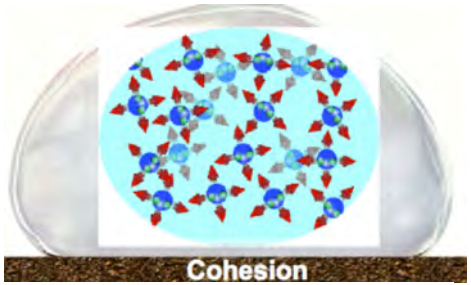
Surface and Bulk Energy

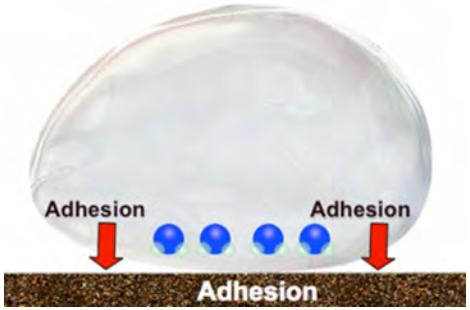
Molecules in the bulk of a material only interact and bond with other bulk molecules (these are called cohesive forces); interaction is generally uniform and balanced, and the energy of bulk molecules is low.

Molecules on the surface of a material only interact with (approximately) *half* the normal amount of other bulk molecules; they are partially exposed to, and interact with, the other phase of matter (these are called adhesive forces)! This leads to unbalanced interaction, and energy that could be used to interact with other molecules is not being utilized. Thus, **molecules at the surface always have higher potential energy than molecules in the bulk.**

Surface energy (denoted by ɣ) is a measurement of the energy at the surface of a material; it is also called surface tension for a liquid, but it applies to all phases of matter.







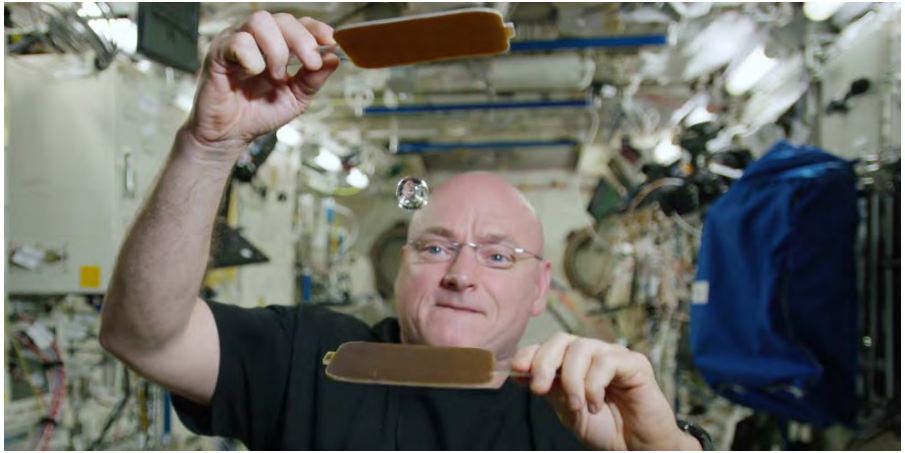
Sources: blog.aquatrols.com, ib.bioninja.com.au

Minimizing Energy

Substances tend to form into shapes that minimize energy. This is accomplished by minimizing the amount of material that is exposed to the surface.

What shape minimizes surface area for a given volume of liquid?

A sphere!



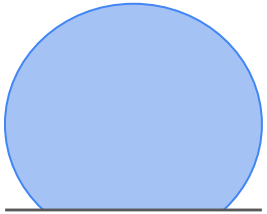
https://www.businessinsider.com/astronaut-scott-kelly-water-ping-pong-2016-1
https://www.permaculturenews.org/2015/03/30/understanding-water-part-1-the-theory-of-flow/

Wetting

Wetting is the contact between a liquid and a solid surface.

High wetting indicates that a large amount of the liquid is in contact with the surface; low wetting indicates the opposite.

The amount of wetting that occurs is determined by the equilibrium point between adhesive forces (which cause the liquid to “spread out”) and cohesive forces (which cause the liquid to “bead up”).



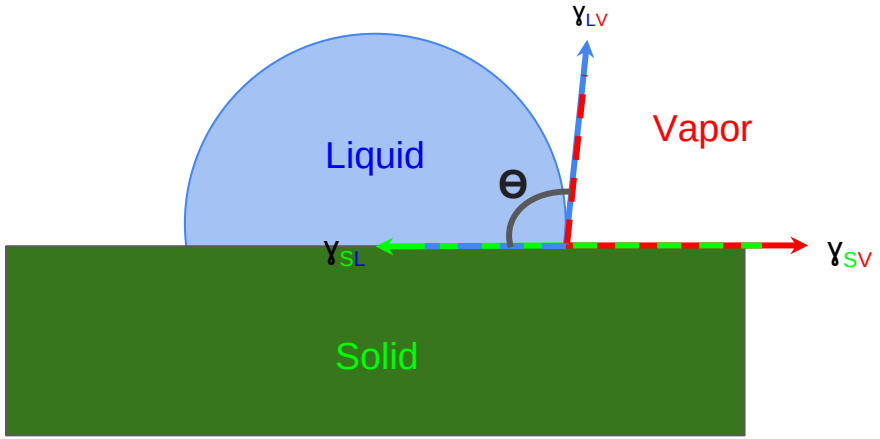
Low wetting

High wetting

Interfaces and Contact Angle

A surface energy exists between each two phases: a solid-liquid (γ_{SL}) surface energy, a liquid-vapor (γ_{LV}) surface energy, and a solid-vapor (γ_{SV}) surface energy.

The angle between the SL and LV surfaces is called the contact angle; it is the most common quantitative measurement of surface energy and wettability.



Equilibrium

When the droplet forms, an equilibrium is found between all three surface energies; the net force acting on the boundary is 0!

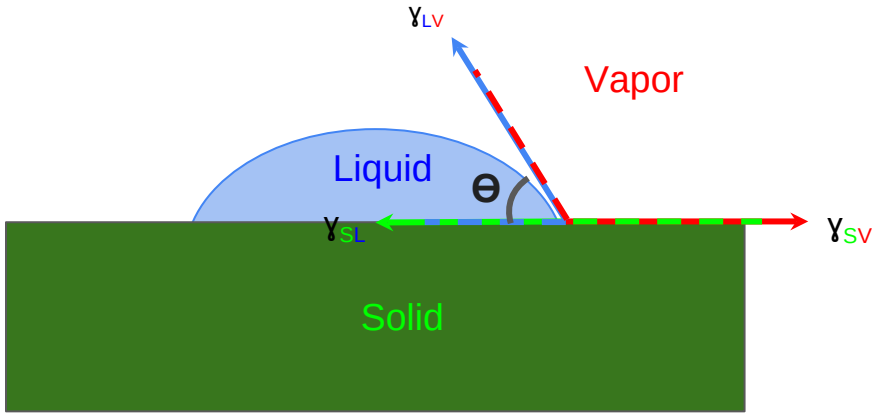
Solving for equilibrium in the x-direction:

$$\Sigma F_x = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \bullet \cos\theta = 0$$

or, more commonly,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \bullet \cos\theta$$

This is a basic equation in wetting, called the Young Equation.

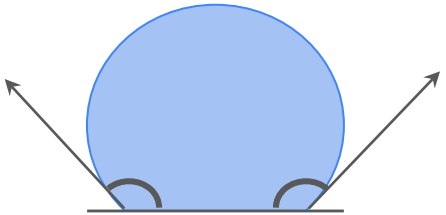


Ideal Models vs. Real Life

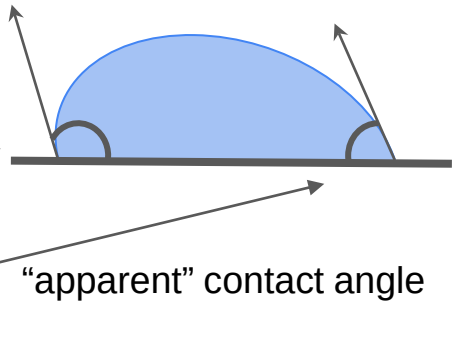
The Young model is useful, but not very realistic. It assumes that the solid surface is completely flat, which is never the case in real life!

A droplet on a surface will never exhibit just one contact angle, but rather a wide variety of contact angles due to surface roughness, or "rugosity".

For a given droplet and solid surface, the maximum possible contact angle is called the advancing contact angle, and the minimum is called the receding contact angle.



"ideal" contact angle



"apparent" contact angle

Realistic Models - Wenzel

The Wenzel model of wetting takes into account the roughness of a surface through the use of a roughness or rugosity factor **r**, defined as:

$$\mathbf{r} = \frac{\text{true surface area}}{\text{apparent surface area}}$$

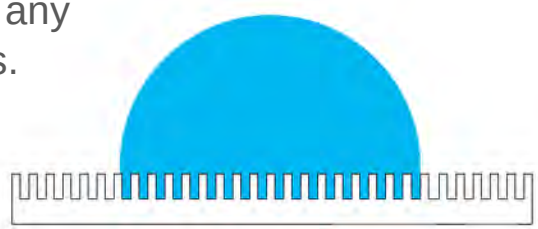
You can see that, since all surfaces have some roughness, r > 1, always.

In Wenzel's model, the liquid seeps into any extra space that forms due to roughness.

Wenzel's contribution to the Young equation is as follows:

The apparent contact angle θ of a droplet in stable equilibrium on a rough surface is equal to the ideal contact angle θ_E multiplied by the roughness factor **r**.*

$$\cos(\theta^*) = \mathbf{r}\cos(\theta_E)$$



https://en.wikipedia.org/wiki/Wetting

Wenzel in Practice

A given substance, when dropped onto a silicon wafer, displays an ideal contact angle of θ_E = **40°**. This contact angle is low, less than 90°, indicating a **hydrophilic** surface with **high wetting**.

