Electrowetting on Super-hydrophobic Surfaces

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Acknowledgements
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Previous Studies of Super-H + EWOD

Torkkeli *et al* (2001) VTT Labs

- Superhydrophobic surface + electrowetting
- Droplet transportation – force reduction

  Sprayed AKD, Sprayed Teflon

  Lithographic pillars + plasma polymerisation

  Lowest V for continuous transport - 124 V rms (64 μm insulator)

  Maximum speed 1 cm/s

- Problem – Drop sticks at higher voltages

Krupenkin *et al* (2004) Bell Labs

- Studying transitions from rolling ball to sticky drop/“film”

  Nanostructured surfaces

Overview of Remainder of Talk

Wetting and Topography

- Superhydrophobicity
- Roughness & Air Trapping/Liquid Penetration
- Our Materials & Methods

  1. Lithography
  2. Etching
  3. Electrodeposition
  4. Sol-Gel

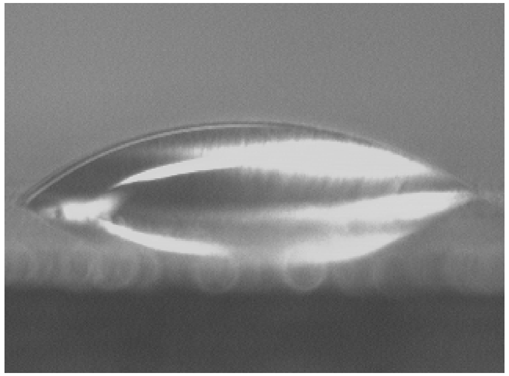
Electrowetting

- Combining with Super/H surfaces

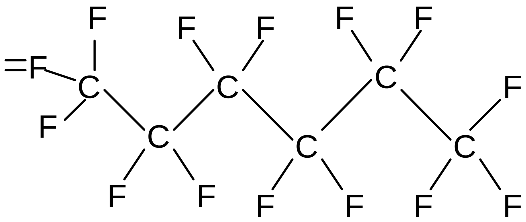
  High Aspect Ratio Patterns

  Wenzel v Cassie-Baxter & Hysteresis

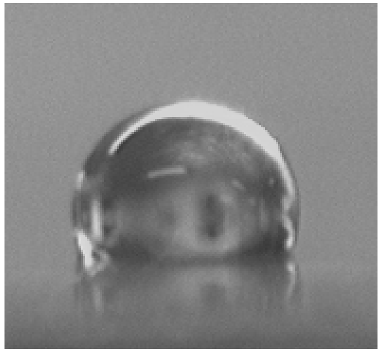
Superhydrophobic Surfaces



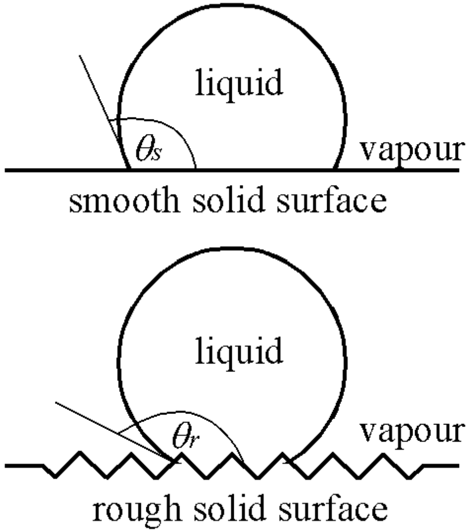
Simple Cu surface



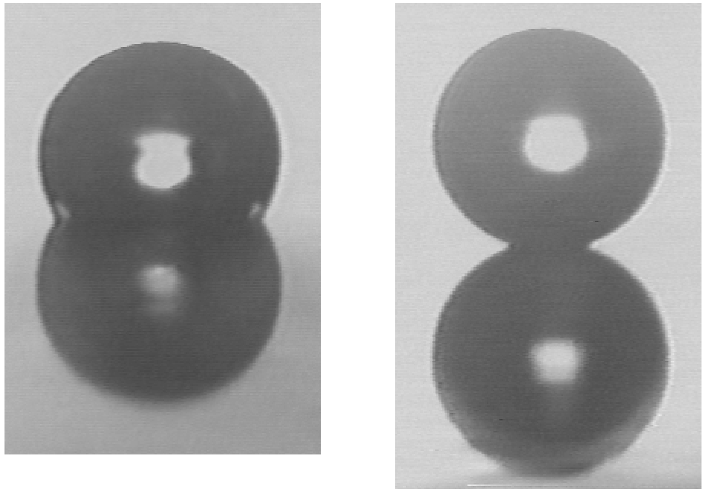
Grangers' molecular chain



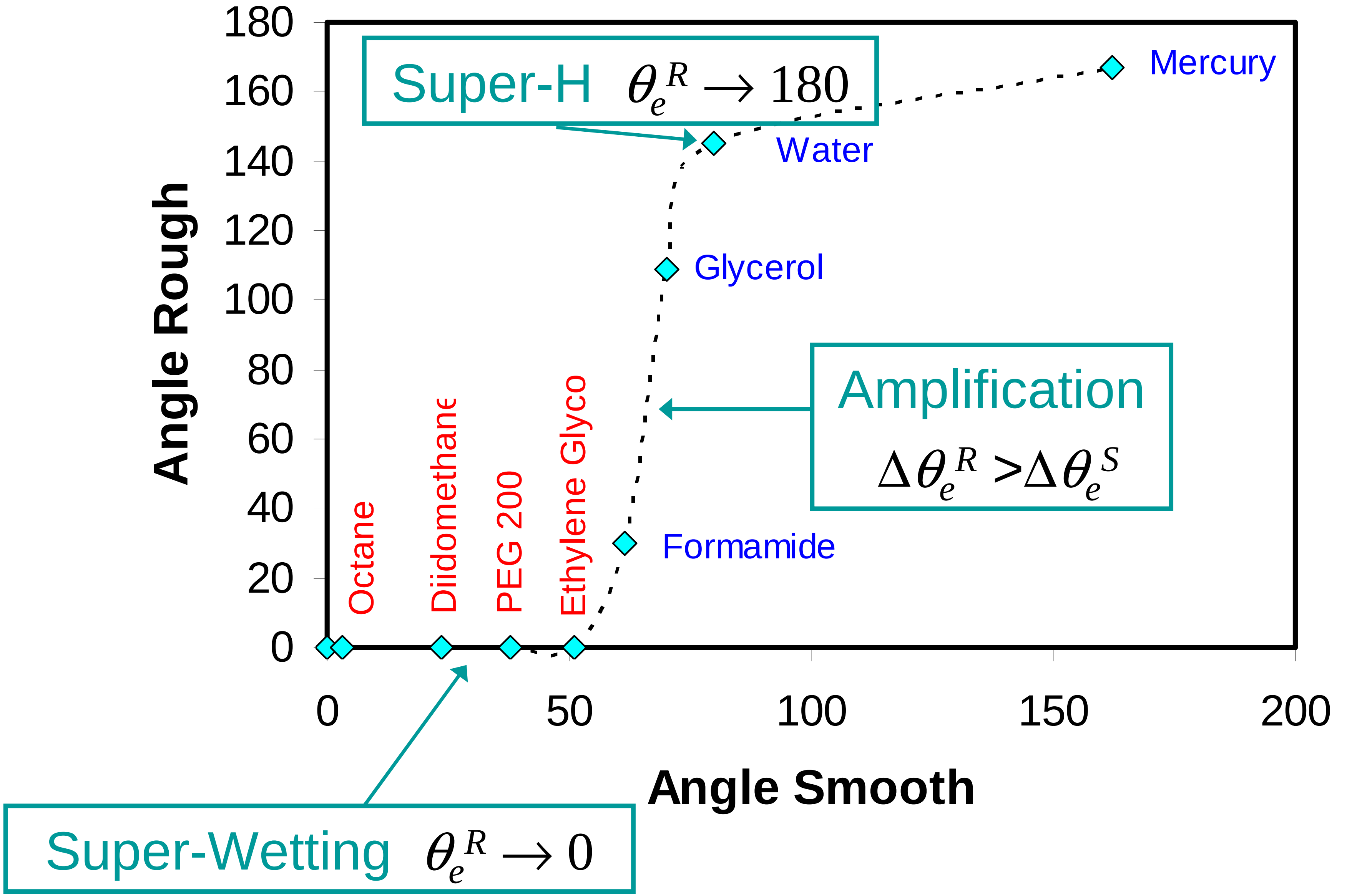
Hydrophobic surface



Water Drop (~ 2 mm)



