Superhydrophobic and Nano-structured Materials

A different type of Nanotechnology

Presented at IAC Meeting

by

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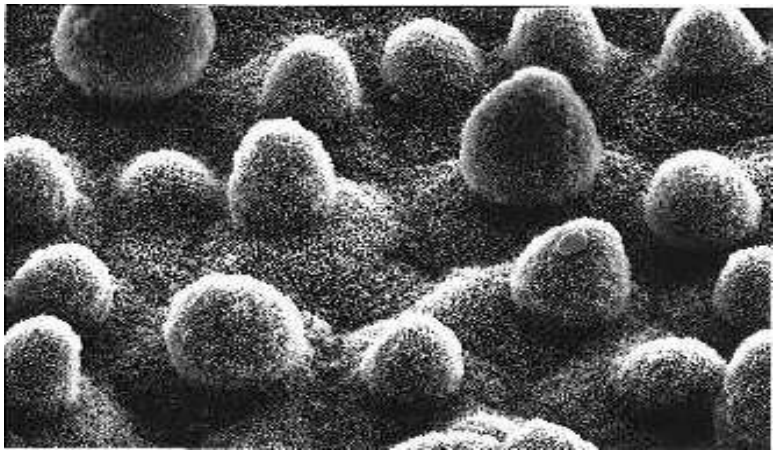
Engineering Science & Technology Division

Natural Superhydrophobic Surfaces



- **Lotus leaf is superhydrophobic.**
  - **Water beads up on surface.**
  - **Waxy hydrophobic material.**
  - **Nanoscale and microscale structure.**

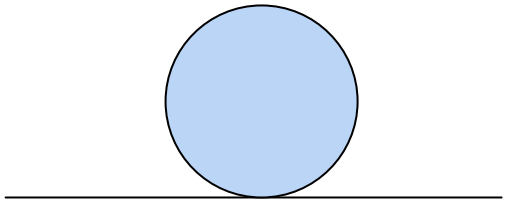
Tennessee State Tree (Tulip Poplar) Leaf

Wetting Phenomena

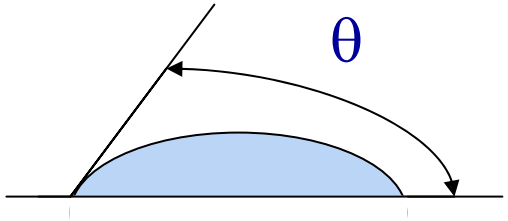
Absolute wetting

$\theta = 0^o$

No wetting

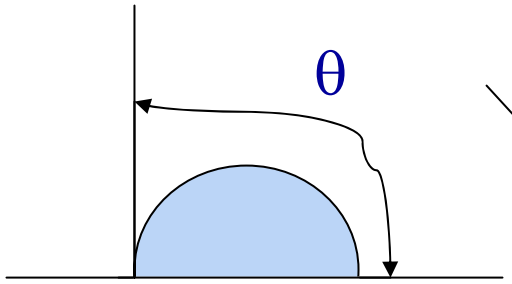


$\theta = 180^o$

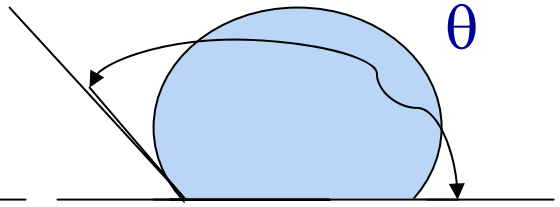


$\theta < 90^o$

Hydrophilic



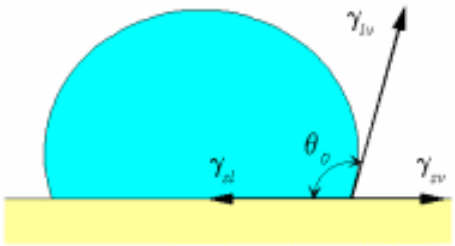
$\theta = 90^o$



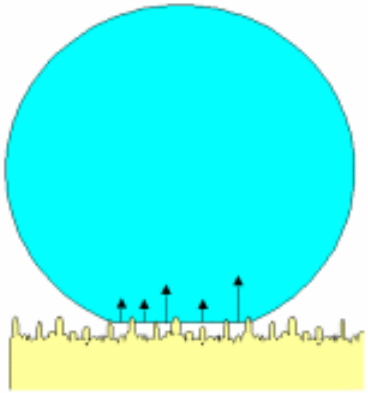
$\theta > 90^o$

Hydrophobic

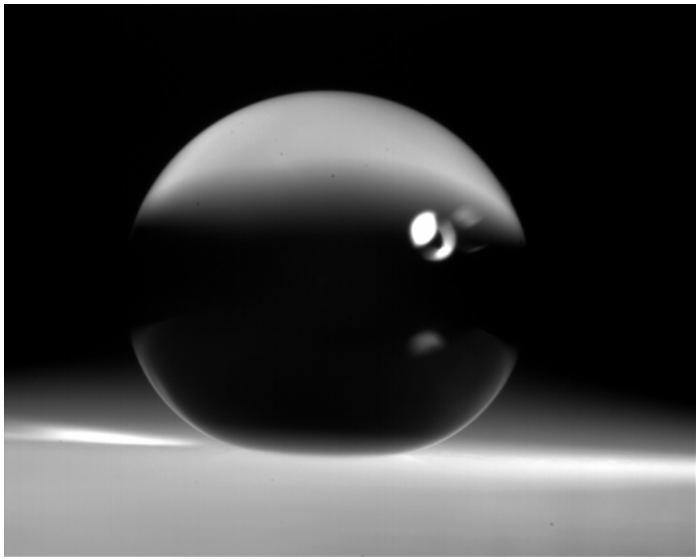
Roughening a hydrophobic surface increases the effective hydrophobicity (contact angle)



Droplet on normal hydrophobic surface

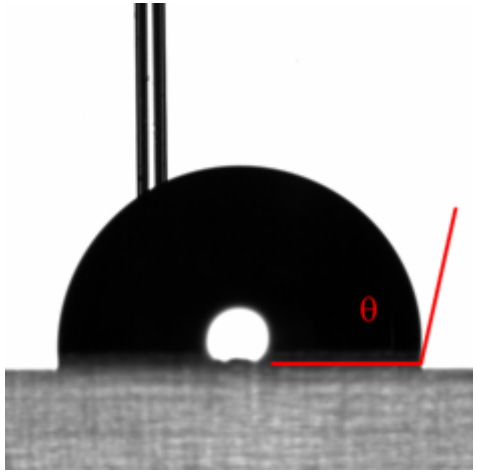


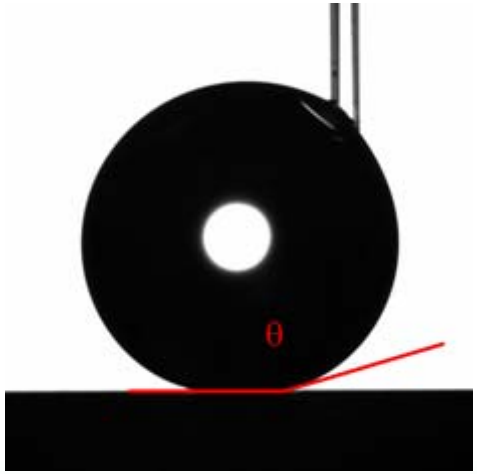
Droplet on superhydrophobic surface



Superhydrophobic Surfaces

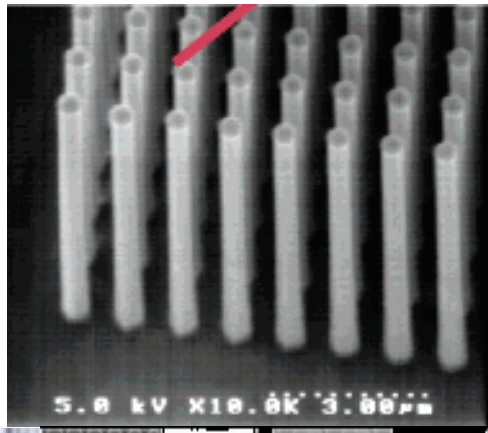
- **Hydrophilic: $\theta < 90^o$.**
  - **Glass (38°).**
  - **Metals, ceramics, some polymers.**
- **Hydrophobic: $\theta > 90^o$.**
  - **Teflon (120°), fluorinated polymers, wax**
  - **Some other polymers.**
- **Surface nanostructure amplifies the hydrophobic properties.**
- **Superhydrophobic: $\theta > 150^o$.**
  - **Natural and synthetic.**
  - **Dramatically different properties.**