Now, let's assume a rugosity factor of **r** = 1.05.

$$\cos(\theta^*) = \mathbf{r} \cdot \cos(\theta_E)$$

$$\cos(\theta^*) = (1.05)\cos(40°)$$

$$\theta^* = 36.4°$$

A droplet on a different surface forms an ideal contact angle of θ_E = **120°**. This high contact angle (> 90°) indicates a **hydrophobic** surface with **low wetting**. We'll assume the same rugosity factor.

$$\cos(\theta^*) = \mathbf{r} \cdot \cos(\theta_E)$$

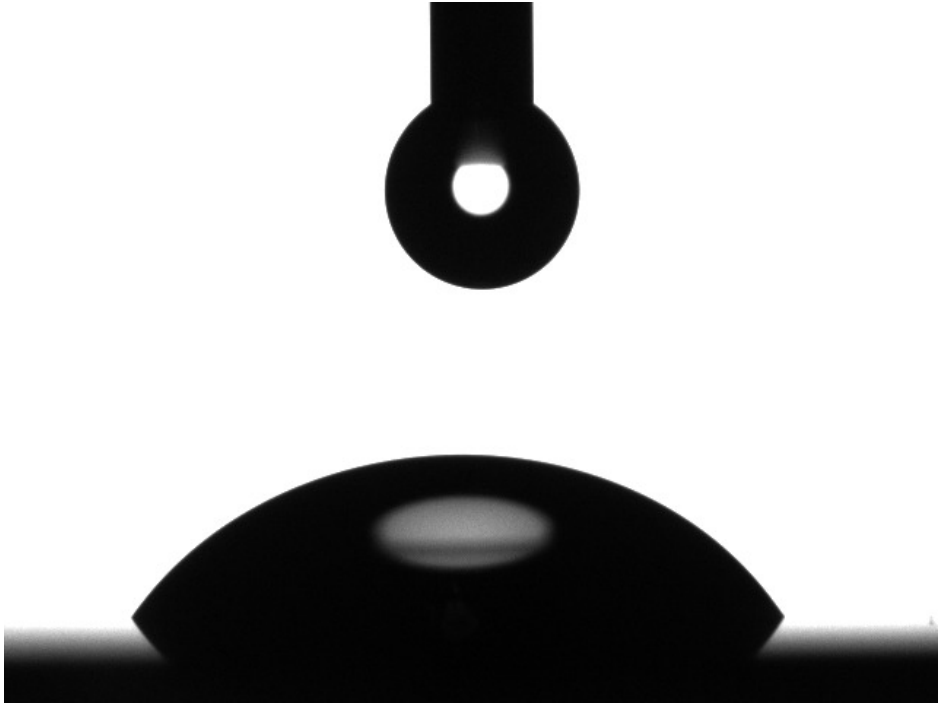
$$\cos(\theta^*) = (1.05)\cos(120°)$$

$$\theta^* = 121.7°$$

Conclusion: Roughness makes a hydrophobic surface MORE hydrophobic and a hydrophilic surface MORE hydrophilic!

Water and Silicon

This is what a drop of water looks like on a smooth silicon wafer.

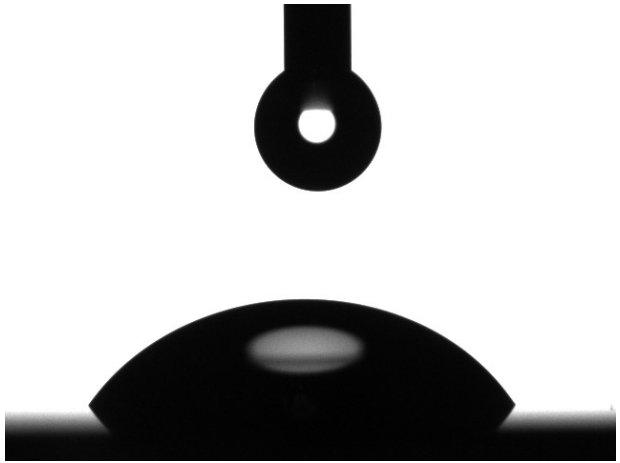


If this solid substrate is roughened, and wetted once again, will the contact angle increase or decrease?

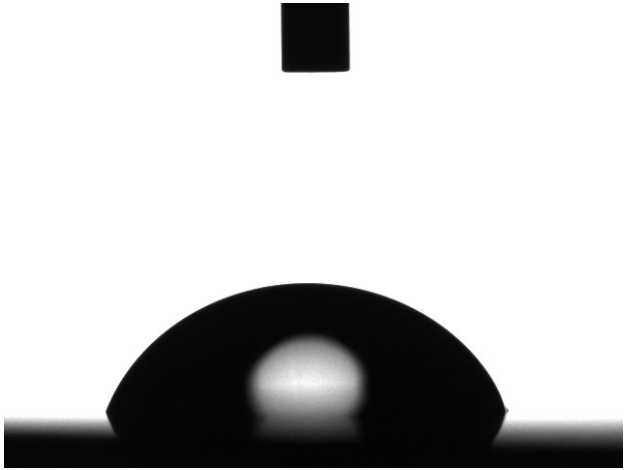
Results - Not what we expected???

From what we learned about the Wenzel model, surface roughness tends to increase contact angle on hydrophobic surfaces, and decrease contact angle on hydrophilic surfaces.

Silicon is a hydrophilic surface...so why does the water “bead up” post-etch?



Pre-roughening (contact angle of about 55°



Post-roughening (contact angle of about 75°

Realistic Models - Cassie-Baxter

The other main model for wetting on rough surfaces is the Cassie-Baxter model.

Unlike the Wenzel model, the Cassie-Baxter model assumes that the liquid does not seep into extra spaces caused by surface roughness; instead, the liquid rests on top of air bubbles trapped between itself and the solid surface.

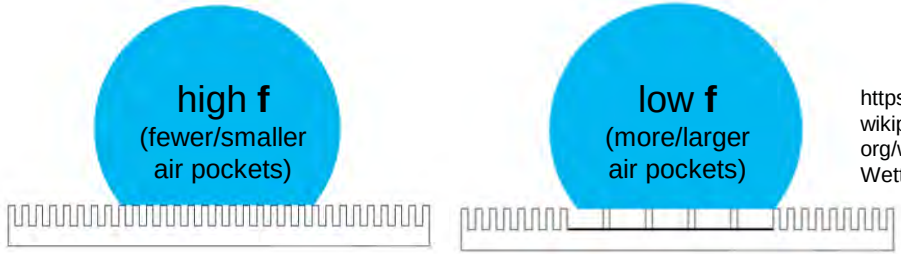
To account for this, Cassie and Baxter introduced a new metric **f**, defined as:

$$\mathbf{f} = \frac{\text{solid surface area wet by liquid}}{\text{total solid surface area}}$$

The Cassie-Baxter metric **f** incorporates into the Wenzel model (and, by extension, the Young equation) like so:

$$\cos(\theta^*) = \mathbf{r} \bullet \mathbf{f}\cos(\theta_E) + \mathbf{f} - 1$$

Notice that when **f** = 1 (indicating that 100% of the surface is wet, leaving no air bubbles), the equation reduces to the Wenzel model. When f = 0, θ* = 180°.



https://en.wikipedia.org/wiki/Wetting

Cassie-Baxter in Practice

The same two substances are used.

θ_E = **40°** and **r** = 1.05; we also introduce the new metric **f** = 0.9.

$cos(\theta^*) = \mathbf{r} \bullet \mathbf{f}cos(\theta_E) + \mathbf{f} - 1$

$cos(\theta^*) = (1.05)(.9)cos(40°) - (.9) + 1$

$\theta^* = 51.4°$

For the second substance,

θ_E = **120°**, **r** = 1.05, **f** = 0.9

$cos(\theta^*) = \mathbf{r} \bullet \mathbf{f}cos(\theta_E) + \mathbf{f} - 1$

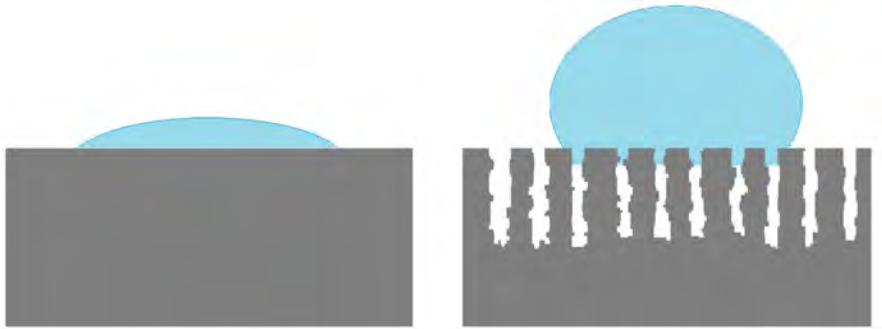
$cos(\theta^*) = (1.05)(.9)cos(120°) - (.9) + 1$

$\theta^* = 124.9°$

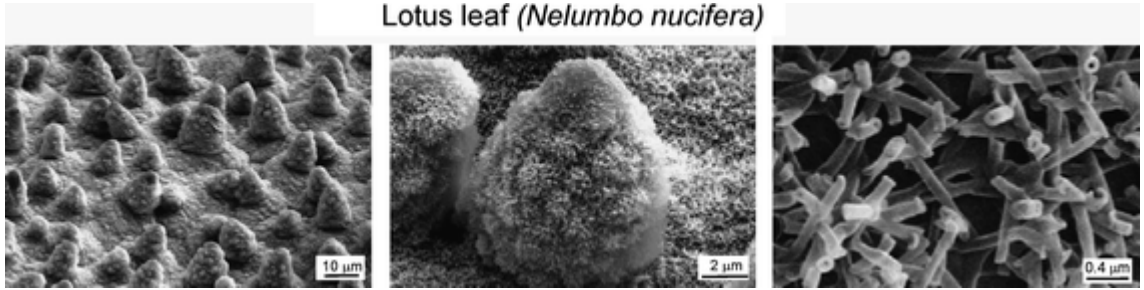
Conclusion: For both hydrophilic and hydrophobic surfaces, **f** increases contact angle and makes the surface MORE hydrophobic.

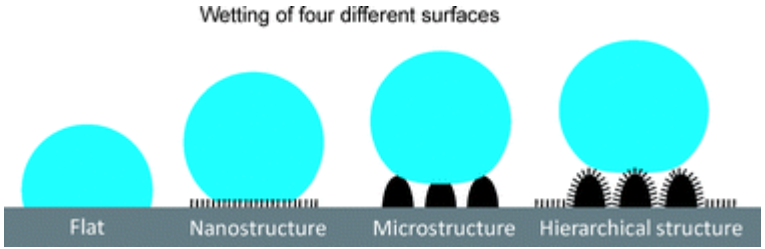
Wetting, Roughness, and Porous Silicon

Etching is a powerful method of achieving an incredibly porous/rough surface at the nanoscale level!