Different Liquids on a Super-H Surface



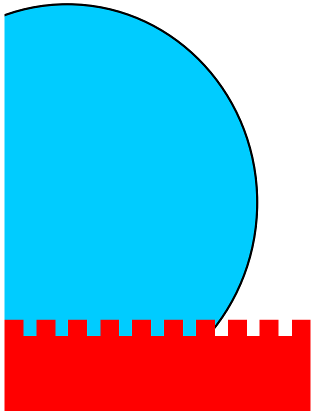
- Pillar Surface - SU-8 photoresist (*D* =15 μm, *L* = 2*D*, *h* = 43 μm)

Wenzel Form of Super-H

Wenzel's Equation

- Based on roughness, *r*

$$\cos\theta_e^W = r\cos\theta_e^S$$



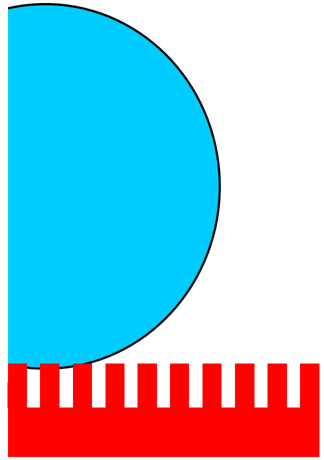
Consequences

- Superhydrophobic when $\cos\theta_e^S \to -1/r$
- Superwetting when $\cos\theta_e^S \to 1/r$
- Amplification in-between $\left(\frac{\Delta\theta_e^W}{\Delta\theta_e^S}\right)_{\theta_e^S} > 1$

Contact Angle Hysteresis

- Super-H with large hysteresis, i.e. "Sticky" surface

Cassie-Baxter Form of Super-H



Cassie-Baxter Equation

- Based on composite air-solid surface, *f*

$$\cos\theta_e^C = f\cos\theta_e^S + (1-f)\cos(180)$$

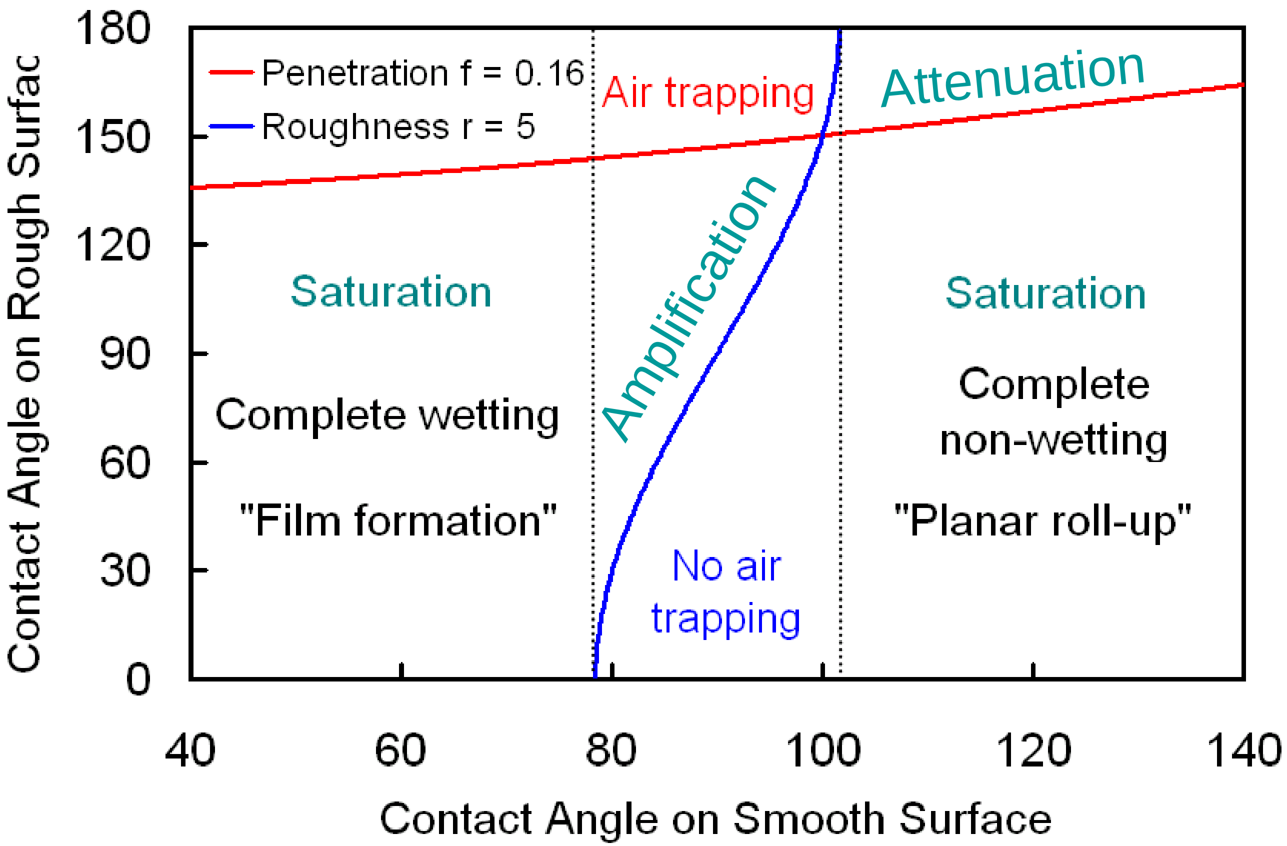
Consequences

- Complete super-H of 180º only reached when θ_e^s=180º
- Easier to obtain >150º than with Wenzel
- Transition to super-H promoted by sharp edges on features

Contact Angle Hysteresis

- Low hysteresis: "Slippy" rather than "sticky" surface

Effect of Topography - Equilibrium



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Super-hydrophobic

Air "trapping" ("Skating case")

⇒ most existing examples

Pressure

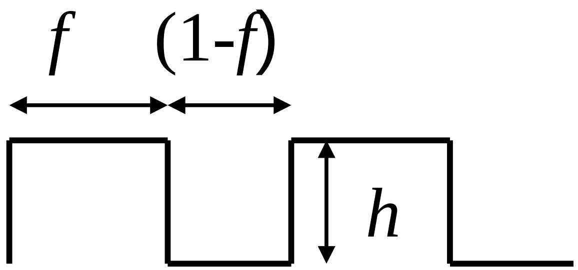
⇒ air trapping disappears

Effect of Topography - Air "Trapping"

- Liquid Penetration into Texture

  f=solid fraction, (1- *f*)=liquid fraction

  r = roughness



Liquid film penetrates when:

Critical angle θ_c is in 0 to 90º range

$$\cos\theta_e^S > \frac{1-f}{r-f} = \cos\theta_c$$

- "Skating" Drop

  Liquid bridges from one peak to next

$$\cos\theta_e^R = -1 + f\left(\cos\theta_e^S + 1\right)$$

- Air "Trapping" and Roughness

  Sinusoidal model gives critical roughness for installation of horizontal contact line

$$r_c = 1 + \frac{\tan^2\theta_e^S}{4}$$

  (e.g. for 120º, r_c=1.75 $\Rightarrow$ jump in θ_e^R to > 150º)

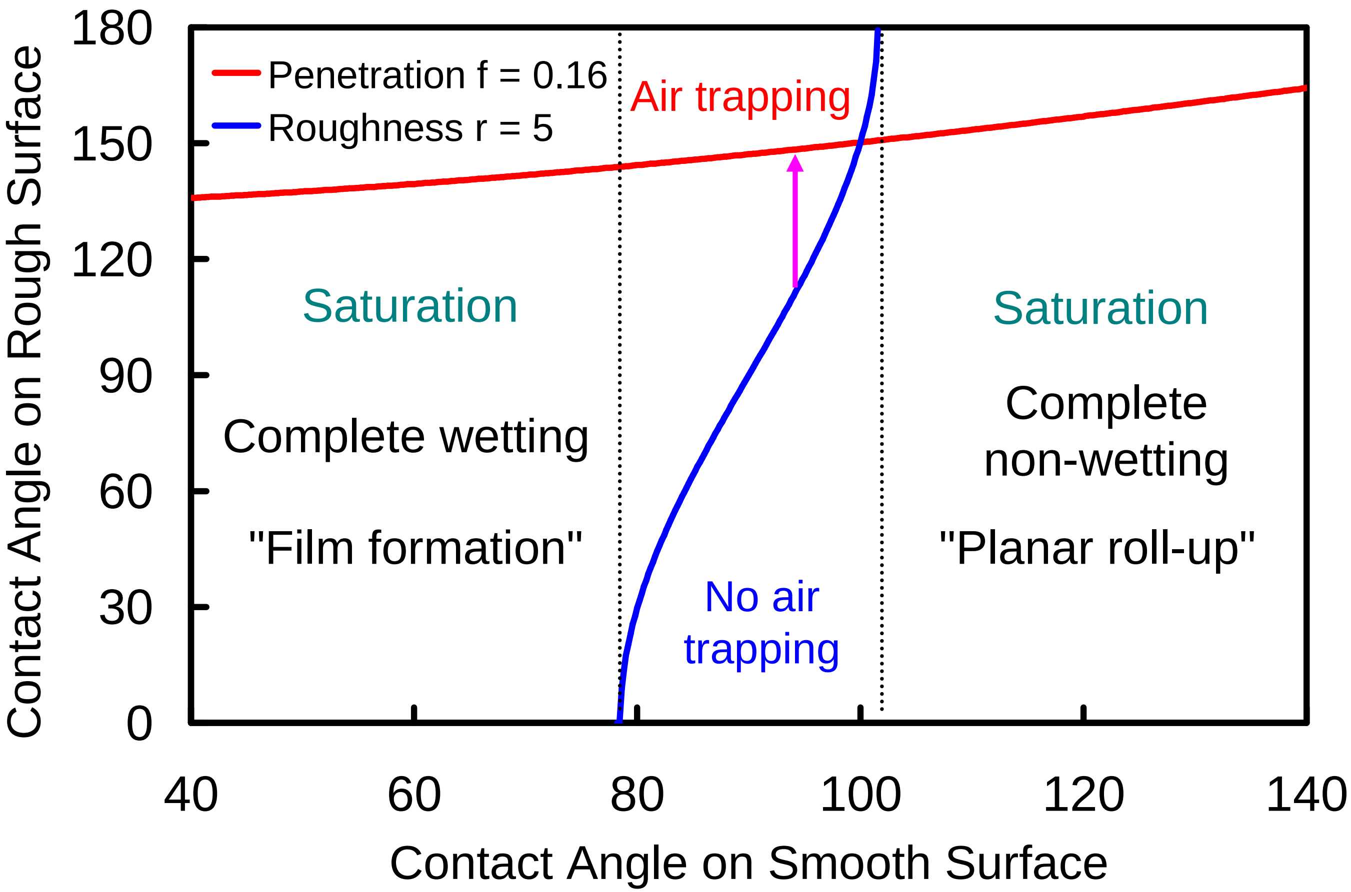
  Also, sharp features promote "skating"

Effect of Topography - Aspect Ratio

- Air Trapping and Aspect Ratio

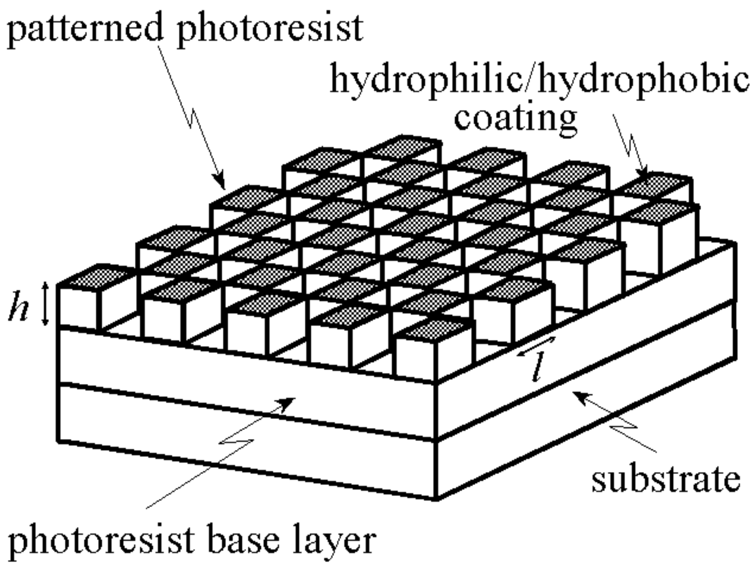
  As roughness increases system jumps from blue to red curve

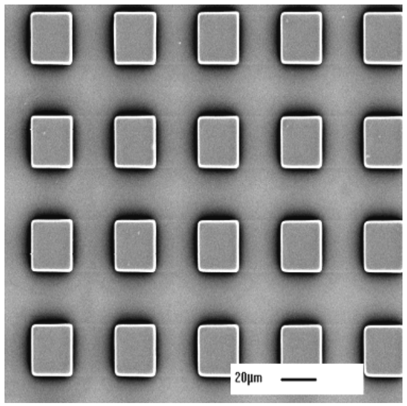
  Alternatively, for given roughness, jump occurs as smooth surface angle increases