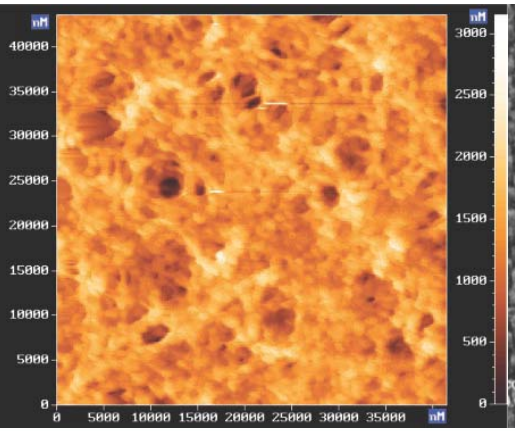


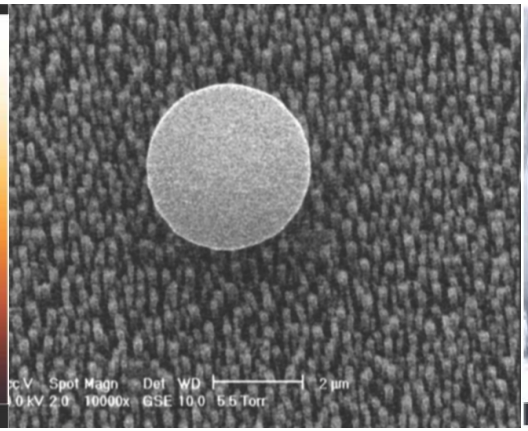


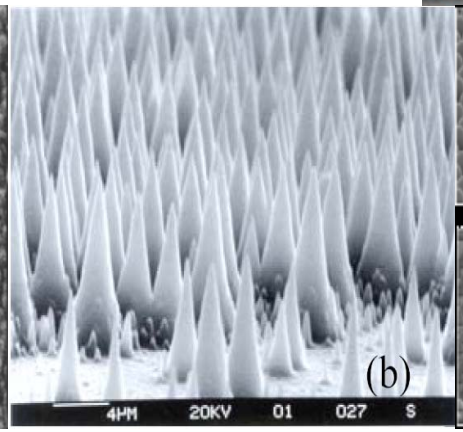
Artificial Superhydrophobic Surfaces

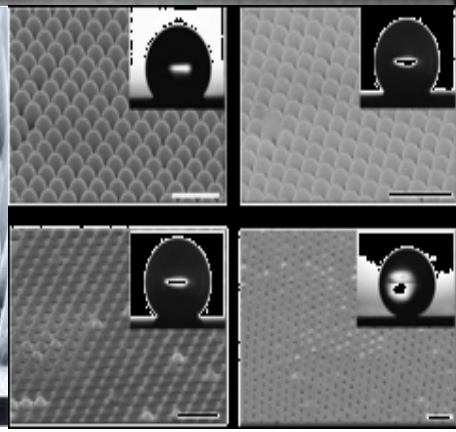
- **Photolithography-based dry etched silicon (Krupenkin et al, Bell Labs).**
- **Porous polymers (Erbil et al, Kocaeli U., Turkey).**
- **Vertically aligned carbon nanotubes (Lau et al, MIT).**
- **Reactive Ion Etched rough silicon (Kim et al, UCLA).**
- **Fluorinated Nanospheres (Jau-Ye Shiu et al,Taiwan, ROC)**





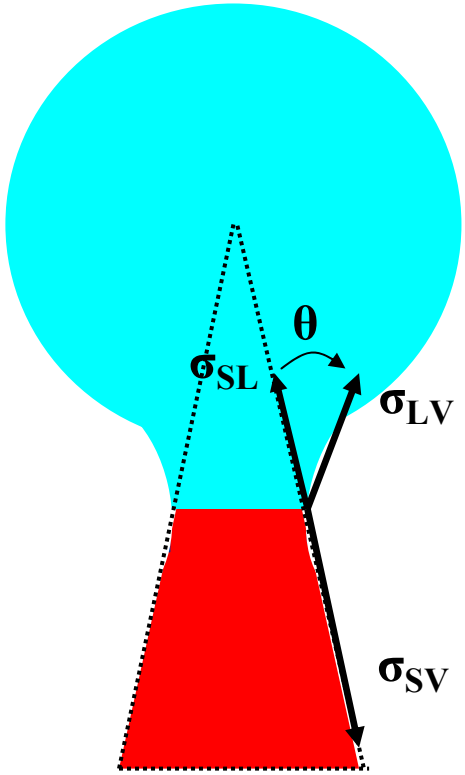






Drop/Spike Dynamics

Young's Equation: $\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cdot \cos\theta$



For hydrophilic material ($\theta < 90^\circ$) : $\sigma_{SL} < \sigma_{SV}$

➔The total energy of the interface is reduced when the interface moves downward

➔It is energetically advantageous for the drop to wet more area (i.e. move downward)

Note that each point on the interface is in equilibrium, but the total interface energy can change with position.

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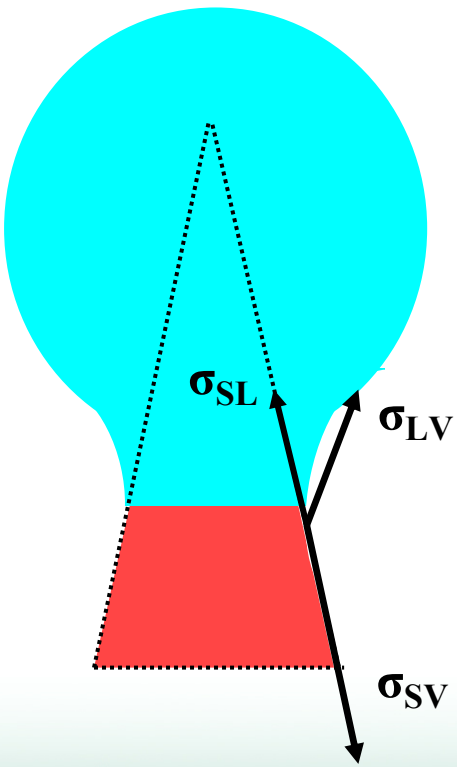

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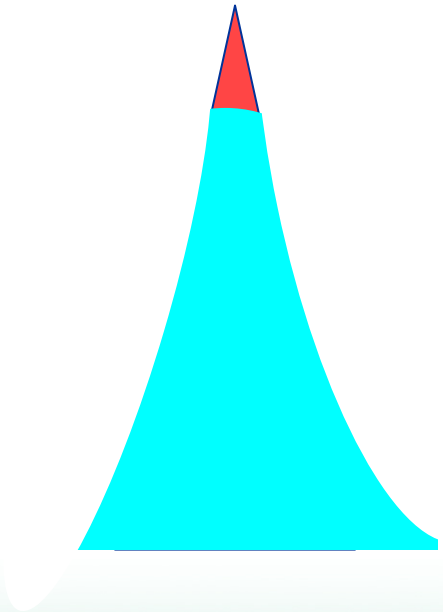

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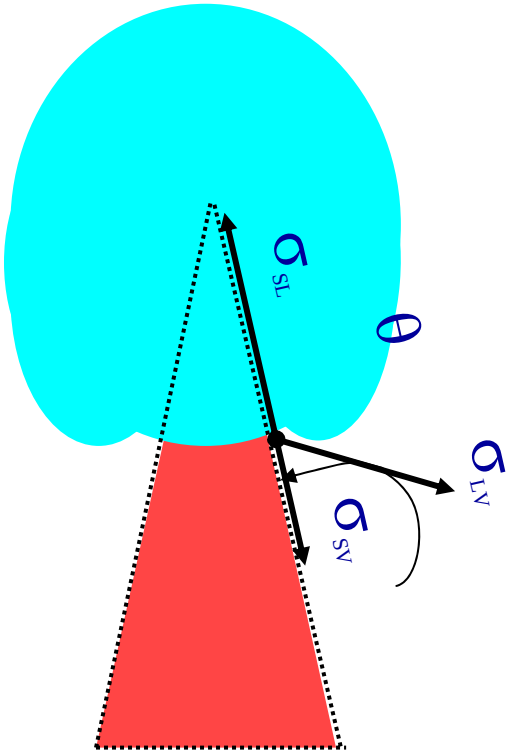

For hydrophobic material ($\theta > 90^\circ$) : $\sigma_{SL} > \sigma_{SV}$

➔The total energy of the interface is reduced when the interface moves upward

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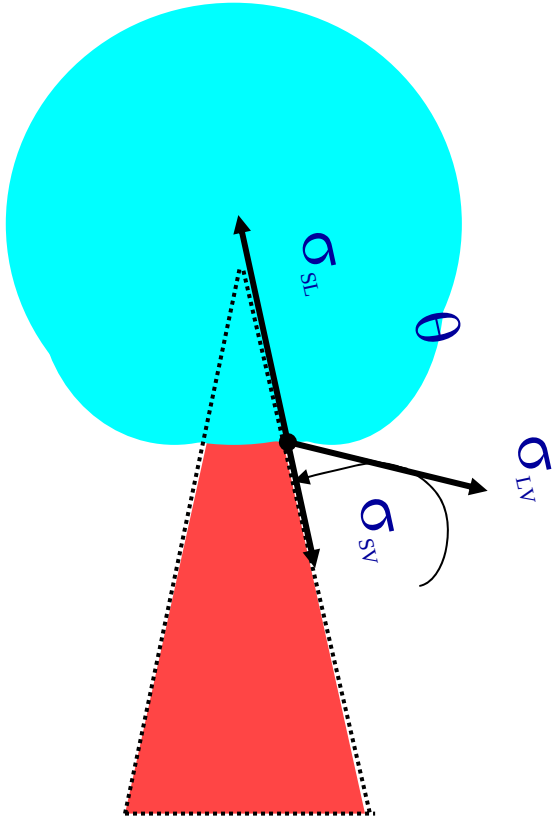
Drop/Spike Dynamics

Young's Equation: $\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cdot \cos\theta$



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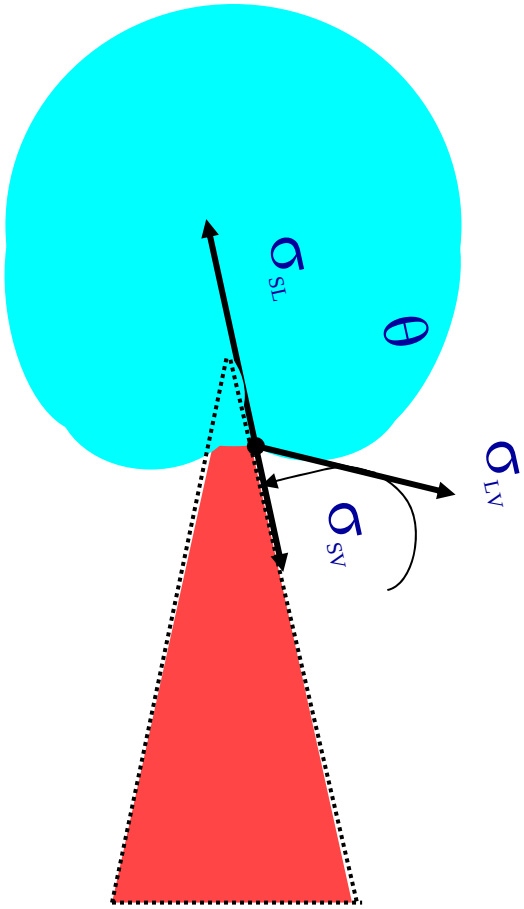