Hierarchical Structure and Hydrophobicity: Lotus Leaf as Example



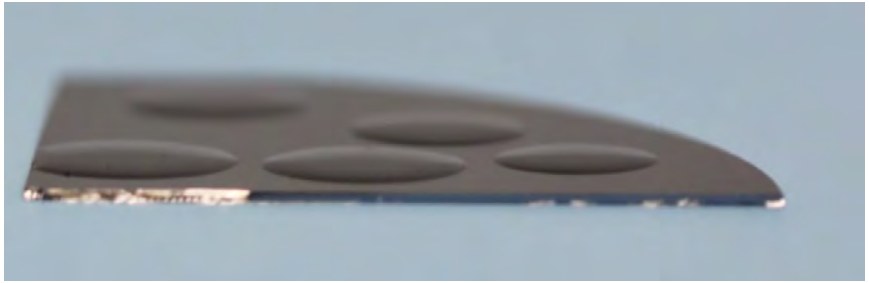


Fabrication of artificial Lotus leaves and significance of hierarchical structure for superhydrophobicity and low adhesion - Soft Matter (RSC Publishing)

Superhydrophobicity, Learn from the Lotus Leaf | IntechOpen

Wetting and Silicon!

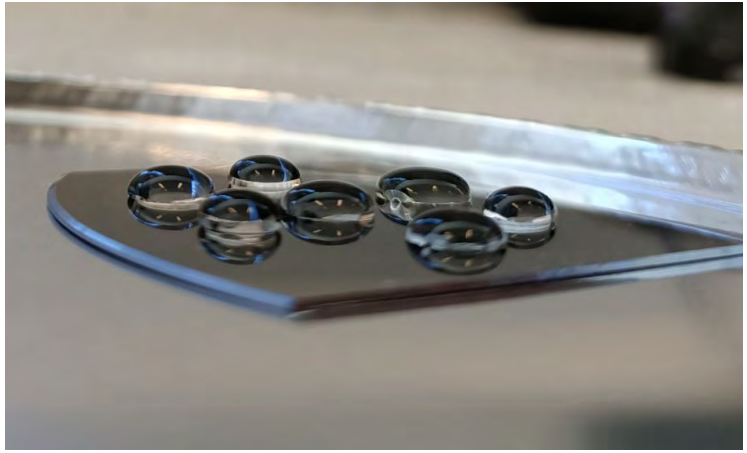
What happens when you drop polydimethylsiloxane (a.k.a. **PDMS** a.k.a silicone) onto a silicon wafer?



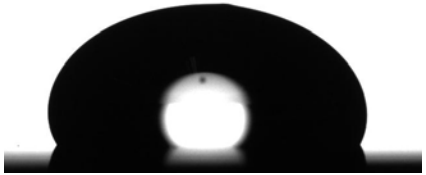
The surface and substance experience almost complete wetting (in other words, a contact angle of 0°).

Wetting and POROUS Silicon!

What happens when you drop PDMS onto an *etched nanostructured porous* silicon wafer?



The same PDMS droplets are now beading up with much higher contact angles than before!

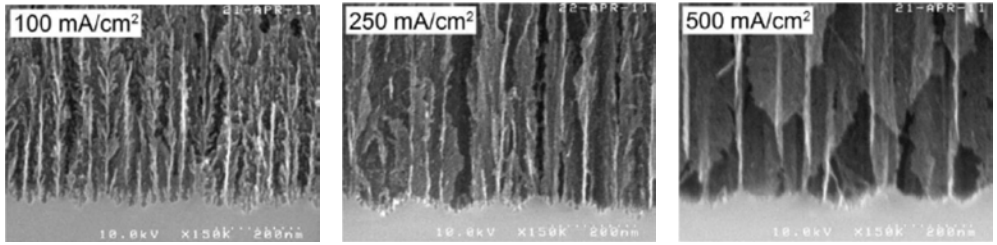


Controlling Porosity Value

*"The **porosity value** of the PSi layer strongly affected both geometrical and optical features of the PDMS lenses … We propose that these diameters were determined by the underlying nanostructure and the degree of infiltration of the liquid PDMS resin into the nanopores of the PSi substrate, in accordance with the Wenzel/Cassie-Baxter hybrid model of liquid wetting of rough surfaces."*

Mariani, S., Robbiano, V., Iglio, R., La Mattina, A. A., Nadimi, P., Wang, J., Kim, B., Kumeria, T., Sailor, M. J., & Barillaro, G. (2020). Moldless Printing of Silicone Lenses With Embedded Nanostructured Optical Filters. *Advanced functional materials*, *30*(4), 1906836. https://doi.org/10.1002/adfm.201906836

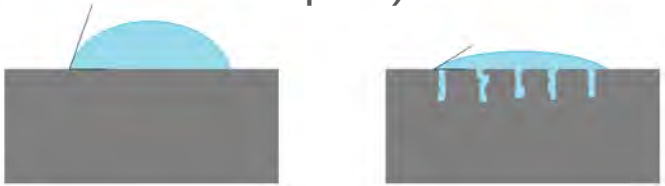
Porosity value (or, in other words, roughness) of the silicon substrate nanosurface is controlled by the current density applied during etching.



Gardner, Donald & III, C. & Liu, Yanki & Clendenning, S. & Jin, W. & Chen, Zhouheng & Moon, B.. (2014). Electrochemical Capacitors Fabricated Using Porous Silicon.

Interpreting the Data

In the Wenzel model, a hydrophilic surface is made *more* hydrophilic by roughening (this **was not** observed in the PDMS samples).



In the Cassie-Baxter model, a hydrophilic surface is made *less* hydrophilic by roughening (this **was** observed in the PDMS samples).

Since we observe decreased hydrophilicity and even a transition from hydrophilicity to hydrophobicity between the two silicon substrates, we can assume that the Cassie-Baxter model is a more effective description of the silicon-PDMS interaction (although the PDMS likely *does* seep into the pores a little bit, as in the Wenzel model).

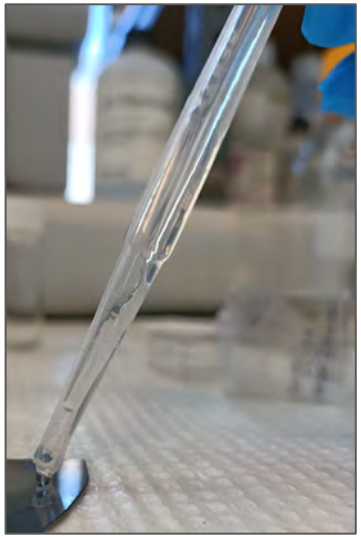
Application

Silicon Lenses that Transform your Cell Phone Into a Microscope!

Introduction to Moldless Nanostructured Silicone Lenses

Conventional preparation of commercial optical lenses relies on mechanical polishing or molding of rigid materials, such as glass and plastics. Optical filter elements and their integration into imaging systems are complex and time-consuming manufacturing processes.

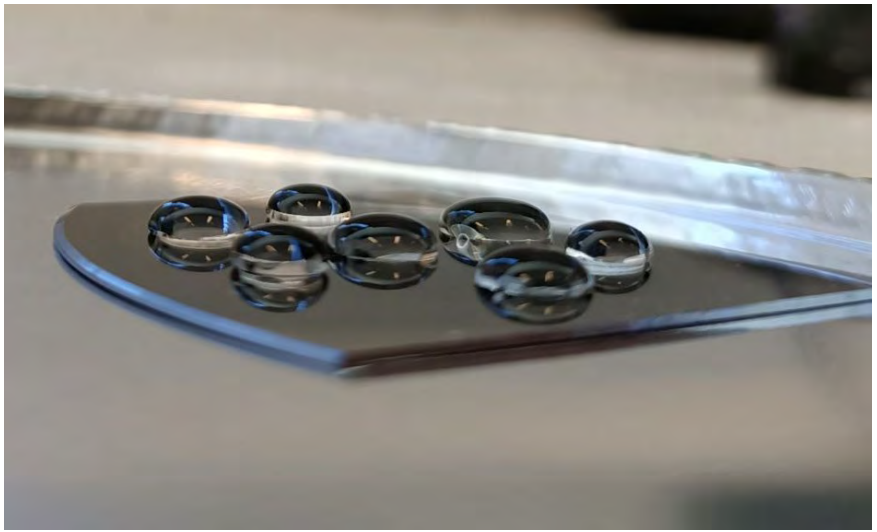
However, more efficient, moldless, low-surface energy production of silicone-based optical lenses is possible. The process involves casting a liquid polydimethylsiloxane (PDMS, aka silicone) pre-polymer solution onto a porous silicon film to generate a droplet, which will have a contact angle that is controlled by the porosity of the silicon nanostructure.



Mariani, S; Robbiano, V; Iglio, R; La Mattina, A. A; et. al: "Moldless Printing of Silicone Lenses with Embedded Nanostructured Optical Filters." Adv. Funct. Mater. 2020, 30, 1906836

Introduction to Moldless Nanostructured Silicone Lenses

PDMS droplets on **porous silicon** vs. **unetched silicon wafers**



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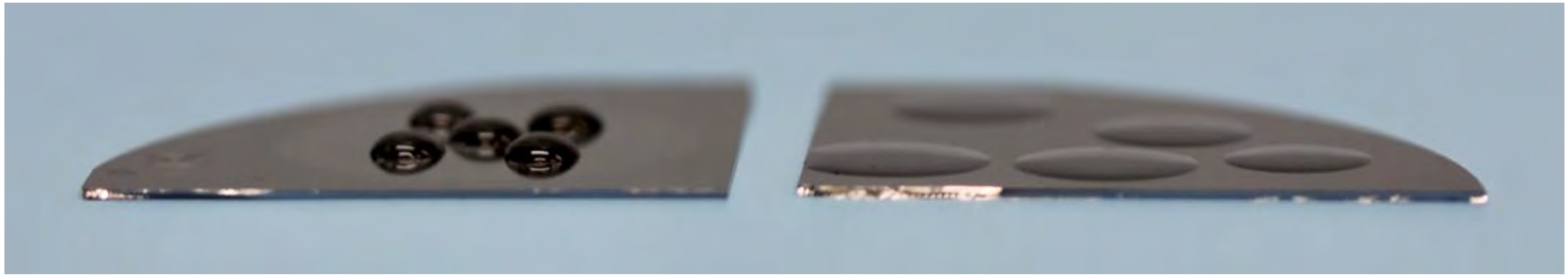
Introduction to Moldless Nanostructured Silicone Lenses