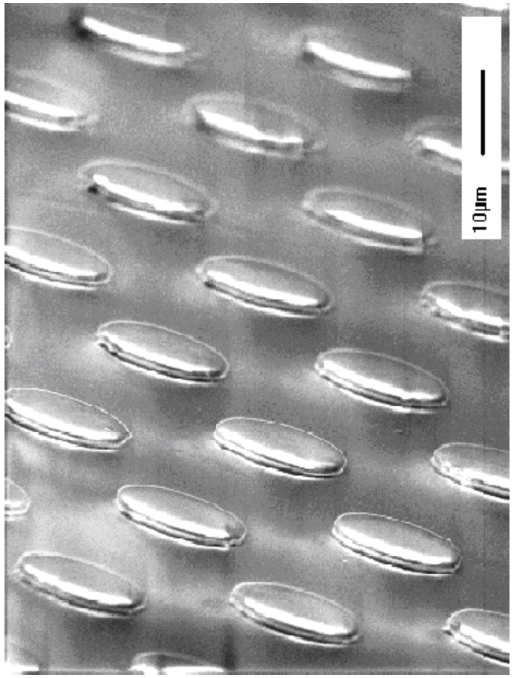
1. Lithographic Structures

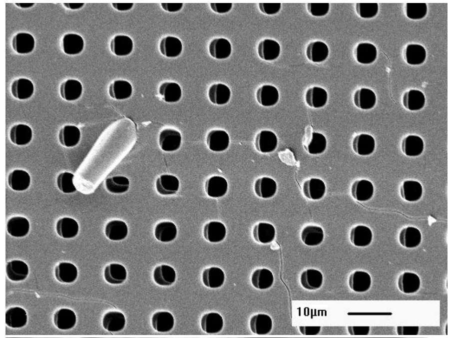
Principles

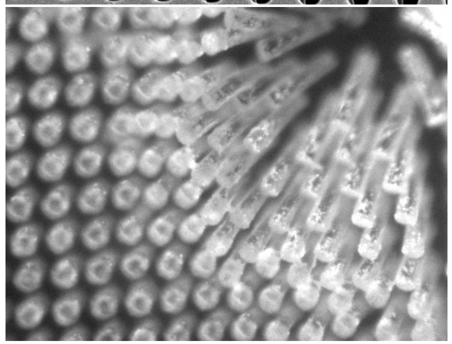


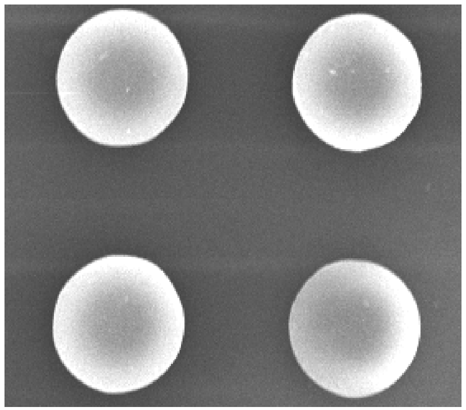


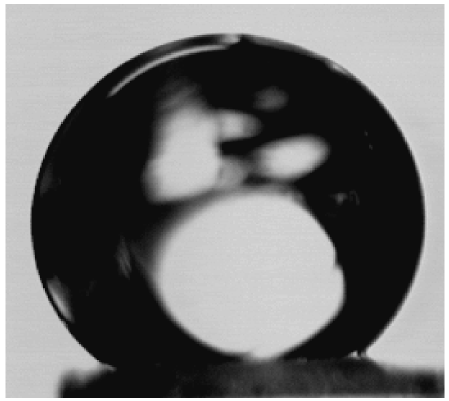
Practice





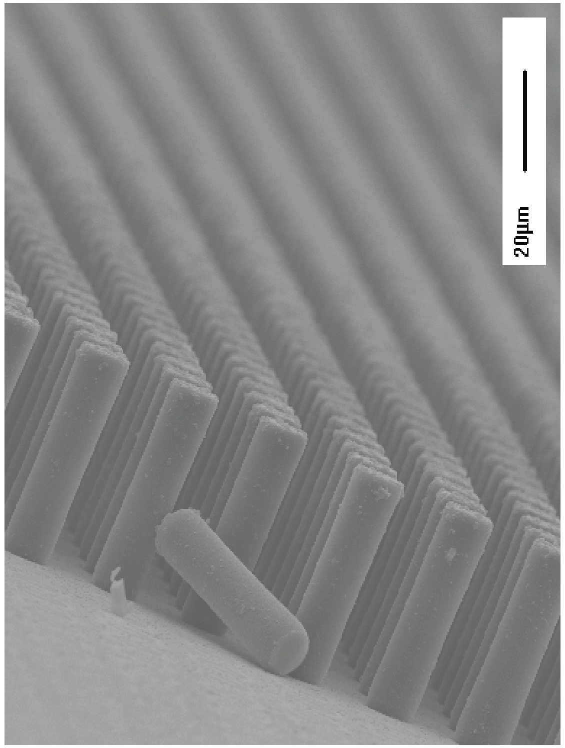


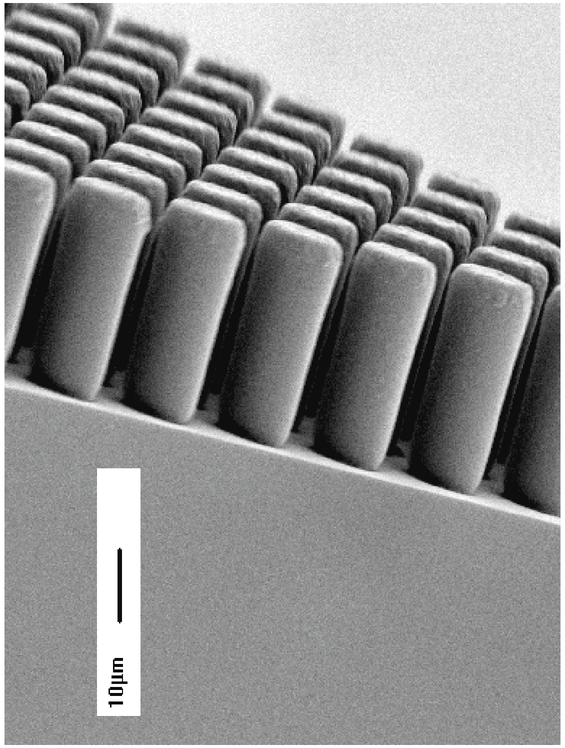




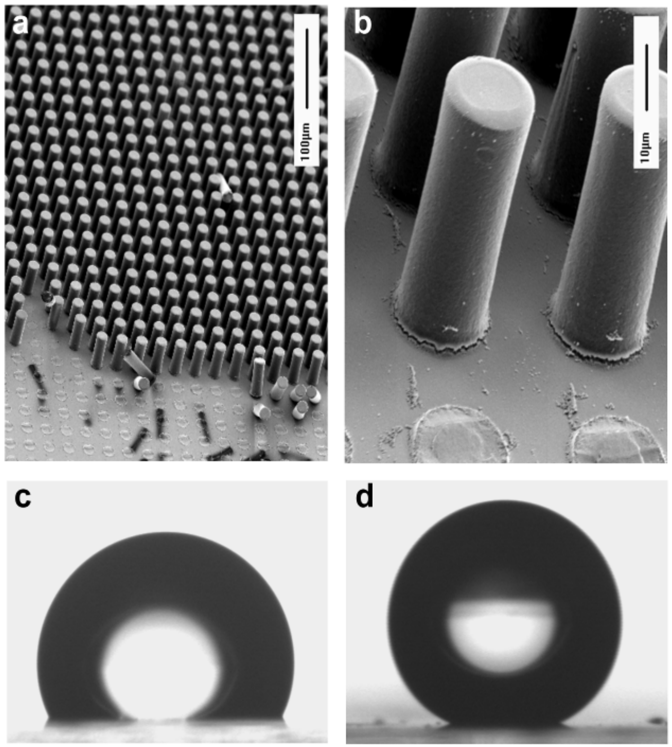
SU-8 Photoresist Pillars

SEMs of Pillars





Effect on Water



Tall structures to 45-75 µm

smooth and straight walls

Aspect ratios up to ~ 7

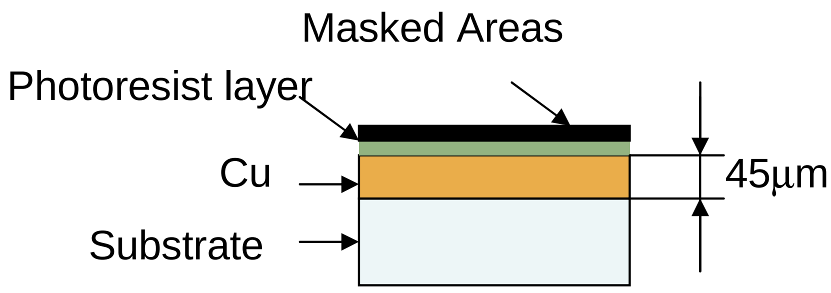
a), b) Pillars *D*=15 µm, *L* = 2*D*

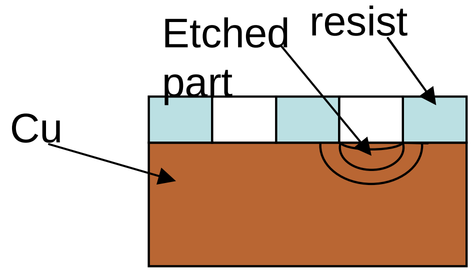
c) Flat and hydrophobic

d) Tall and hydrophobic

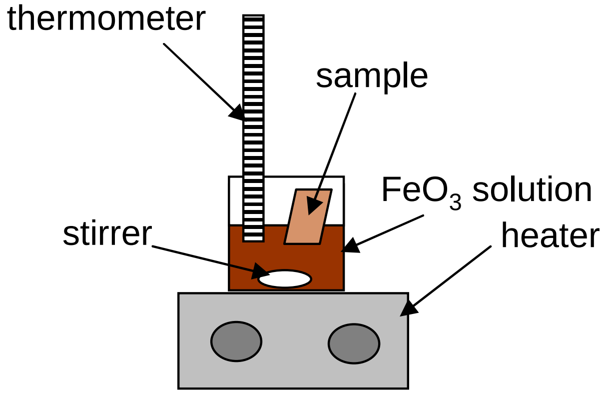
2. Etching of Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