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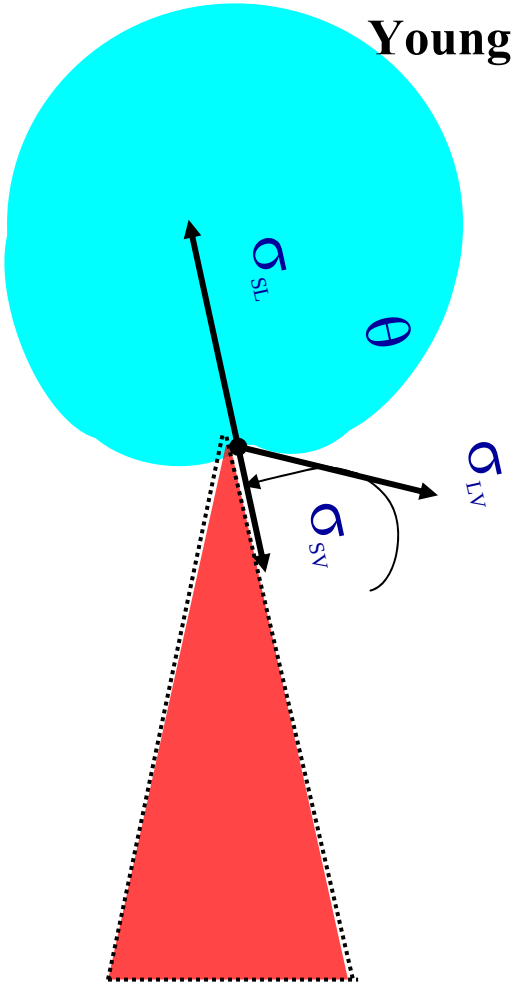

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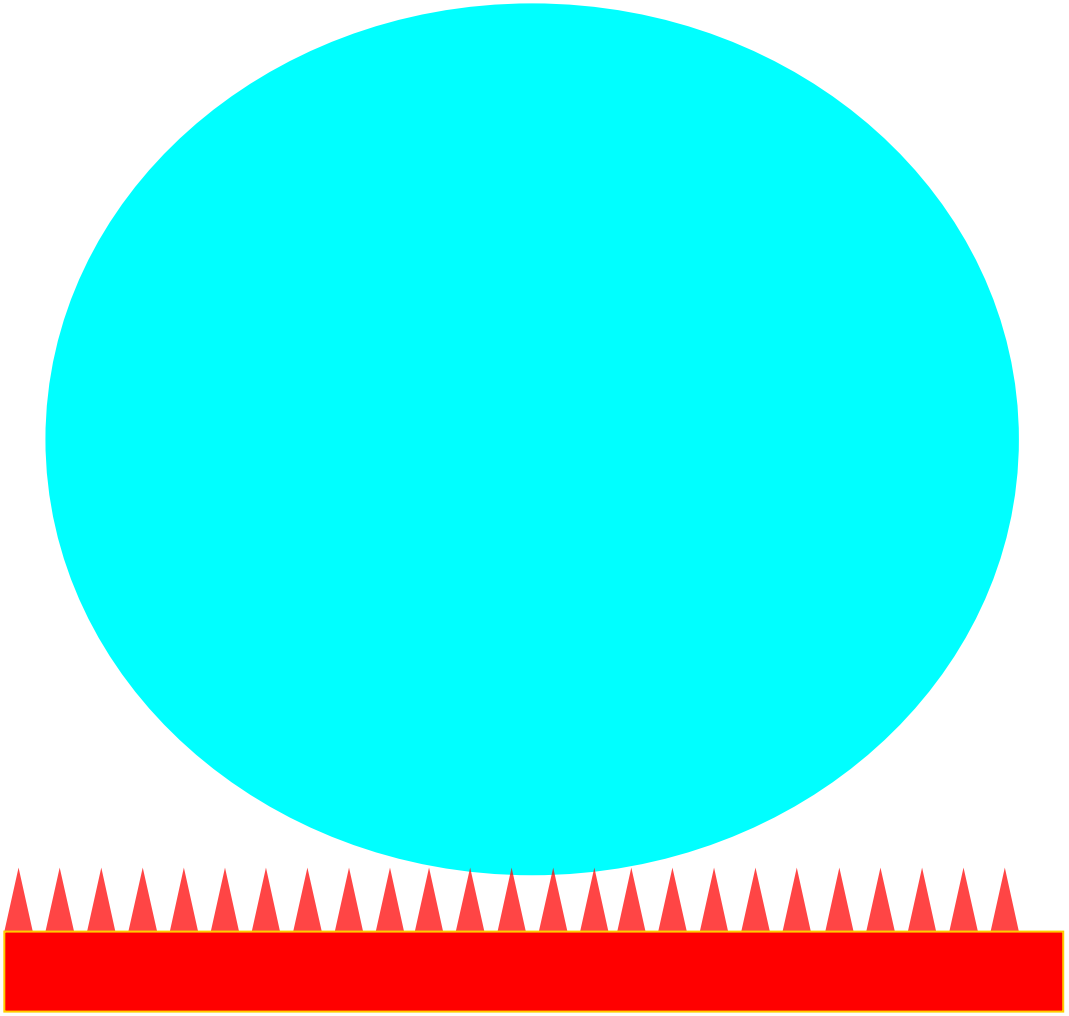
Drop on Hydrophobic Coned Spikes

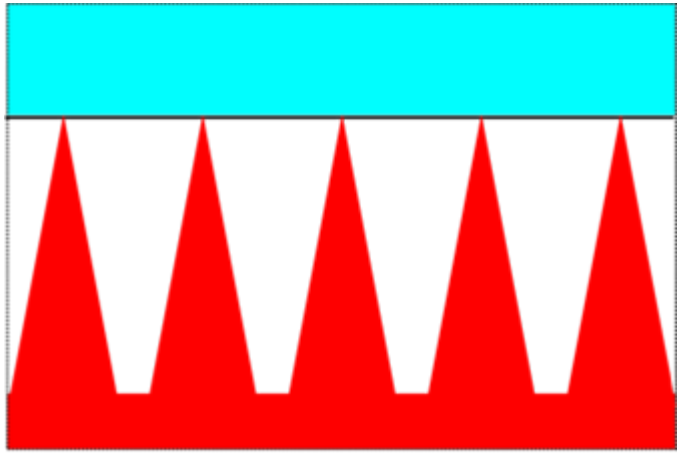


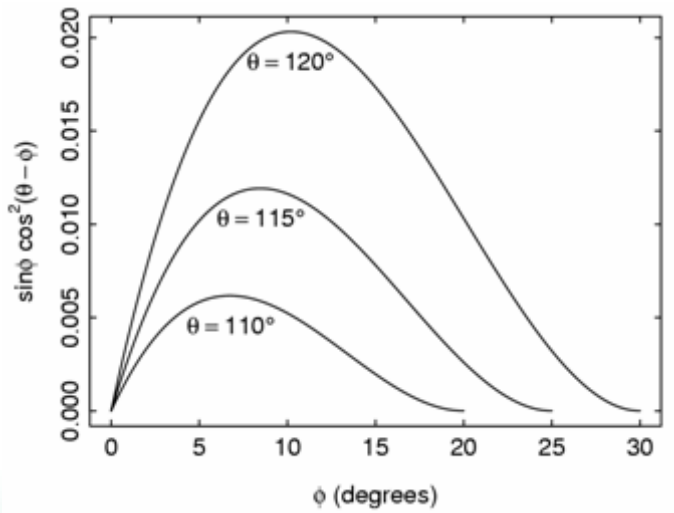
Optimized Superhydrophobic Surface Structure

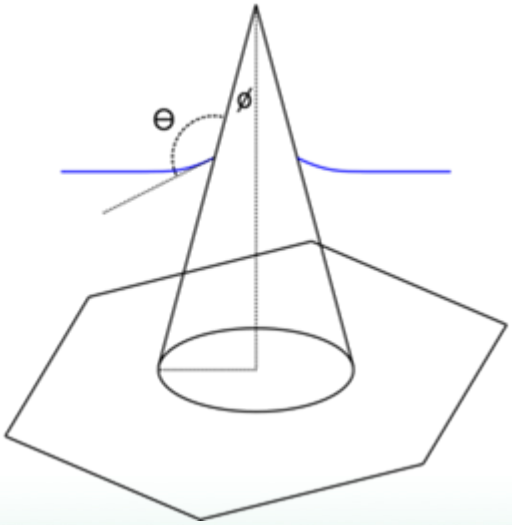
- **Optimal surface:**
  - **Minimum solid-liquid contact → sharp points.**
  - **Maximum vertical force per contact area.**
    - **Vertical force:**
    - **Contact area for given force:**