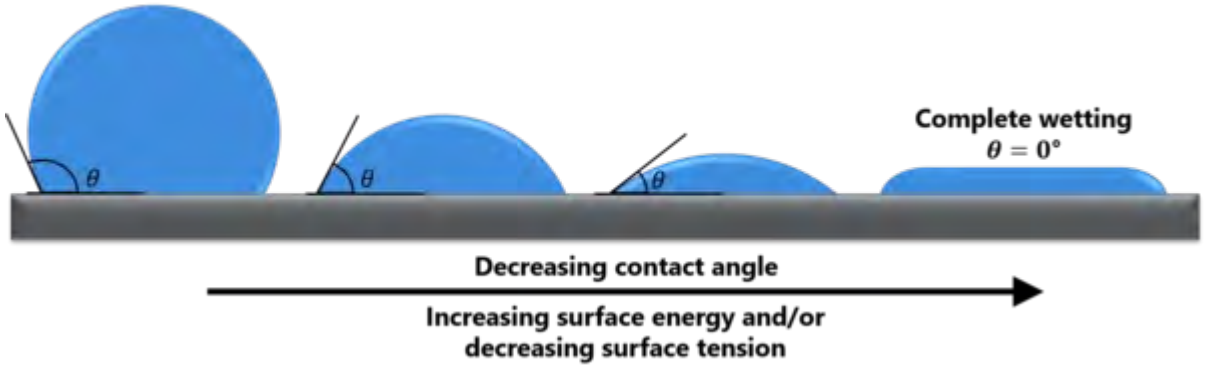
PDMS droplets on **porous silicon** vs. **unetched silicon wafers**

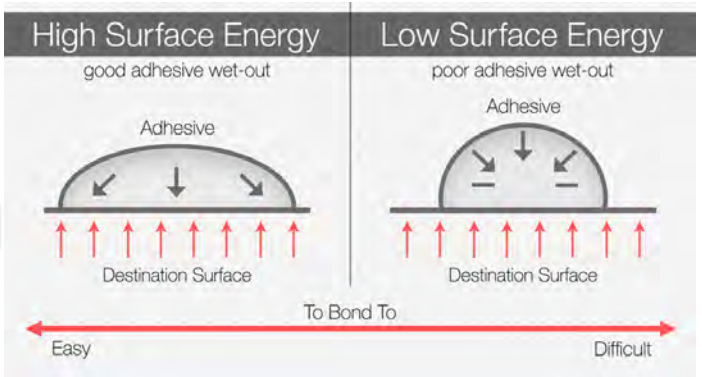


Generally, the higher the porosity of the substrate, the greater the contact angle.

Introduction to Moldless Nanostructured Silicone Lenses

On an unetched silicon wafer with zero porosity, there is almost complete wetting of the surface by the PDMS pre-polymer solution due to the hydrophilicity of the surface. The contact angle is very small, and there is low surface tension of the PDMS solution and high surface energy. Nonetheless, PDMS solution has a large contact angle with increased surface tension on porous silicon material as well as low surface energy due to the material's hydrophobicity as porosity increases.





Source: https://www.ossila.com/pages/a-guide-to-surface-energy

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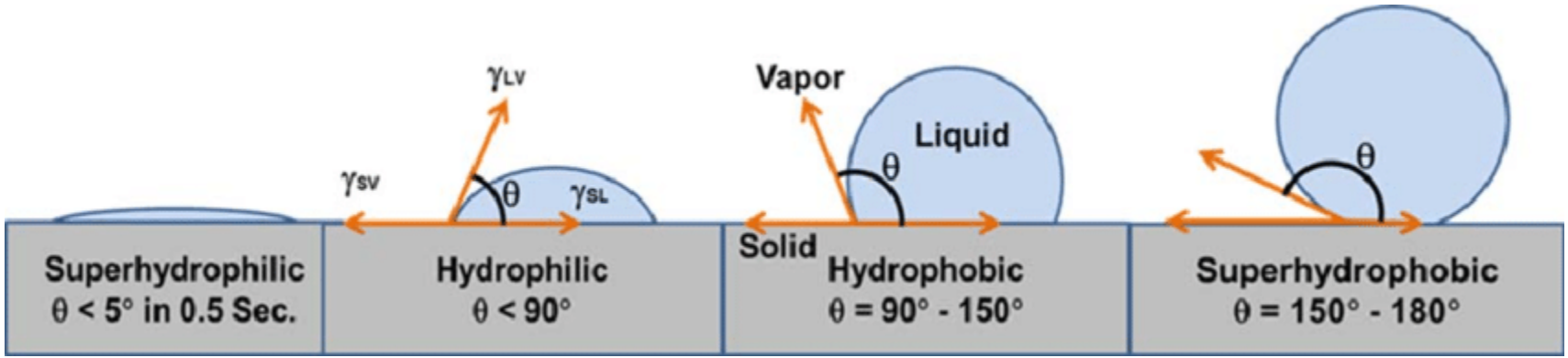
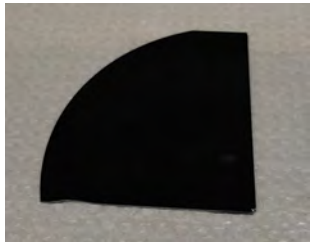


Asmatulu, R. & Khan, Waseem & Reddy, Ramya & Ceylan, Muhammet. (2016). Synthesis and Analysis of Injection-Molded Nanocomposites of Recycled High-Density Polyethylene Incorporated With Graphene Nanoflakes.

Materials

- One large etch cell

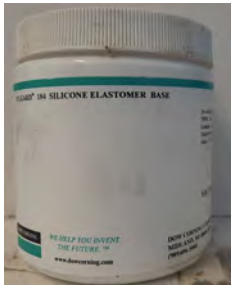
- One large silicon wafer



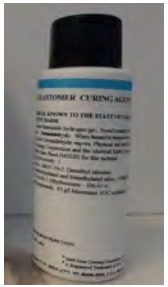
- 3 plastic pipettes

- Cleaving tool

- Silicone elastomer base



- Silicone elastomer curing agent



- 1 aluminum weighing/drying pan

- 1 plastic boat

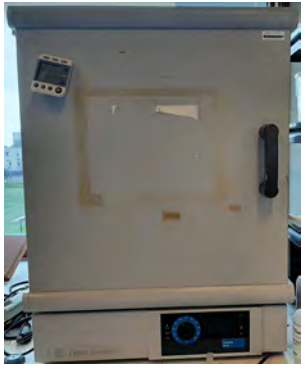
Equipment

- A fume hood

- A power supply

- Scale

- Isotemp oven

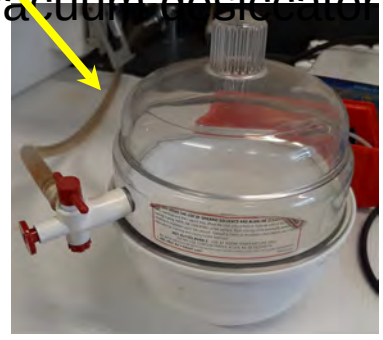


- Tweezers

- Mini Spatula

- Isotemp vacuum oven

OR vacuum desiccator



Equipment (cont.)

KOH **waste** container
Marked by green & white tape
May contain:
- *KOH (potassium hydroxide)*
- *Ethanol*
- *Deionized water*

HF container
Marked by red tape
May contain:
- *3:1 HF-ethanol solution (do not use 1:1!)*

HF **waste** container
Marked by red and white tape
May contain:
- *HF*
- *Ethanol*

KOH container
Marked by green tape
May contain:
- *KOH*

Ethanol container
Marked by color and writing on container

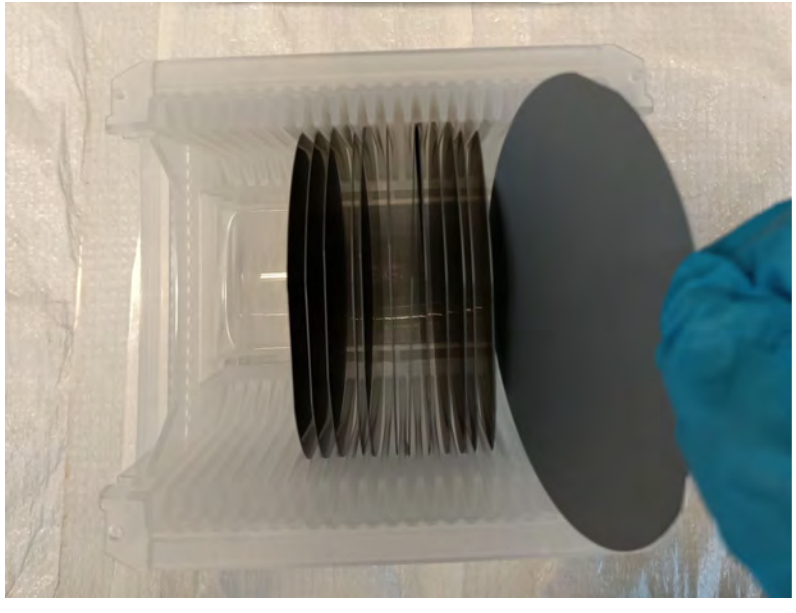
Deionized water container
Marked by color and writing on container

Step 1

Substrate Production

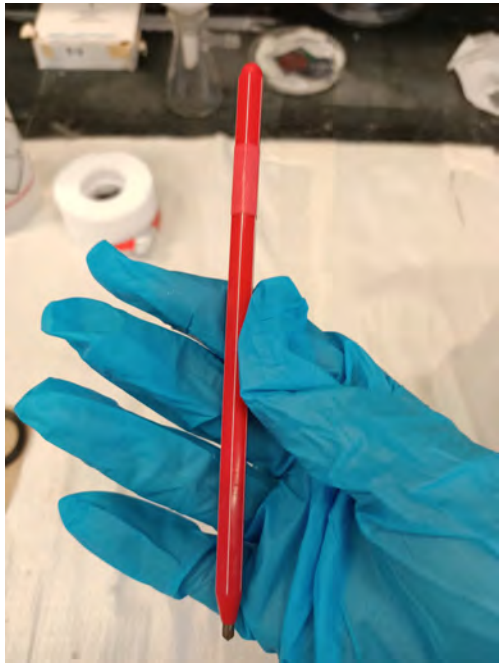
Selecting a Silicon Wafer

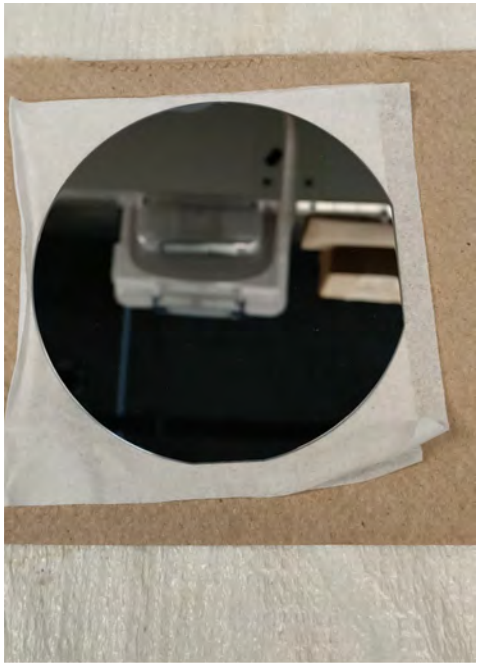
For demonstration purposes, we will select a 1 mΩ-cm wafer for our waveform. Depending on the resistivity of the wafer of your choice, you need to adjust the current density of your waveform accordingly.