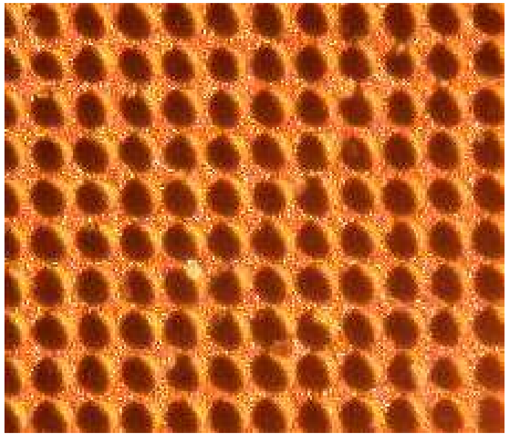




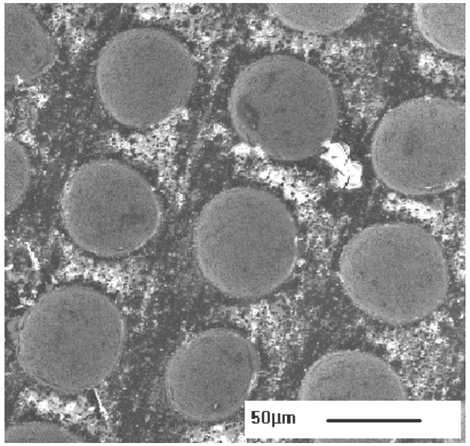
hole growth



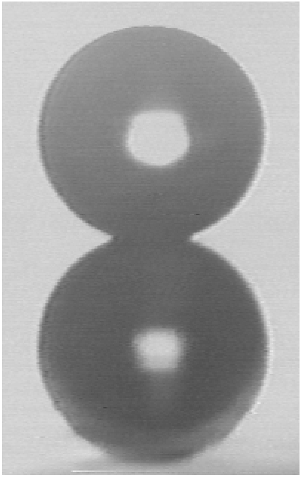
Setup of the copper etching



Copper sample etched through a 30 µm pattern



SEM picture of the pattern of the etched copper surface

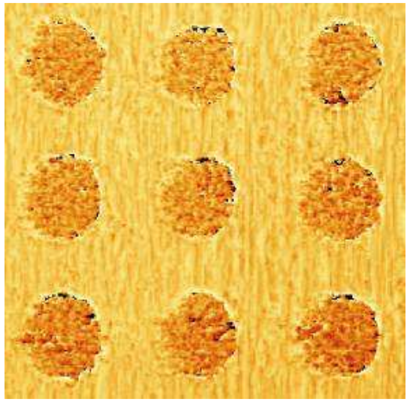


Water drop and reflection on an etched copper surface

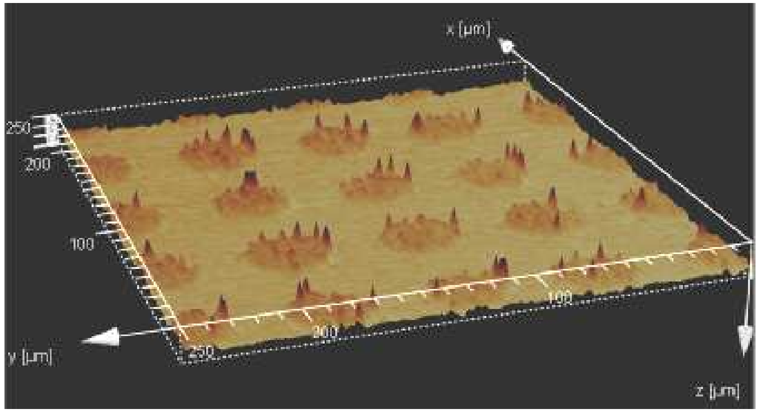
3. Electrodeposited Textured Surfaces

- Electroplating through a mask – acid copper bath

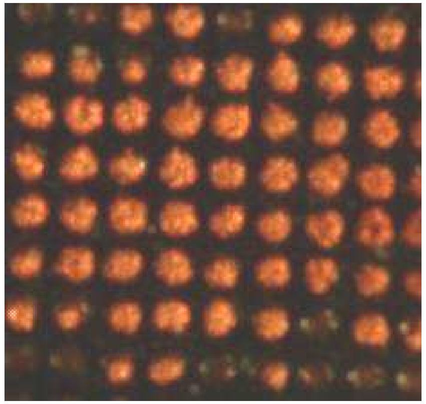
Base Cu electroplated surface



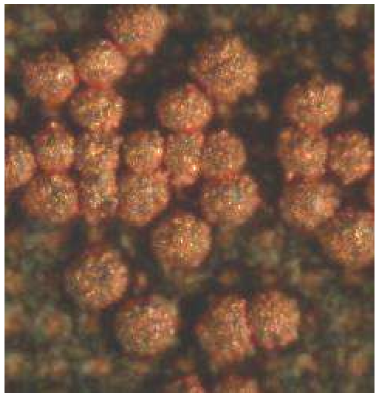
Confocal image of a 30μm textured electroplated Cu



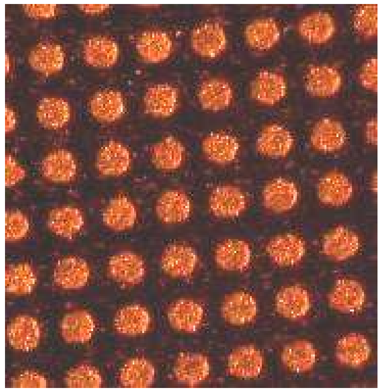
3D view of a electroplated copper sample