$$F \propto \cos(\theta - \phi)$$

$$A \propto \left[\sin\phi \cos^2(\theta - \phi)\right]^{-1}$$



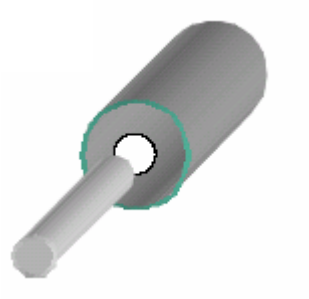




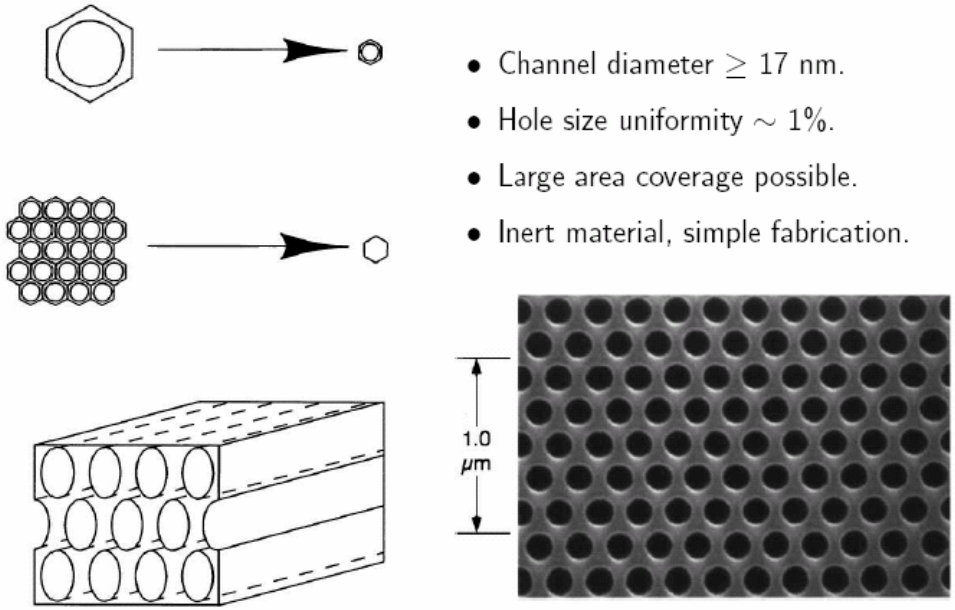
Our Goal: Make the Highest Quality Superhydrophobic Material Possible (i.e. contact angle ~ 180°)

- **Method:**

  Modify nanochannel plate fabrication technology in order to make uniform arrays of spiked cones having the theoretical best superhydrophobic structure.



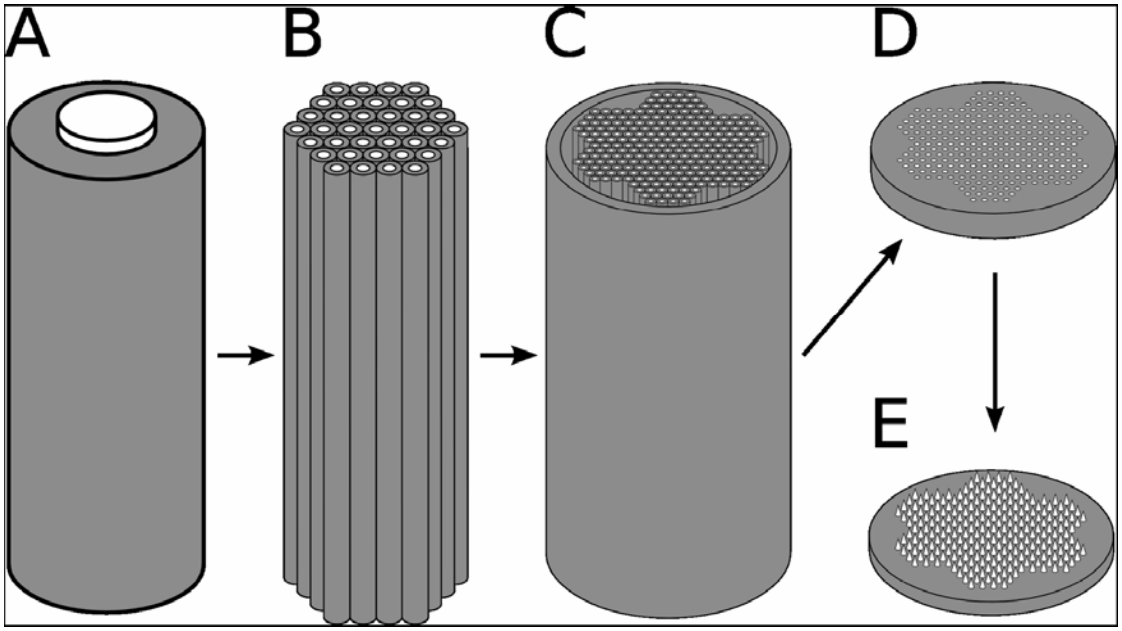
Nano-Channel Glass Process



- Channel diameter $\geq$ 17 nm.
- Hole size uniformity $\sim$ 1%.
- Large area coverage possible.
- Inert material, simple fabrication.

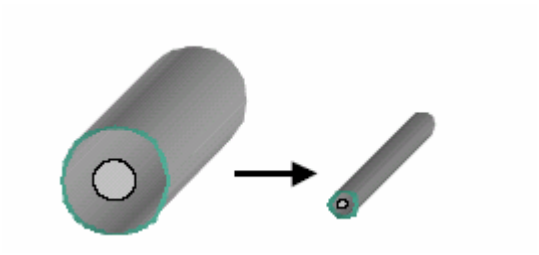
R. J. Tonucci, B. L. Justus, A. J. Campillo, and C. E. Ford, Science vol. 258, p. 783 (1992).

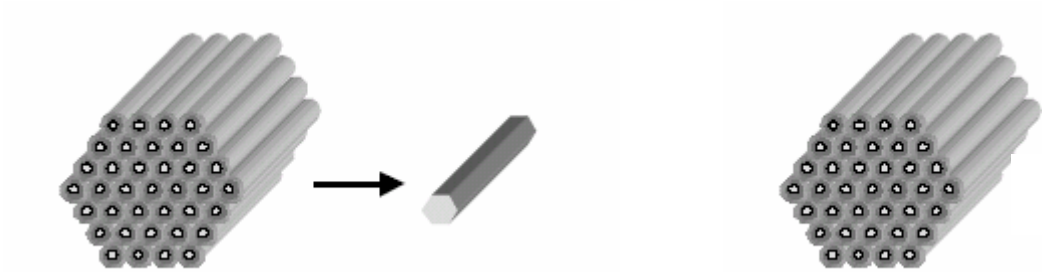
Micro/Nano Glass Array Fabrication

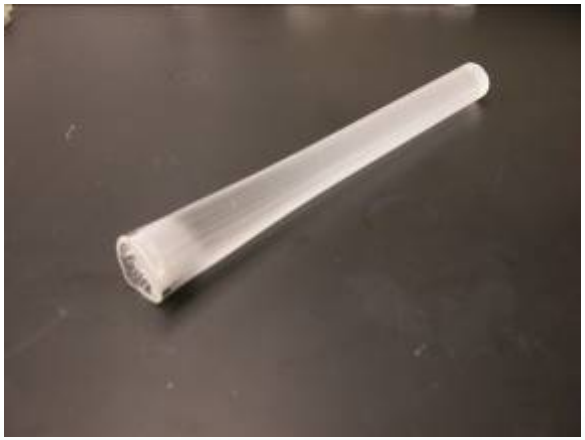


Micro/Nano Glass Array Fabrication

1. **An etchable tube and less etchable rod are drawn at elevated temperature to a fiber which is cut into short pieces.**
2. **The fiber is (repeatedly) bundled, and redrawn into a fiber, and cut.**
3. **The fiber pieces are bundled and fused without drawing to make a larger bundle, which is sliced into wafers.**

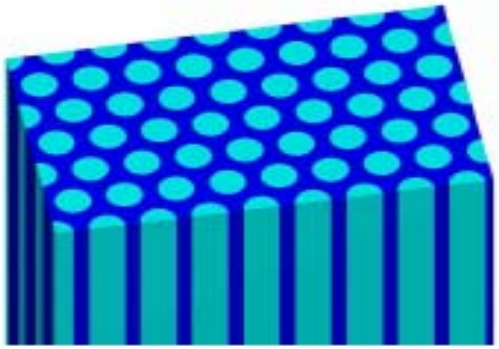






Superhydrophobic Micro/Nano-Cone Glass

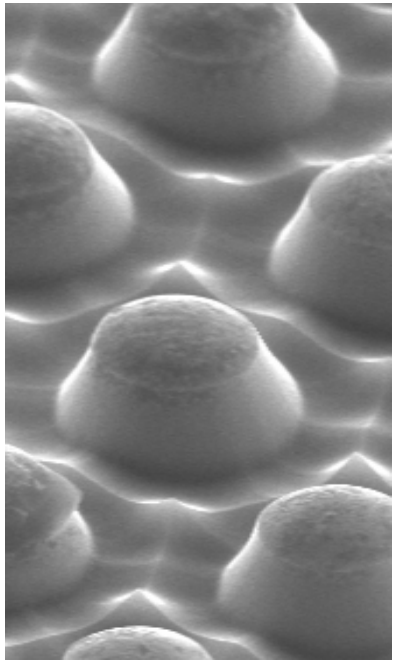
- Slice final bundle into wafers and polish surface
- Wet etch surface with moderate selectivity ~ 10:1
- Coat surface with hydrophobic material

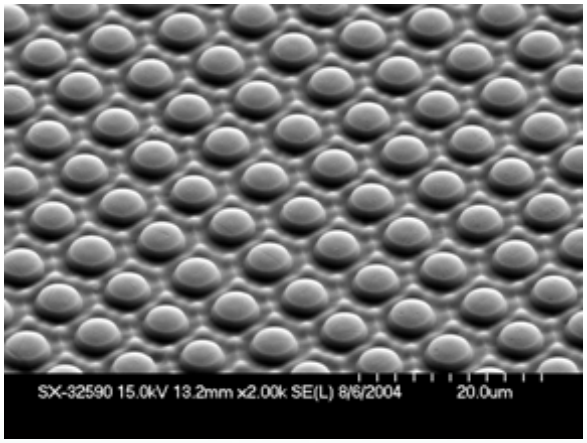


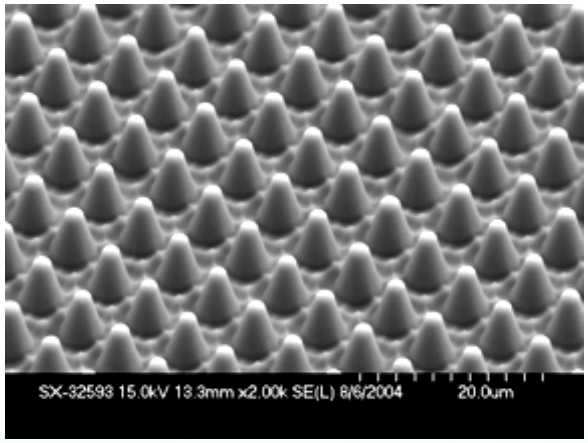
- **Simple Fabrication** (no photolithography, no vacuum processing)
- **Uniform spacing and height**
- **Large area, small features**