Preparing for Cleaving Wafers

You will need a cleaving tool (red), a whole wafer, and a large etch cell.





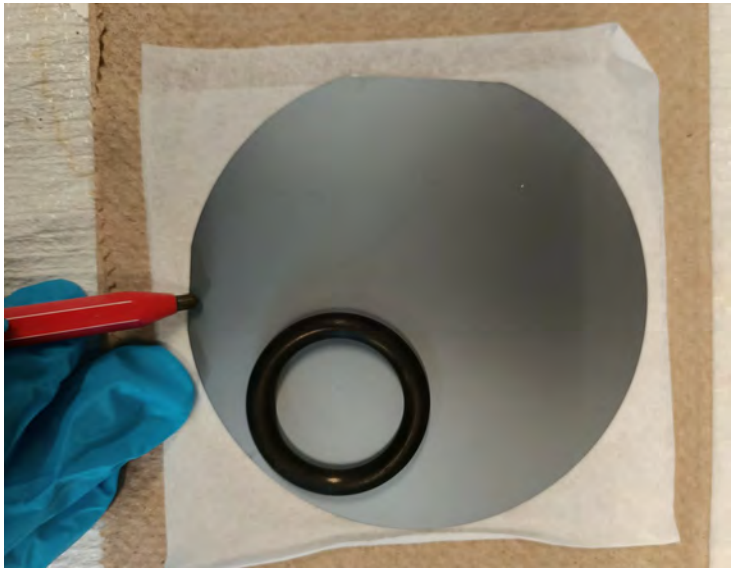
Cleaving a Silicon Wafer

Wafers cleave along the flat edges, and we will use this fact to help cut wafers into usable pieces of silicon. We will make large silicon samples for making PDMS lenses, so our goal is to cut the wafer into four large pieces.

First, find two paper towels and a kimwipe and stack them on your lab bench.

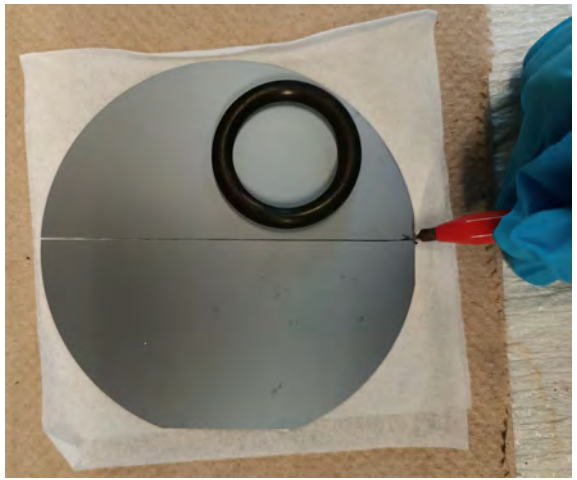
Second, place your silicon wafer on the kimwipe with the matte side facing up and the shiny side in contact with the kimwipe.

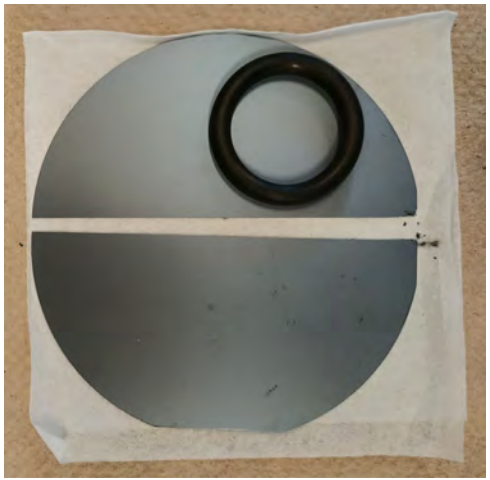
Third, grab an O-ring from a large etch cell assembly as well as a wafer cleaving tool (red) (the tip is a tiny piece of diamond!).

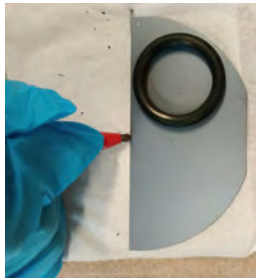


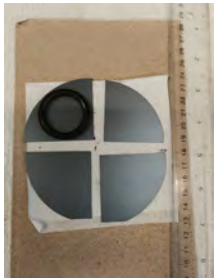
Cleaving a Silicon Wafer

Use the cleaving tool to gently scratch the edge of the wafer in the desired direction parallel to the flat edge. Cut from the middle of the wafer to leave enough space for the o-ring. The wafer cleaves very easily and can leave Si residue on the wipes. Dump any powder-like residue/pieces of Si waste into the blue waste bucket labeled “Silicon Wafer/Chips only”.









Repeat this step until you obtain four pieces of the silicon wafer with approximately identical size. Alternatively, if you don’t want to measure using an o-ring, use a ruler to help cleave the wafer such that the cleaving lines intersect in the center.

Prepare the Wafer on the Etch Cell

Locate the large etch cell and mount one piece of silicon wafer on the cell exactly as outlined in the *Porous Silicon in Practice* textbook.

Set up a large etch cell (8.6 cm^2) and mount all parts using screws. Tighten the screws.

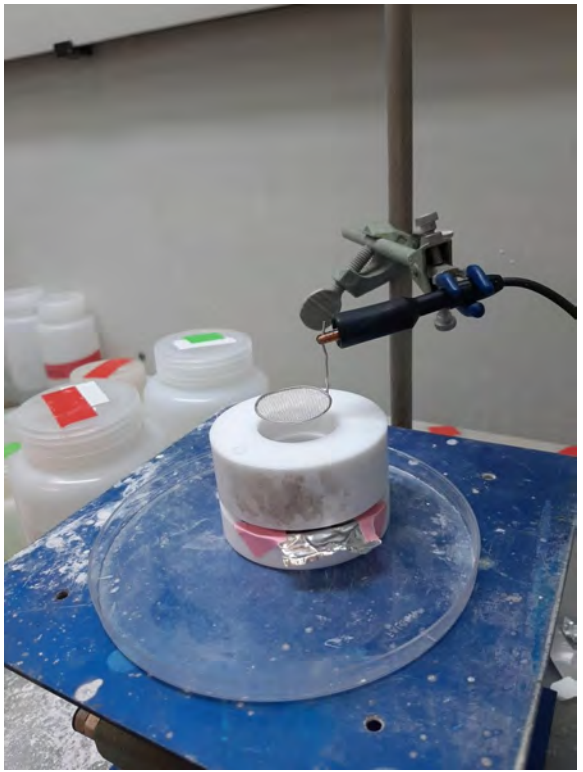
Conduct a leak test on the etch cell. Pour ethanol into the etch cell and wait for 5-10 mins. Then, slide a kimwipe towards the o-ring and check if there is any liquid leakage. If not, proceed to step 3. Otherwise, repeat the above steps.

Sacrificial Etch

Make sure to wear all necessary PPE (apron, safety goggles, lab coat, face shield, latex gloves, and large protective gloves for etching). Place the etch cell in the fume hood and prepare the platinum mesh. Add 3:1 HF:ethanol to the etch cell until the mesh is immersed in the solution. Turn on the switch of the etching system, complete the circuit by connecting the red cord to the aluminum foil on the etch cell, and close the fume hood.

Then, perform sacrificial etch for 30 seconds at a current density of 30 mA/cm^2.

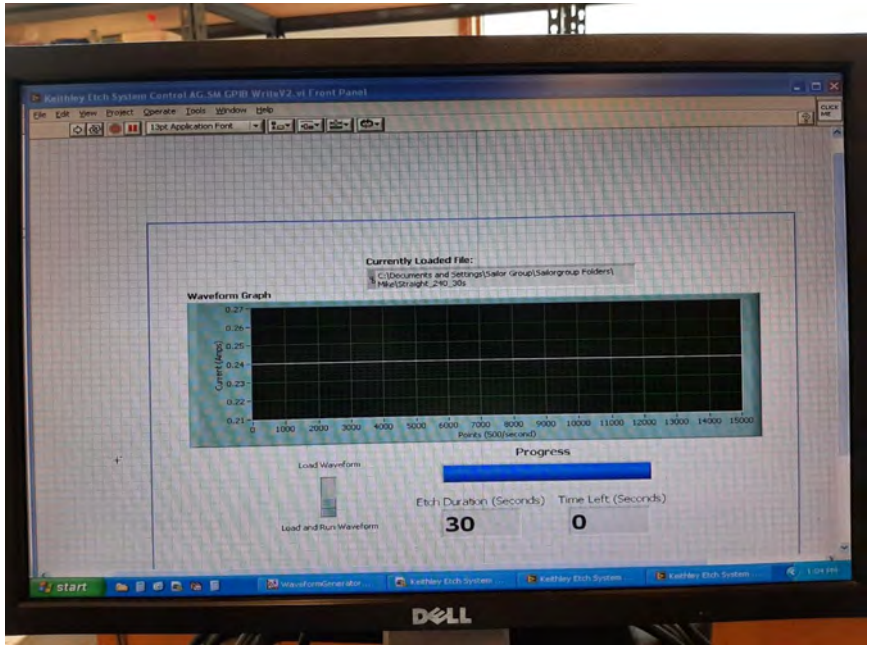
You can find the waveform in Desktop > Shortcut to Group Folder > Claire > PDMS Project > Large_Sacrificial.



Sacrificial Etch

The exposed area on the etch cell is approximately 8.6 cm^2, so a current of 1720 mA is needed.

Etch for 30 seconds. The etch system will alert you when there are 10 seconds of etching left. Be prepared to turn off the switch on the etching system and disconnect the circuit by removing the red clip from the etch cell’s aluminum foil.