Deposition time too short



Deposition time too long - mushrooms touch

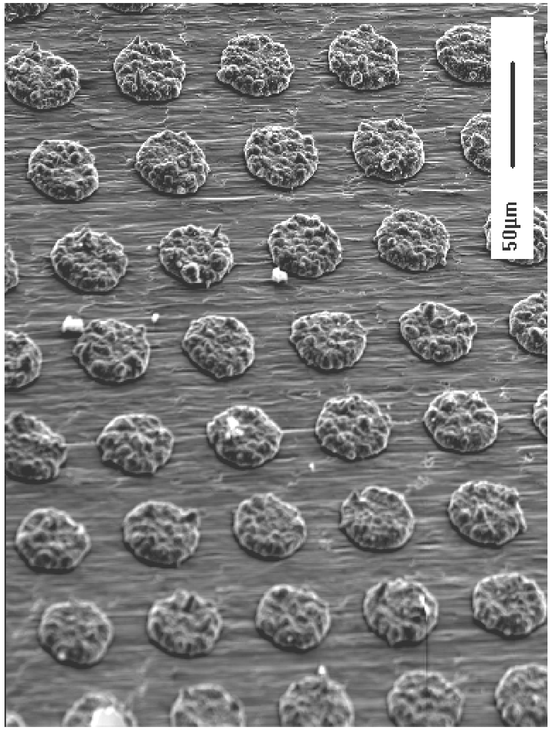


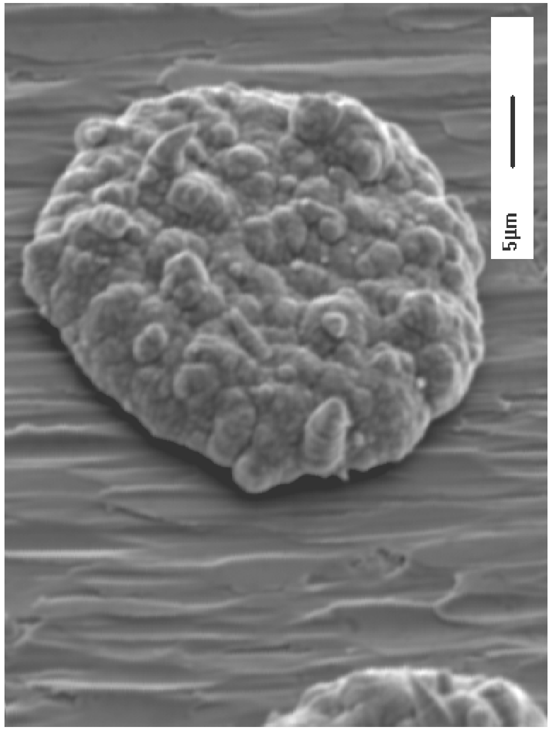
Deposition time OK

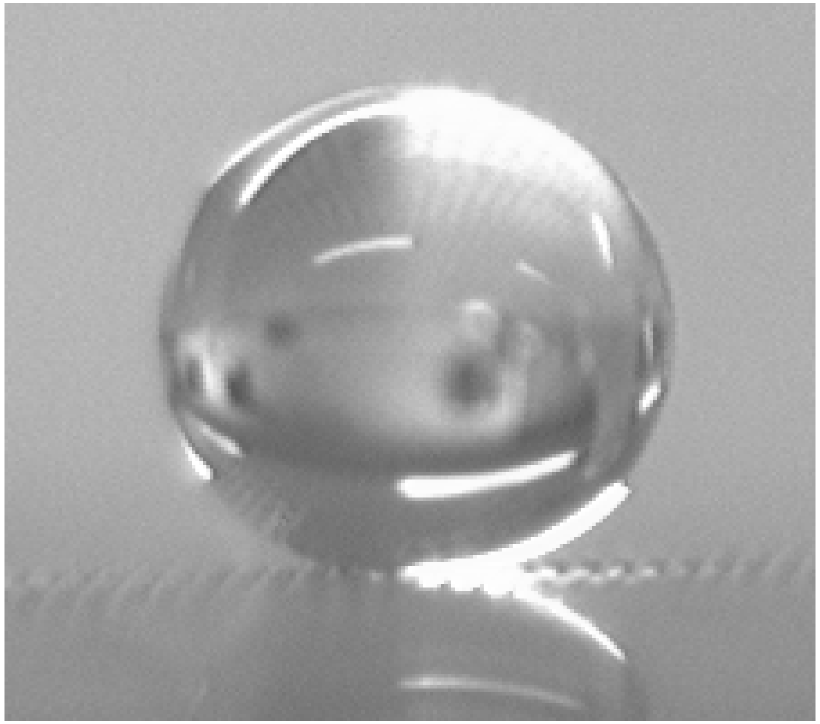
Electrodeposited Surfaces

"Chocolate Chip Cookies"

Water Drop







Contact angles of 160-180º

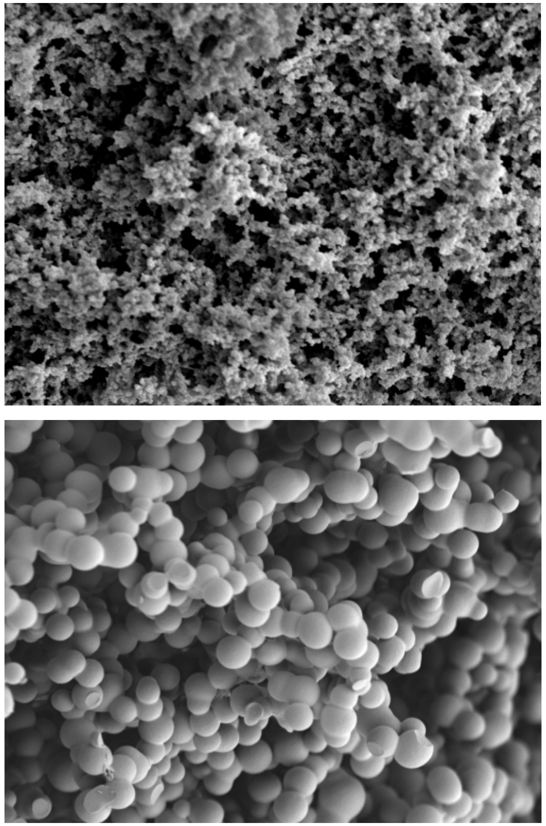
Electroplating can achieve 180º even without texturing

– use current to obtain a fractally rough surface

4. Organo-Silica Sol-Gel Foam Surfaces

- Sol-Gel = preparation of oxide materials from solution
  - Usually organosilicon compounds hydrolysed to form intermediates
  - Partially & fully hydrolysed silicates can link together
  - Solvent creates porous structure unless complete phase separation occurs
  - Hydroxide and organic groups usually present until thermally treated
  - MTEOS sol-gel using 1.1 M & 2.2 M ammonia

- Advantages
  - Intrinsically hydrophobic
  - Hydrophobic to hydrophilic transition by heating
  - Pore size controllable nano- to macro-porous
  - Contact angle hysteresis as low as 4^{o}