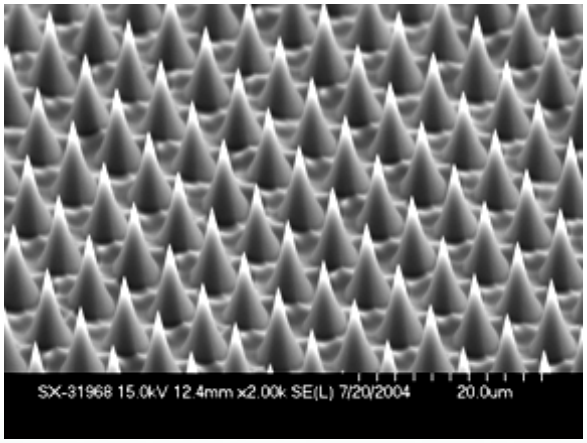
Differential Etching

- Glasses in composite etch at different rates.
  - May depend on etchant.
- Core etches more slowly than matrix glass.
- Duration of etch is not critical.
- Pattern continues in bulk material.
  - Surface can be easily regenerated if damaged.



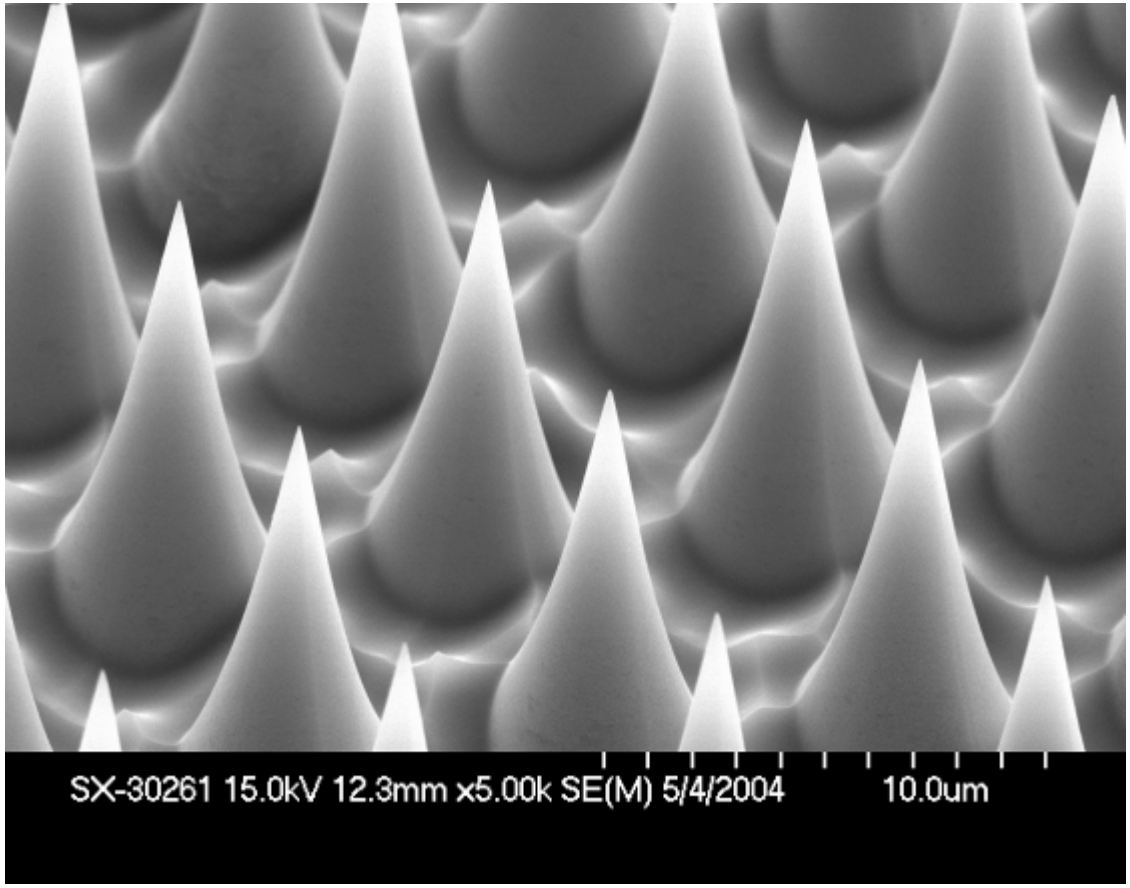






SEM image of cones (looking at ~45 degrees)

> 1 million spikes per cm^2



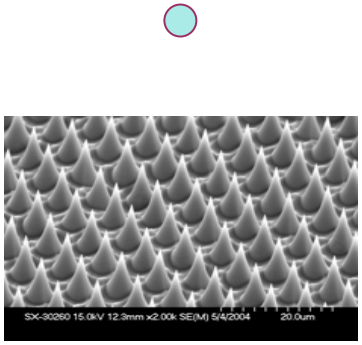
Advantages of this approach

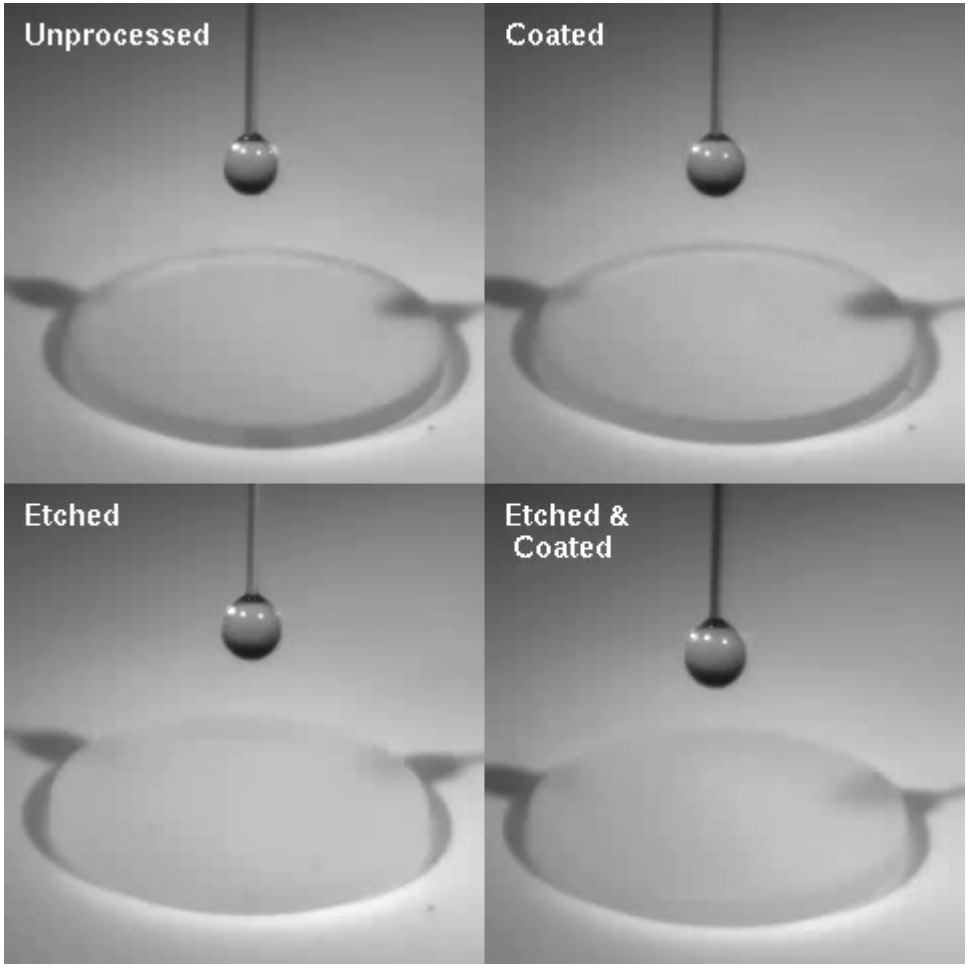
- **Amazing uniformity**
- **No photolithography required**
- **No vacuum processing required**
- **Can use environmentally and biomedically friendly glass**
- **Scalable**
- **Inexpensive material and processing equipment**
- **Elegantly simple process**
- **Robust**

Water Drop on Glass Movies

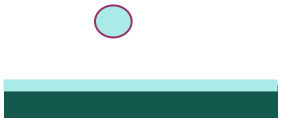
"hydrophilic"

"Super-hydrophilic"

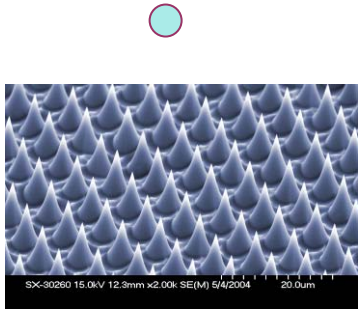




"hydrophobic"