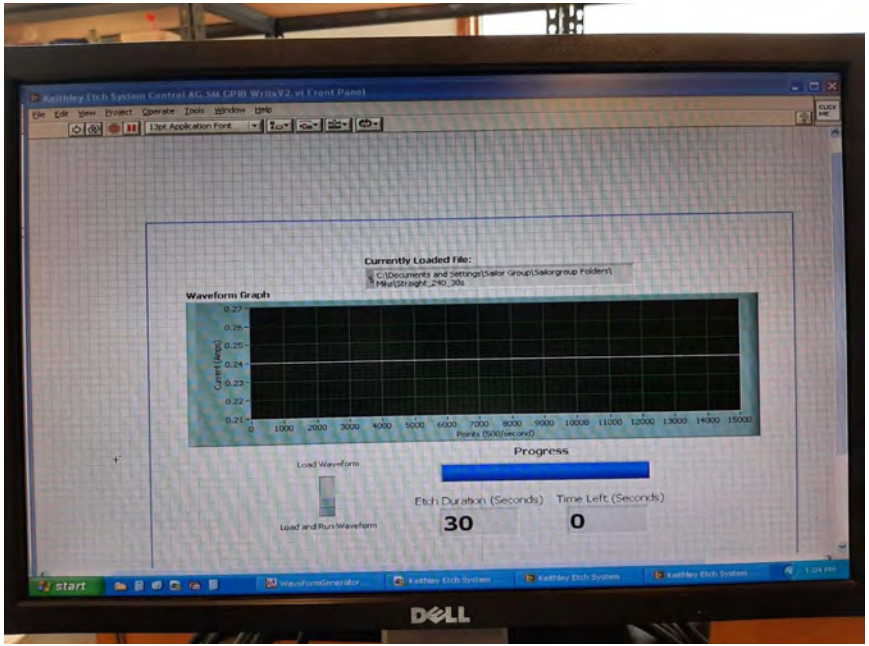
Sacrificial Etch (cont.)

Once the 30 second etch is completed, remove the HF, rinse the cell with ethanol (2-3 times), and dry with nitrogen flow.

Next, add a small amount (2-4 pipettes) of KOH to the cell; bubbles should appear as it reacts with the surface, dissolving the etched layer. Wait a few minutes, then move it to the KOH waste container and rinse: first with deionized water, then twice with ethanol. Dry with nitrogen.

Why do a sacrificial etch?

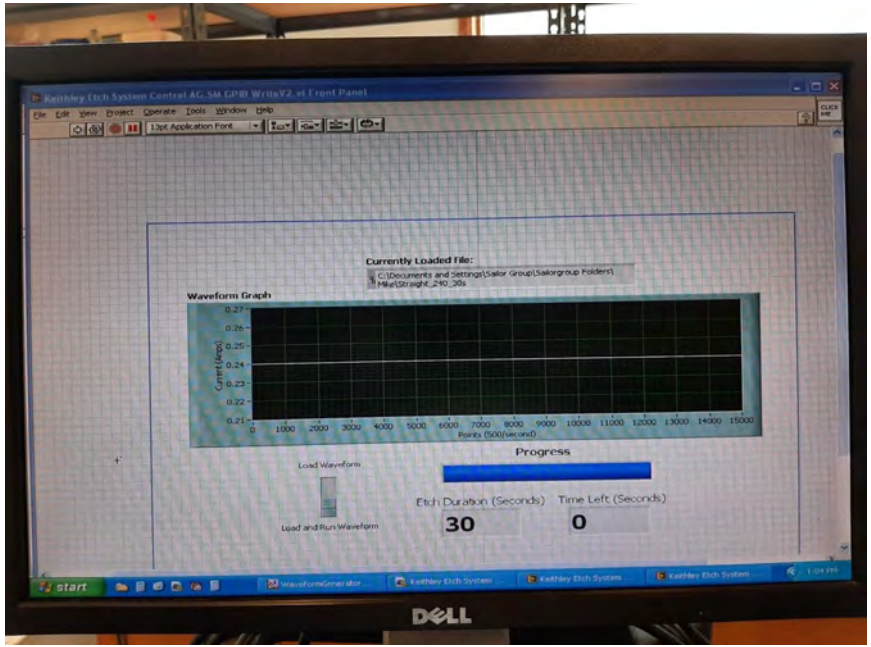
The top surface of a silicon wafer may be scratched or uneven, so “sacrificing” this layer and dissolving it off with KOH forms a more uniform layer and more consistent results.



Etching of the Porous Silicon Layer

Perform electrochemical etching of the porous silicon layer. Etch using a current of 928 mA (over an area of 8.6 cm^2) in 3:1 HF:ethanol solution for 625 seconds.

You can find the waveform in Desktop > Shortcut to Group Folder > Claire > PDMS Project > Large_Porous.

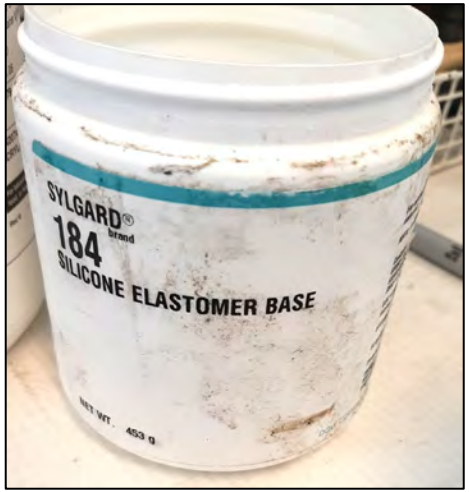


Step 2

Lens Production

Preparing the PDMS Solution

Locate the silicone elastomer base (large) and the elastomer curing agent (small) on the shelf. Find three disposable plastic pipettes: one for the base, one for the curing agent, and one for mixing. Use scissors to cut 1 cm from the tip of the plastic pipette for the elastomer base, which is very viscous.



Weighing the Ingredients

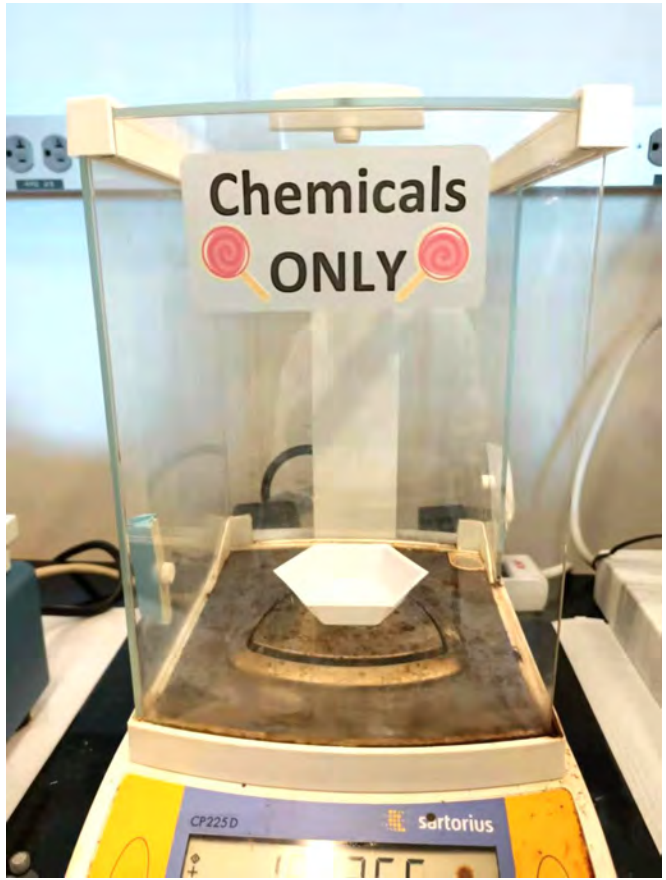
Locate the scale. Place a plastic boat on the scale and press “TARE” to zero the scale. Then, press “F” to refine the measurement by increasing the number of significant figures on the scale’s display.

Weighing the Ingredients

The optimal base-to-curing agent ratio was found to be 10:1 by mass.

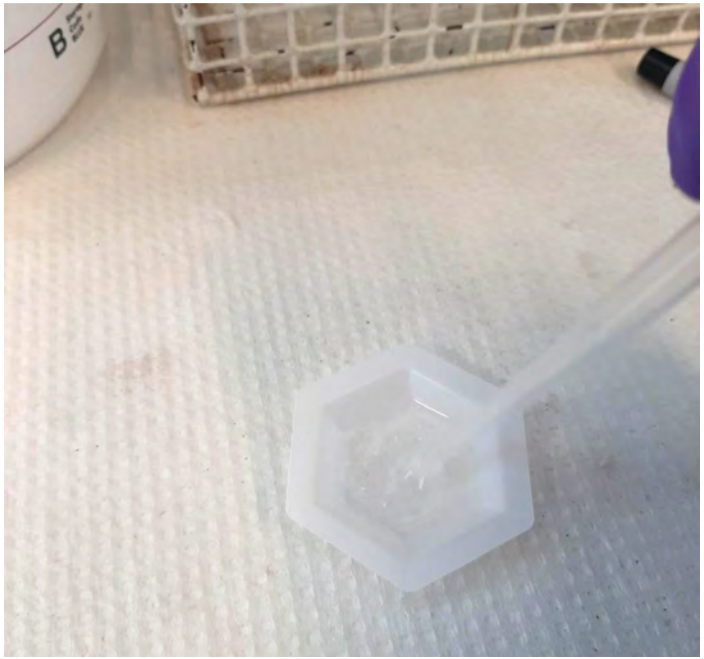
Pipette 2 grams of elastomer base solution from the bottle to the plastic boat. Then, pipette 0.2 grams of curing agent from the bottle to the plastic boat. Make sure to use separate pipettes for each ingredient.

Keep track of the numbers displayed on the scale as you pipette.