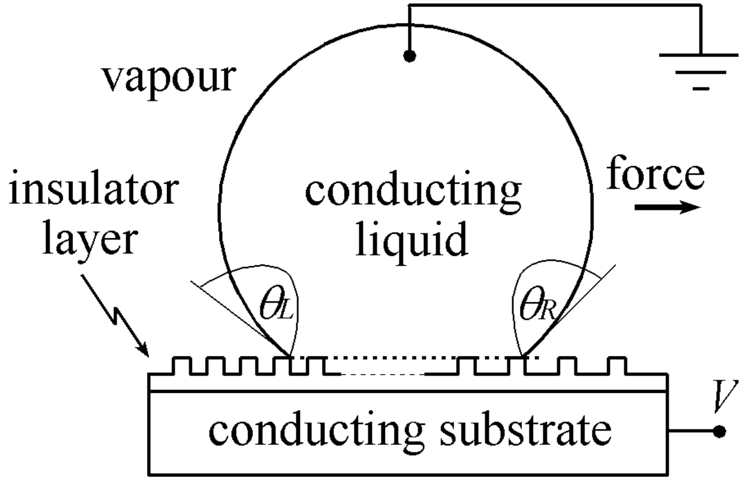
10 µm

Electrowetting on Superhydrophobic Surfaces

- Electrowetting Principle
  - Voltage Reduces Contact Angle

$$\cos\theta_e(V) = \cos\theta_e(0) + CV^2/2\gamma_{LV}$$

  - Difference in angles at edge of droplet reflects an actuating force



- Thin Insulator
  - Capacitance ∝ 1/insulator thickness
  - Thin insulator for lower voltages

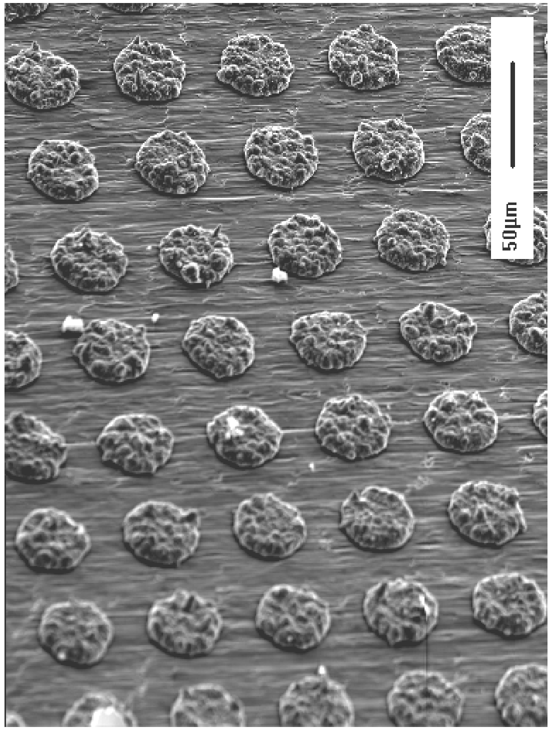
But Super-H via patterning insulator needs high aspect ratio

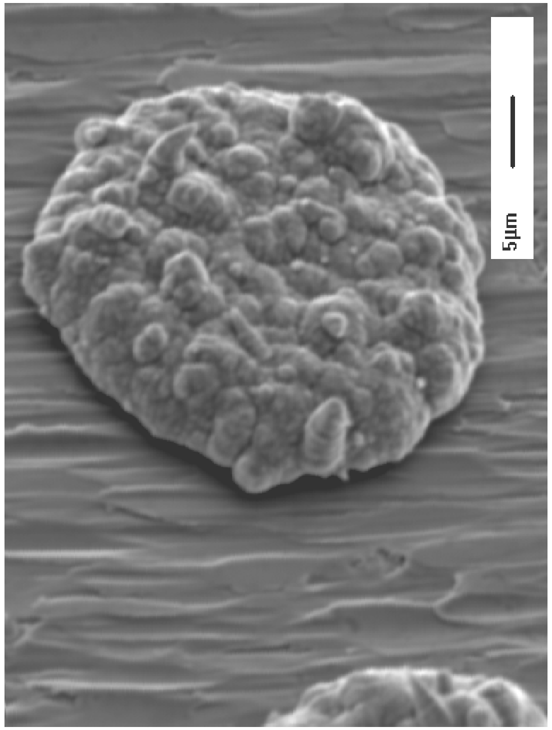
- Electrowetting
  - Applying voltage causes electrocapillary pressure into surface texture (Wenzel)

But low hysteresis requires Cassie-Baxter

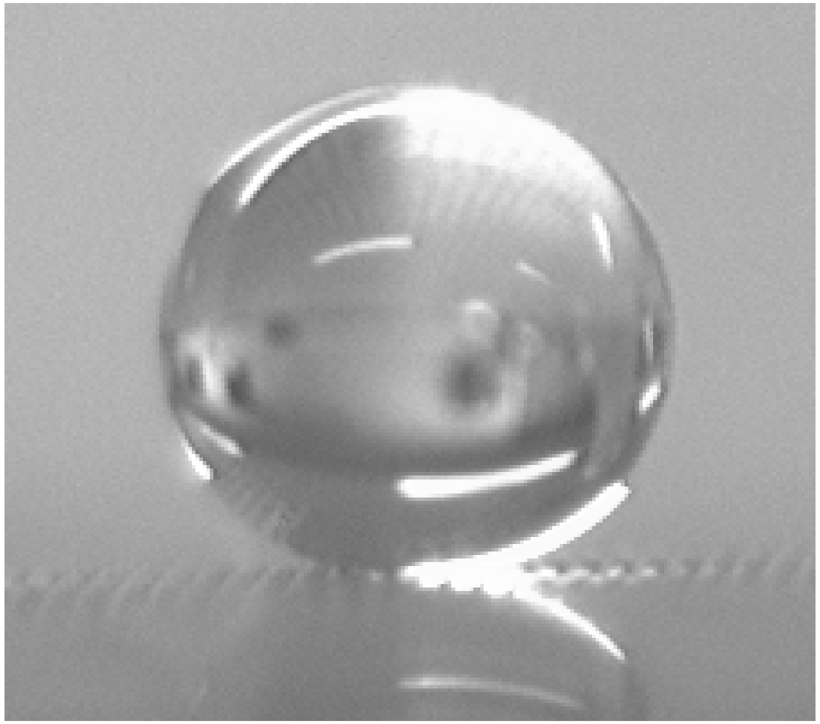
Electrodeposited Surfaces

“Chocolate Chip Cookies”