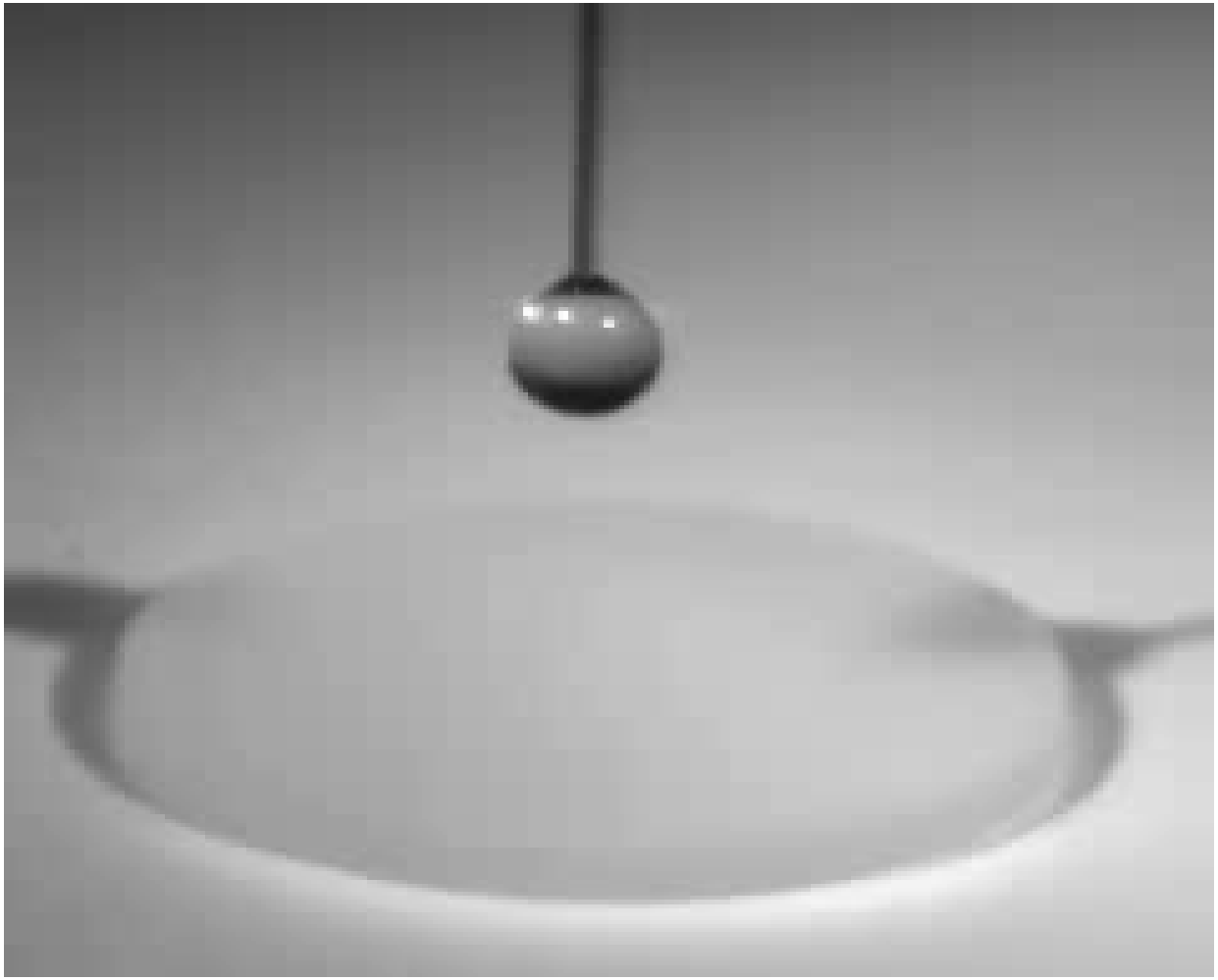


"Super-hydrophobic"

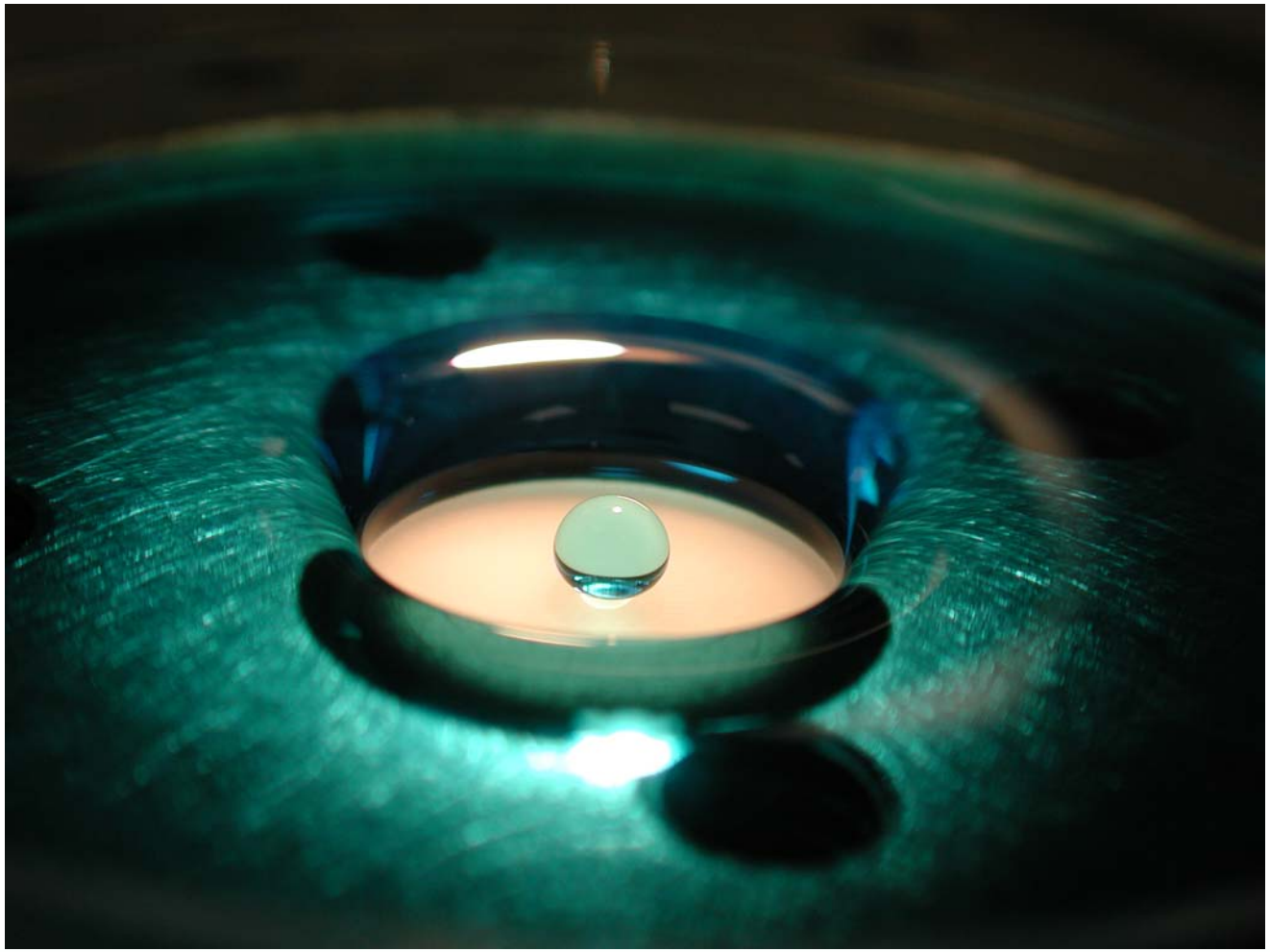


Nanostructure amplifies surface property.