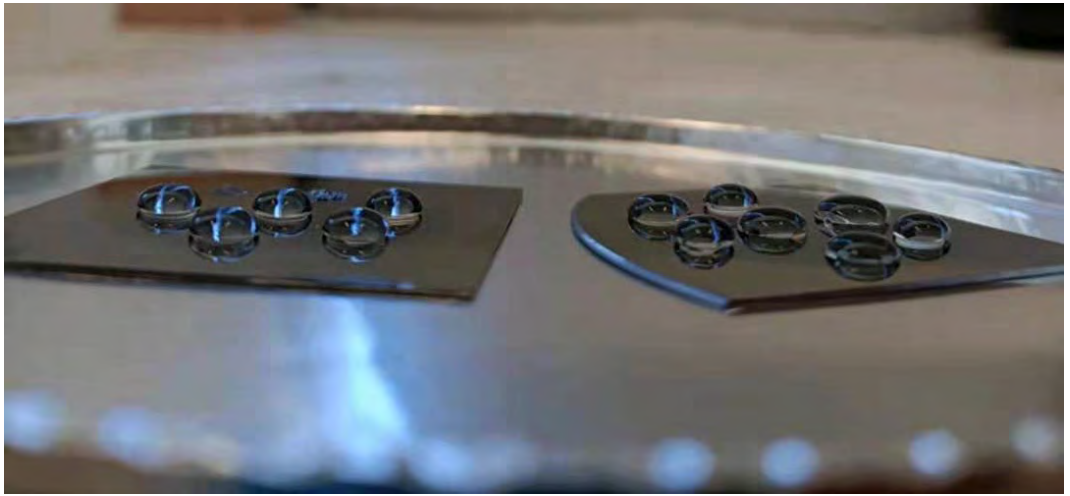
Stirring the PDMS Pre-Polymer Solution

Mix the PDMS pre-polymer solution using your designated mixing pipette for two minutes.



Moldless Production of Lenses

Find your etched silicon sample on the aluminum platter and your silicone mixture in its plastic boat. Use the mixing pipette to drop the silicone droplets on the porous silicon material.



Removing Air Bubbles in the Lenses

Locate the vacuum desiccator and place your silicon samples with PDMS droplets on the semi-transparent plastic platform in the desiccator.

Remove the clear plastic domed lid from the desiccator assembly.

Carefully place the aluminum plate with samples (and lenses) on the plastic platform. Put back the clear lid and push it down to seal tightly.

Connect the rubber pipe from the desiccator and the vacuum pump labeled “VAC” in yellow.

Turn on the faucet of the vacuum pump.

Turn the red nozzle such that it points in the direction of the pipe.

Vacuum the lenses for 30 minutes. Then, switch off the vacuum pump and red nozzle on the pipe. Take your samples out of the vacuum dessicator.

Heating Up the Lenses

Keep your samples on the aluminum plate and place the plate in the oven to heat up silicone lenses.

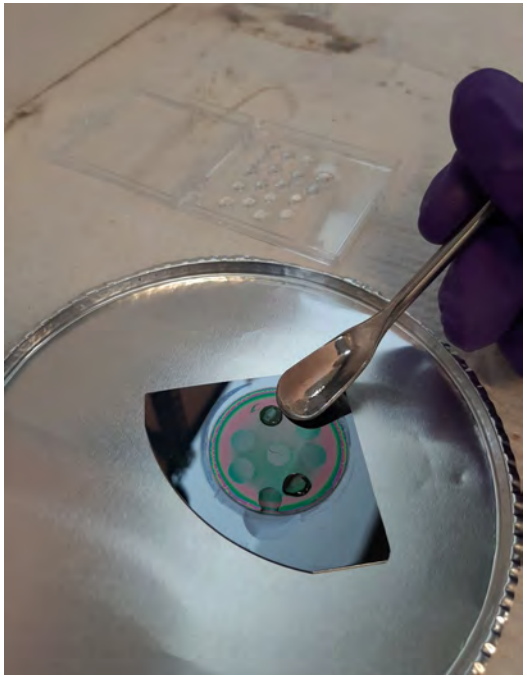
Heat up for 60 minutes at 100˚C **OR** 70 minutes at 80˚C **OR** 50 minutes at 120˚C.

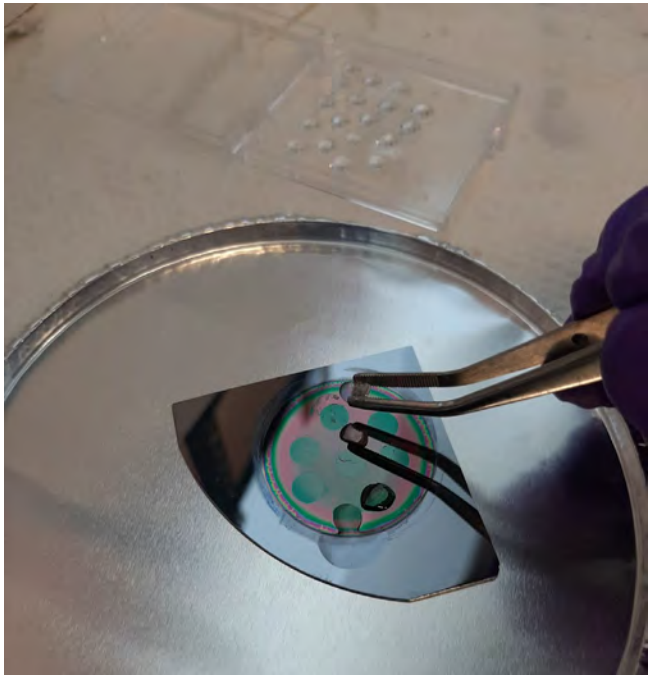
When the time is over, take out the aluminum plate using tongs or heat-insulating gloves and let the lenses cool for 1-2 minutes.

Peeling Off the Lenses

Peel each of the lenses off using the mini-spatula and place them in a safe spot using tweezers.

Finally, your lenses are ready! Test them on your cell phone cameras :)





Your Next Step - Learning Contact Angle Measurements

Start with a Si wafer.

In the fume hood, soak it in HF for 1 minute to dissolve the SiO_2 layer, exposing SiH.

Measure and record the contact angle of a water droplet on the sample's surface.

Etch the wafer.

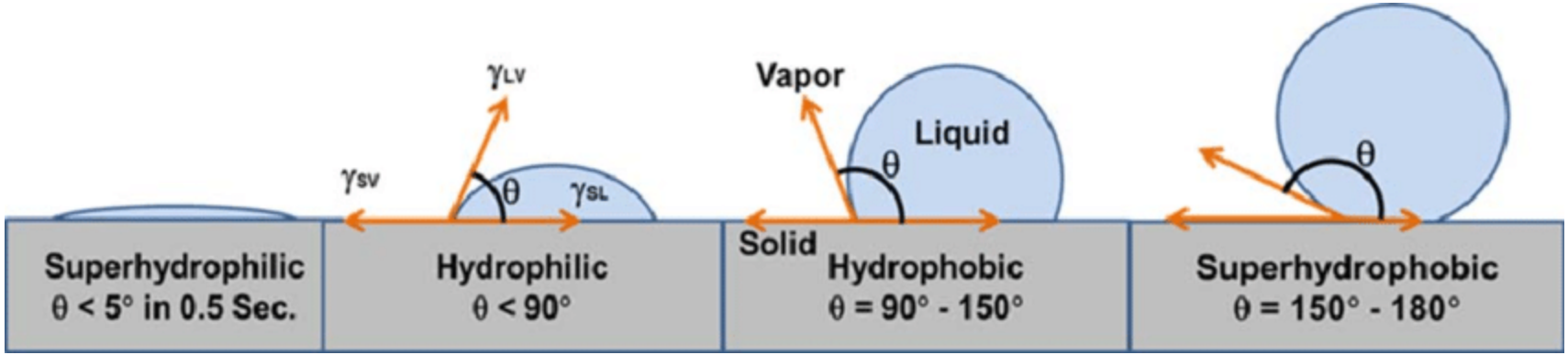
Take another contact angle measurement of water droplet. Record it.

Compare them!

Once you have experience using the contact angle instrument, you can move on to synthesizing your own PDMS lenses!

Measuring Contact Angles On Your Own Phone!!

Compare Your Numbers:

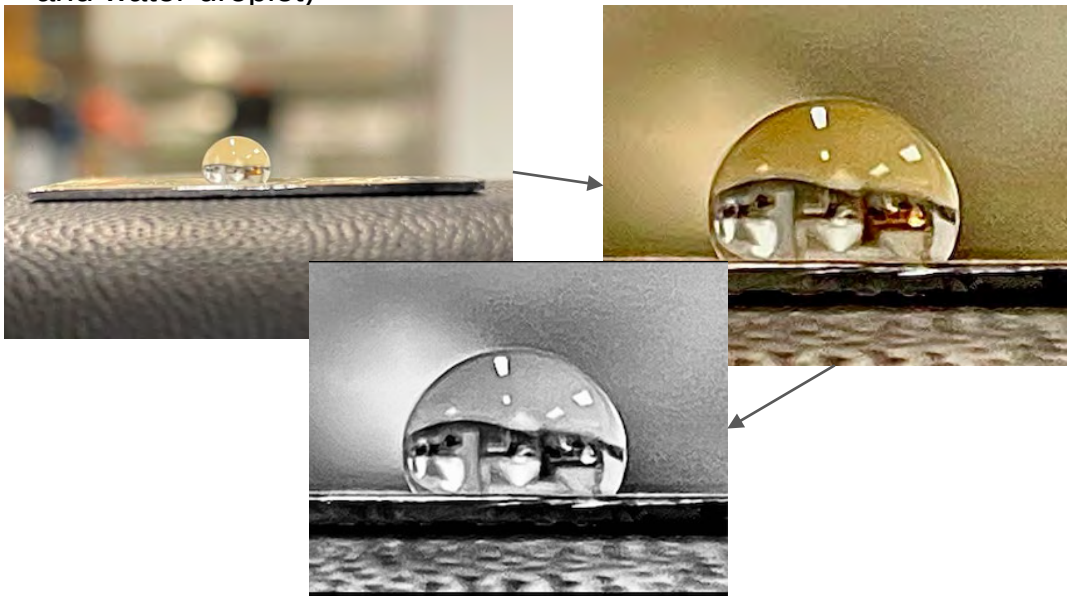


Measuring Contact Angles On Your Own Phone!!