Water Drop



Contact angles of 160-180º

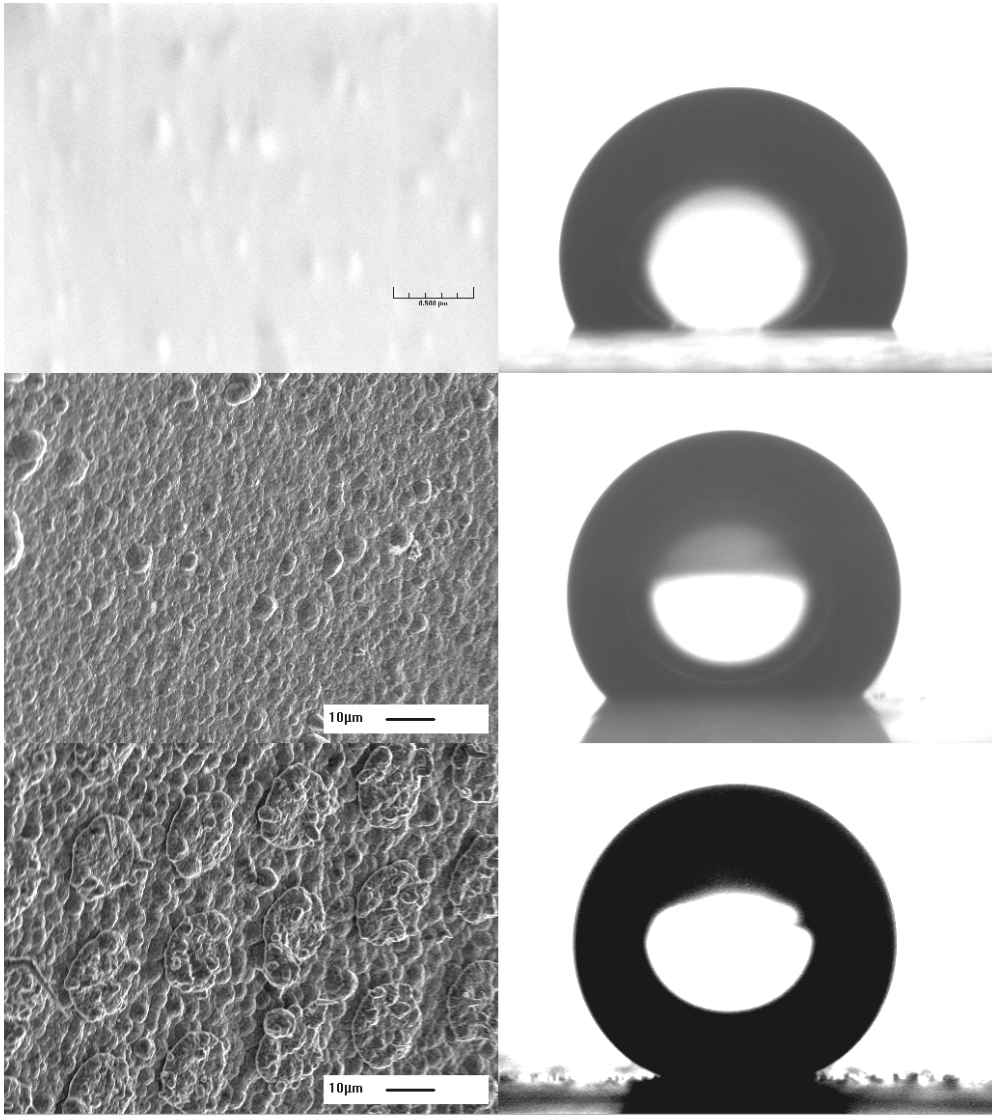
Electroplating can achieve 180º even without texturing

– use current to obtain a fractally rough surface

Overcoming Conflicting Requirements?

- Smooth and Hydrophobised 115°
- Slightly Rough and Hydrophobised 136°
- Slightly Rough, Textured and Hydrophobised 160°

Two Length Scales is extremely effective



Future Work on Electrowetting

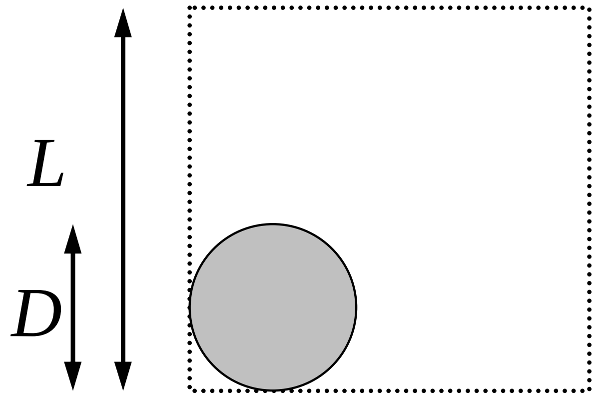
1. Pillar surfaces with/without base photoresist
2. Low aspect ratio texture with top roughness
3. Hysteresis $\Rightarrow$ rough base layer with pillars on top
4. Characterise slippy-to-sticky transition
5. Pattern shape variation to investigate effect on local electric field

The End

Texture Example

Cylindrical Pillars

- Diameter *D*, box side *L*, height *h*



$$f = \frac{\pi D^2}{4L^2} \qquad r = 1 + \frac{\pi}{4}\left(\frac{h}{D}\right)$$

Example

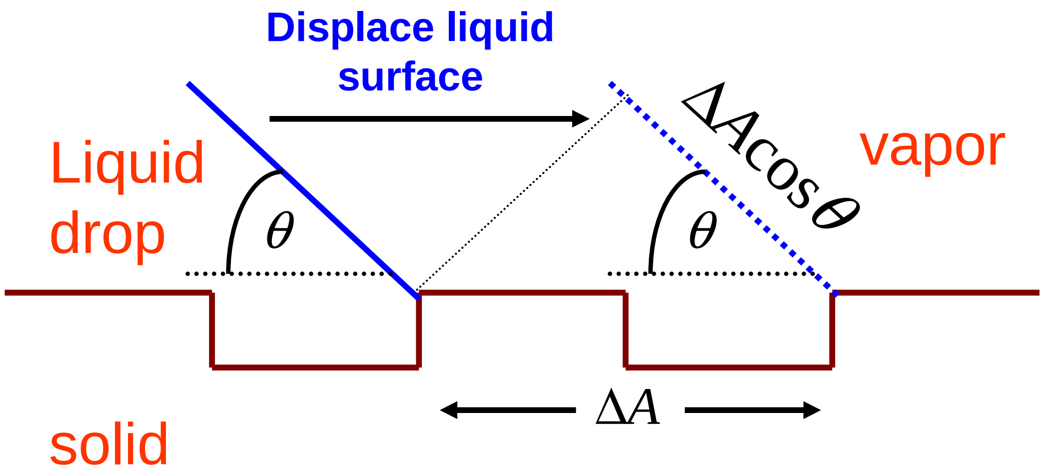
L=2D f=0.196 $\theta_e^s=115^o$ $\theta_e^c=152^o$

D=15 µm *h*=21 µm before $\theta_e^w=152^o$

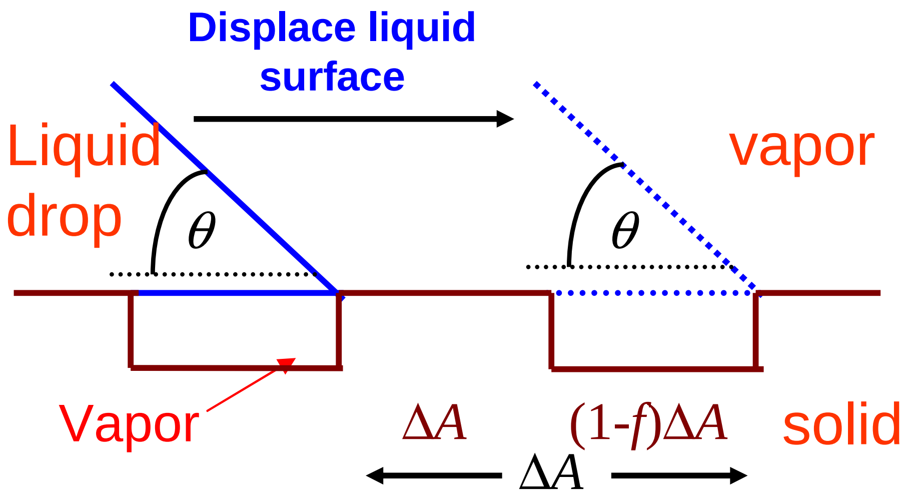
D=5 µm *h*=21/3=7 µm before $\theta_e^w=152^o$

Wetting and Topography

Complete Penetration



Air "Trapping"



Surface Free Energy Changes

$$\Delta F = (\gamma_{SL} - \gamma_{SV})r\Delta A + \gamma_{LV}\cos\theta\Delta A$$

$$\Delta F = (\gamma_{SL} - \gamma_{SV}) f\Delta A + \gamma_{LV}(1-f)\Delta A + \gamma_{LV}\cos\theta\Delta A$$

Wenzel's Eqn

$$\cos\theta_e^R = r(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = r\cos\theta_e^s$$

$r = \Delta A_{true}/\Delta A$ = roughness factor

Modified (Cassie Style) Eqn

$$\cos\theta_e^R = f\cos\theta_e^s - (1-f)$$

f = fraction of "rough" surface wet