Water Drop Movies



Moses Effect

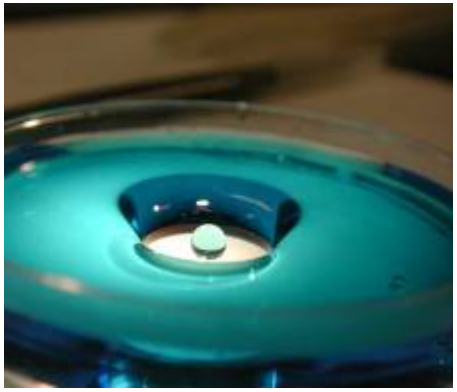


Moses Effect Movie

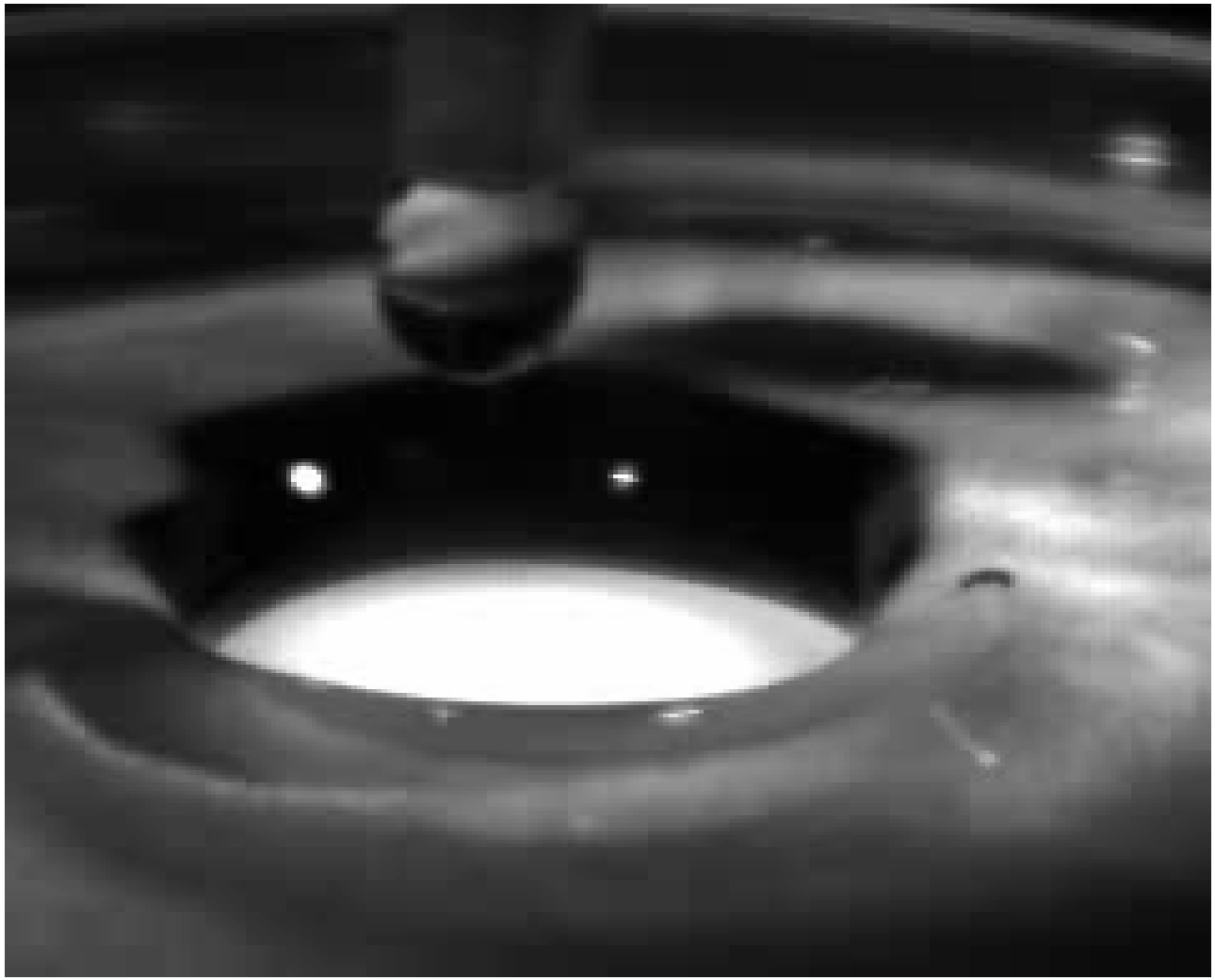
Coated and etched wafer

Surrounded by colored water

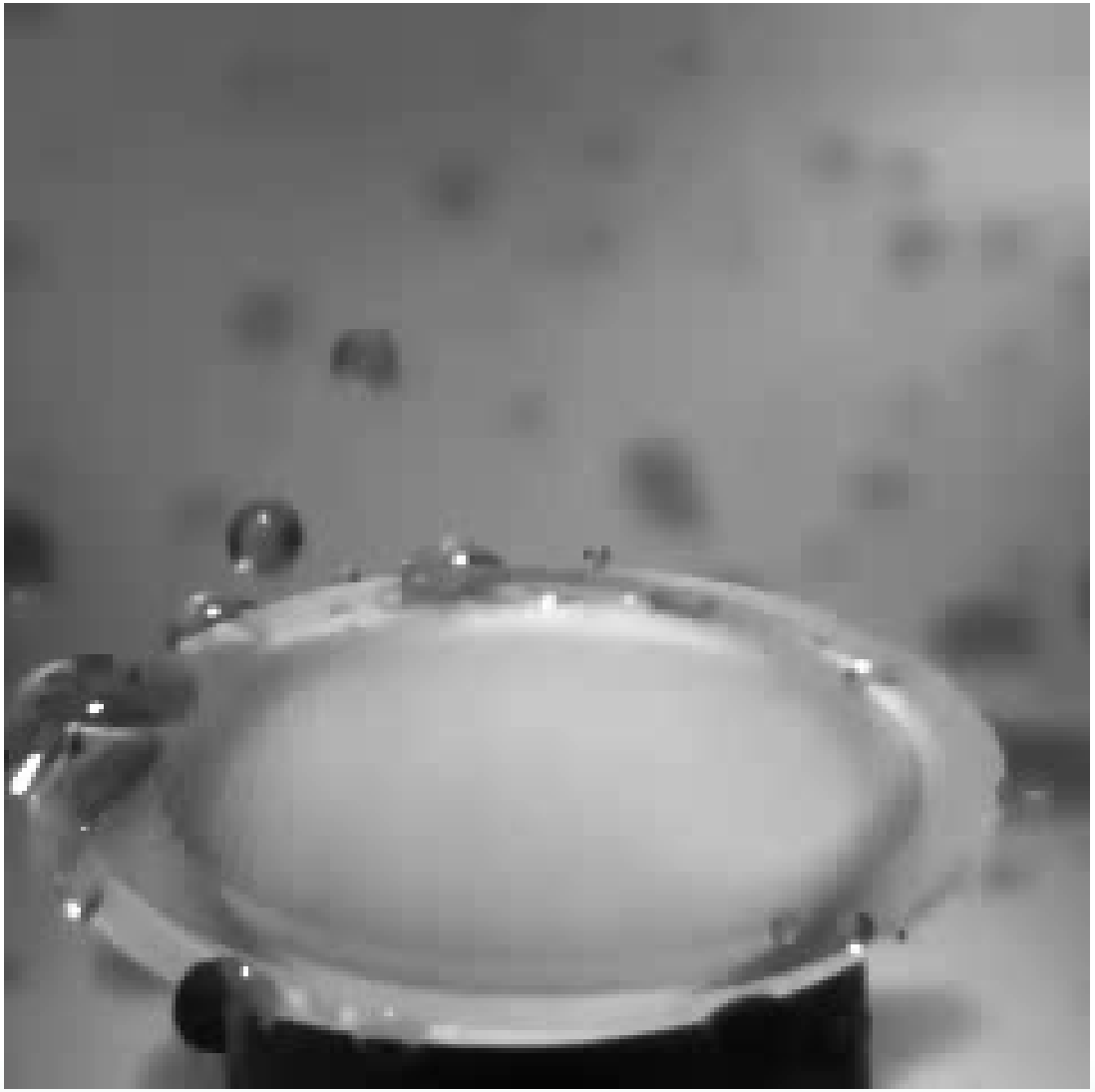
"super-hydrophobic"



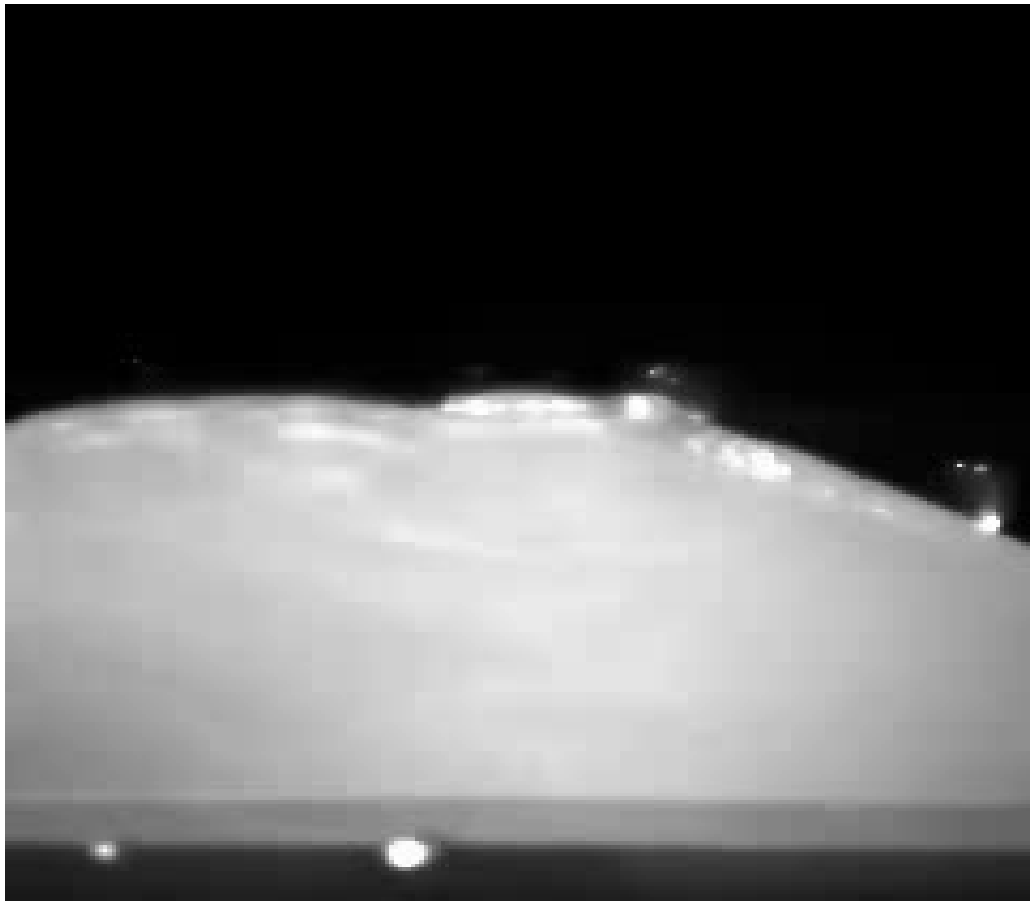
- **Air column over material.**
- **Surface tension holds back water.**
- **Air column is revived by adding air.**
- **Surface was never wet!**