1) First download the Protractor App by searching “protractor” in the App Store

2) Get Your Image Ready by taking a photo and editing as needed to have

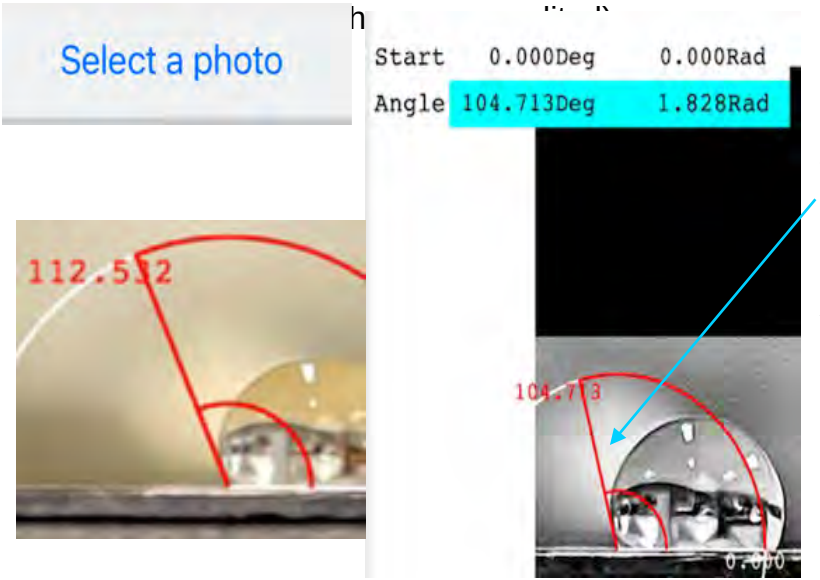
- Good background contrast (darker background)
  - If needed you can make the image black and white
- Zoomed In
- Eye level (phone should be at the same level as the substrate and water droplet)



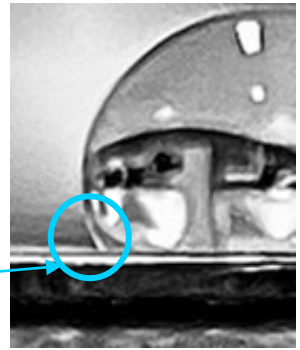
Measuring Contact Angles On Your Own Phone!!

3) Open the App and Upload Your image

- Click the Camera button in the bottom corner



4) Place the Protractor in the Correct Position



Move- use this to place the origin of the protractor at the area where the water droplet meets the substrate

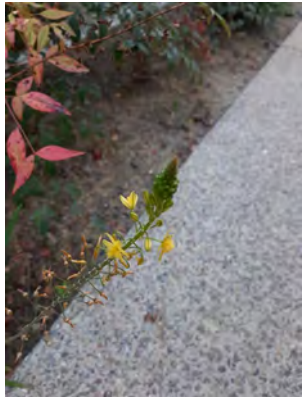
Start- Move the ray of the protractor so it follows the edge of the droplet - it should be touching the outer edge of the droplet

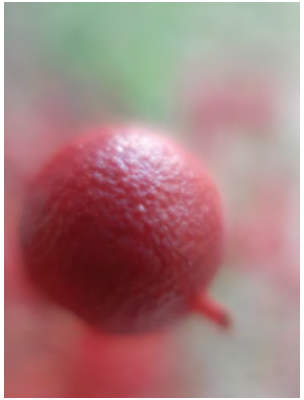
Angle- Do not touch this setting unless the base of your droplet is not level

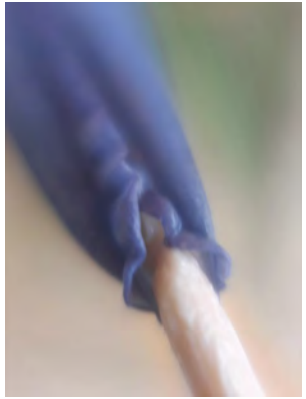
Record Your Angle and Use the Table To Check How Hydrophobic Your Substrate Is!!

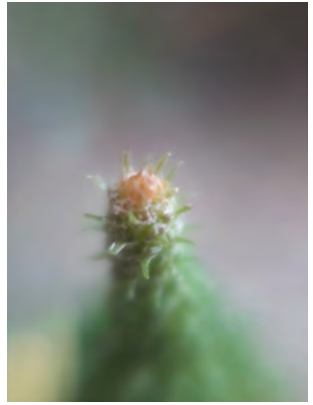
Team Number + Initials	Contact Angle of Water on Si wafer after 1-minute HF soak	Contact Angle of Water on Si wafer after etch	Contact Angle of PDMS on Si wafer after 1-minute HF soak	Contact Angle of PDMS on Si wafer after etch

Images taken using lens on cell phone camera

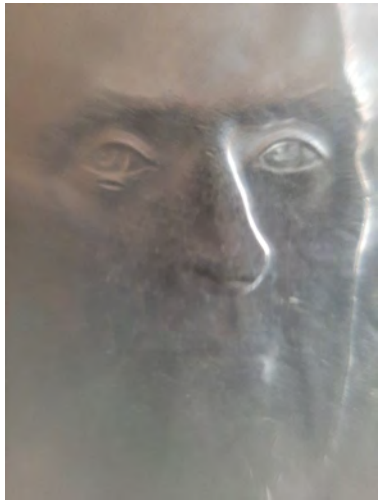


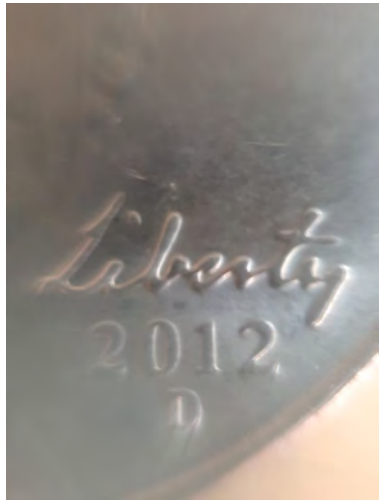




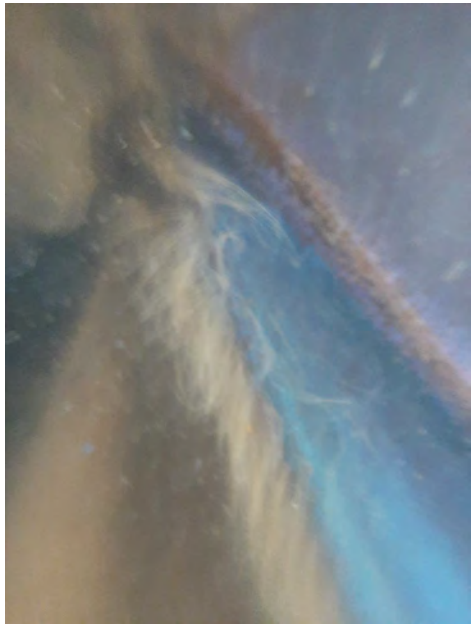


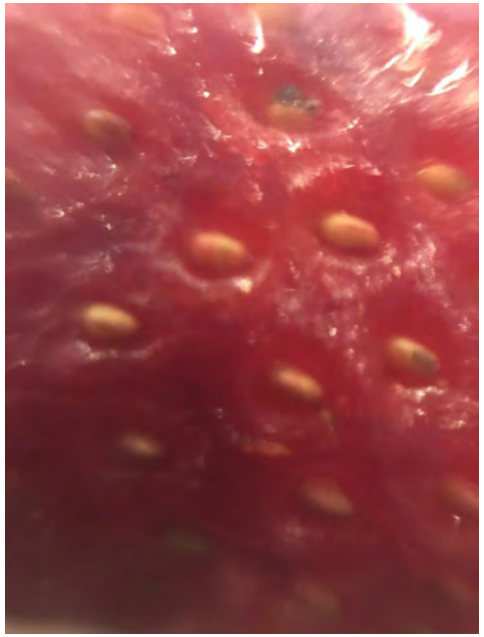
Images taken using lens on cell phone camera



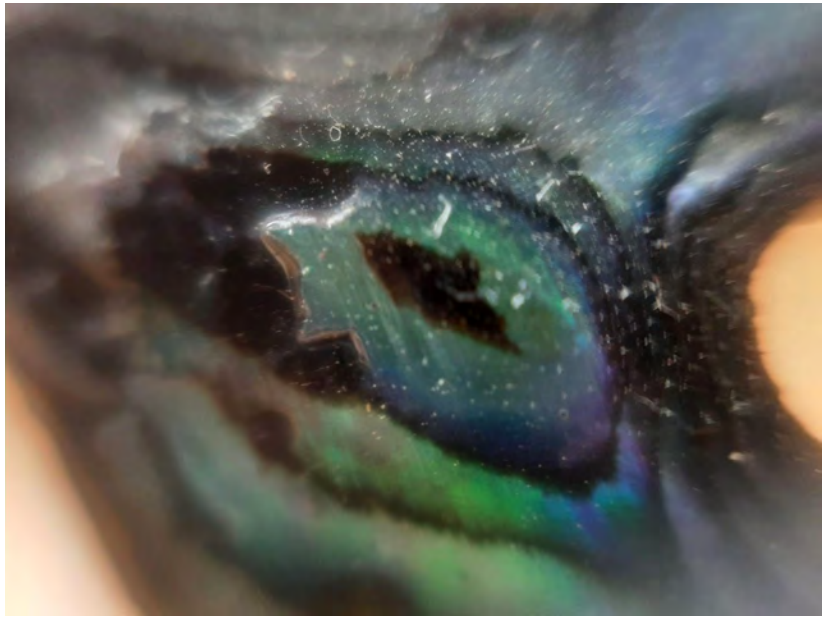


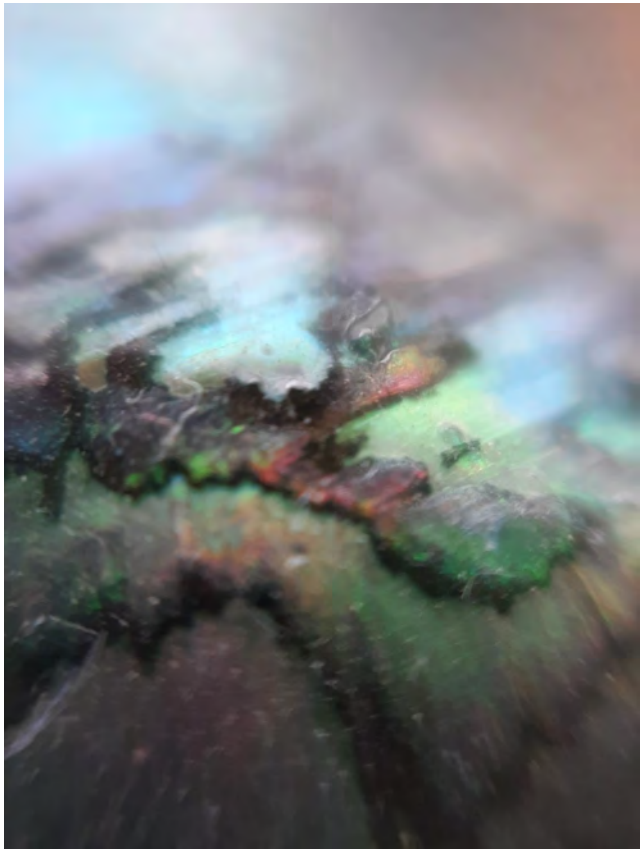
Images taken using lens on cell phone camera





Images taken using lens on cell phone camera





Images taken using lens on cell phone camera