High Velocity Water Drop Movie



Stream of Water Demonstration



Self Cleaning Demonstration

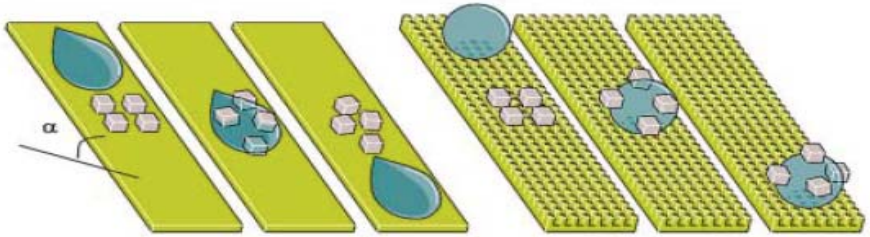
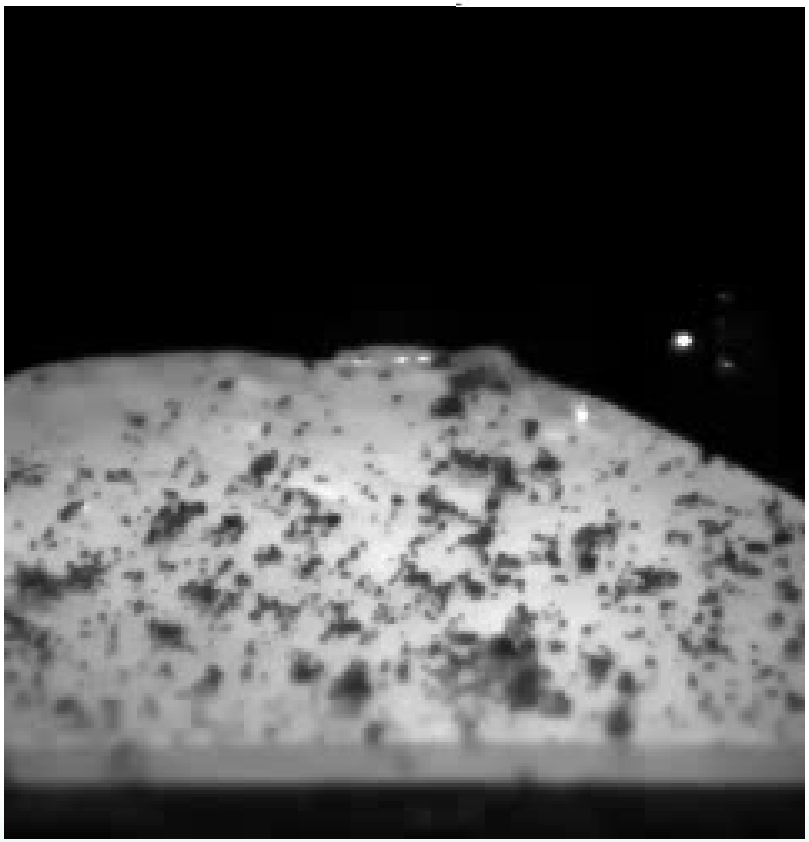
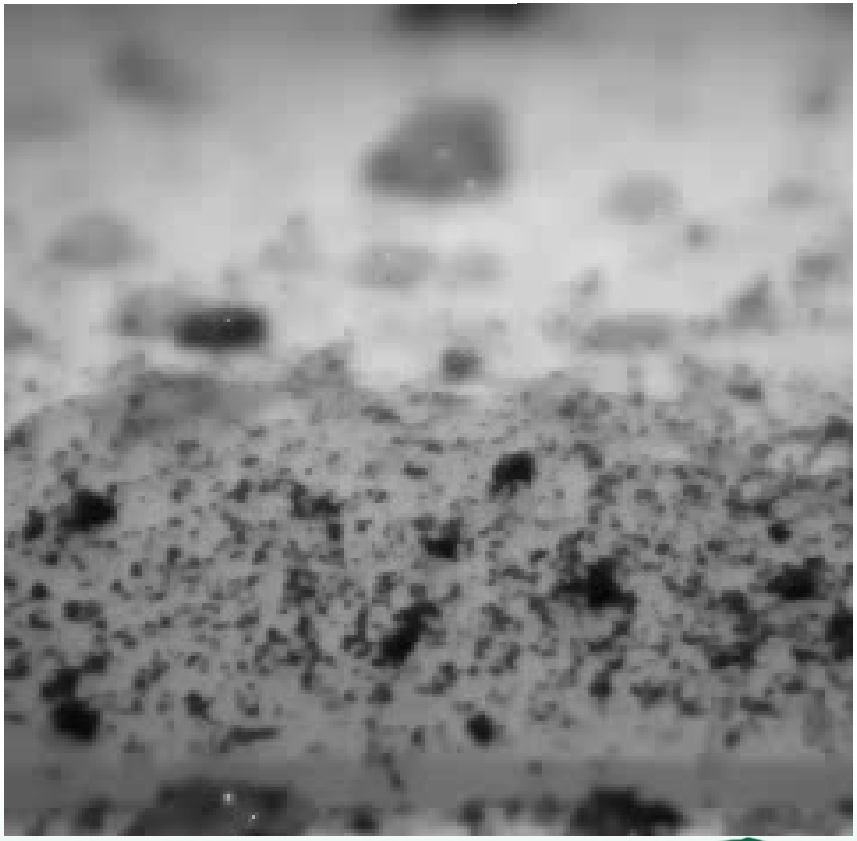


Fig. 4
Surface roughness and selfcleaning by rinsing with water.



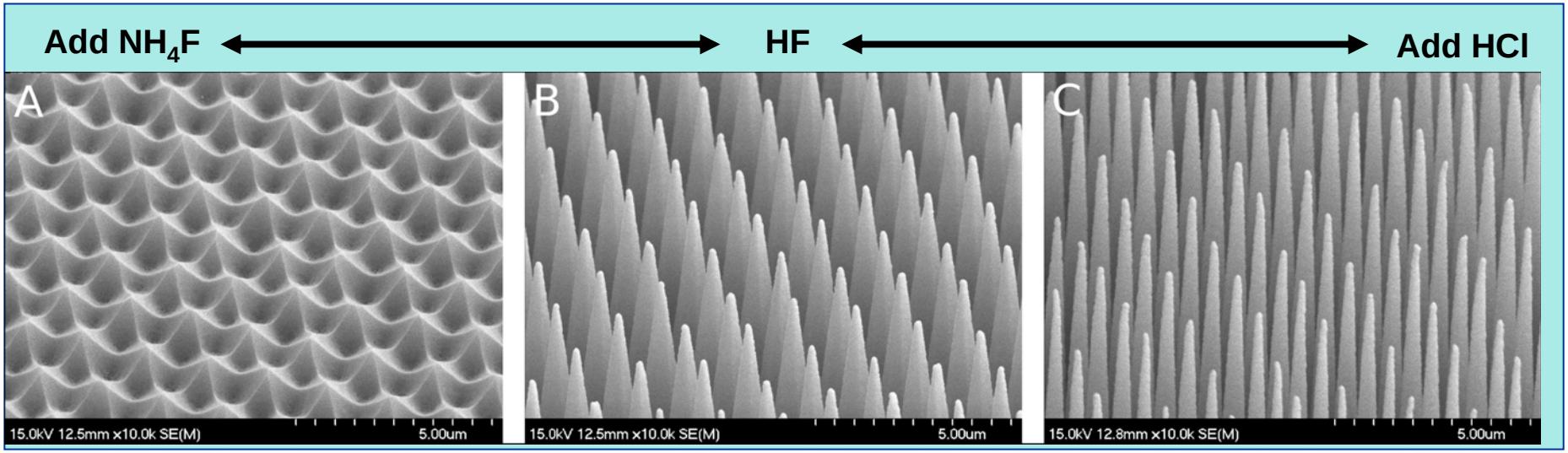


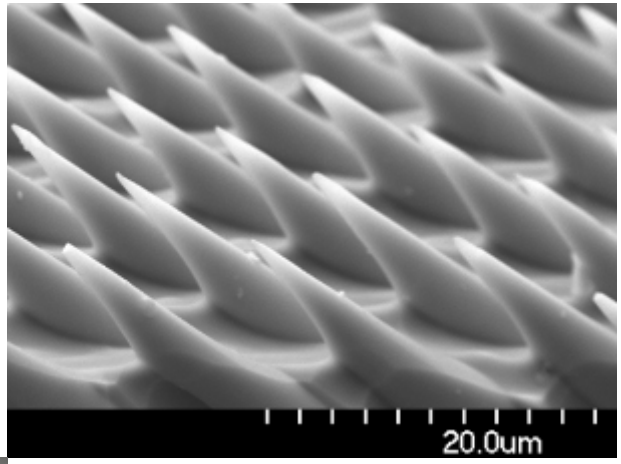
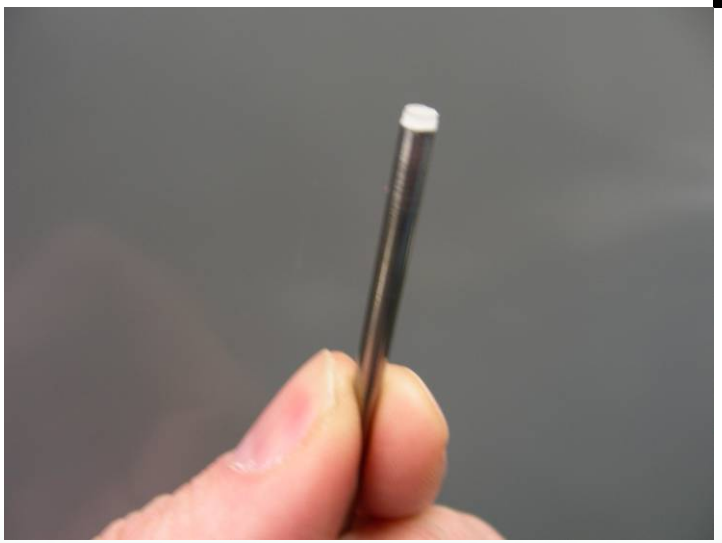
A word about this fabrication process:

- **Using this fabrication method we can control:**
  - **The cone array pitch**
  - **We can vary the array pitch from location to location**
  - **The cone size (i.e. fill factor)**
  - **Aspect ratio (base length vs. height)**
  - **We can insert holes along with the cones**
  - **Cones can be angled**
  - **Optical properties**
  - **Doping properties**

Tunable Etching Contrast

- **Additional mechanism for controlling features: Tuning the etching contrast through the etchant chemistry.**
- **Etch contrast depends on [HF], [HF_2^-], [H^+].**
- **Tune concentrations by adding NH_4F or HCl.**
  - **Dramatic tuning in borosilicate glasses from 1:1 to 30:1.**
  - **Roughness from limited solubility of $(NH_4)_2SiF_6$ with NH_4F.**
    - **Large etchant volume and agitation required.**



Tools for Minimally Invasive Surgery

- **Nano-Velcro for Retinal Eye Surgery**
- **Tools for Endoscopic Surgery**
  - **Easy to integrate**
    - **Optics**
    - **Tubes**
    - **Conductors**