Lithographic and Electrochemical Approaches to Super-hydrophobic Surfaces

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Acknowledgements
EPSRC Grant GR/R02184/01

Overview

1. Superhydrophobic Surfaces
    - Etching - Cu surfaces 20-50 μm
    - Electrodeposition - Fractal, textured, 2 length scales
    - Lithography - designer surfaces 2-50 μm

      - Wenzel to Cassie transition
2. Characterisation
    - Contact angles (Kruss DSA10)
    - Electron and confocal microscopy
3. Measurements and Theory
    - Static angles
    - Dynamic angles

Superhydrophobicity – Wenzel Form

Wenzel's Equation

- Based on roughness, *r*

$$\cos\theta_e^w = r\cos\theta_e^s$$

Consequences

- Superhydrophobic when

$$\theta_e^s > \cos^{-1}(-1/r)$$

- Superwetting when

$$\theta_e^s < \cos^{-1}(1/r)$$

- Amplification in-between

$$\left(\frac{\Delta\theta_e^w}{\Delta\theta_e^s}\right)_{\theta_e^s} > 1$$

- Super-H with large hysteresis

  i.e. "Sticky" surface

Superhydrophobicity – Cassie Form

Cassie-Baxter Equation

- Based on composite air-solid surface, φ_s

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

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

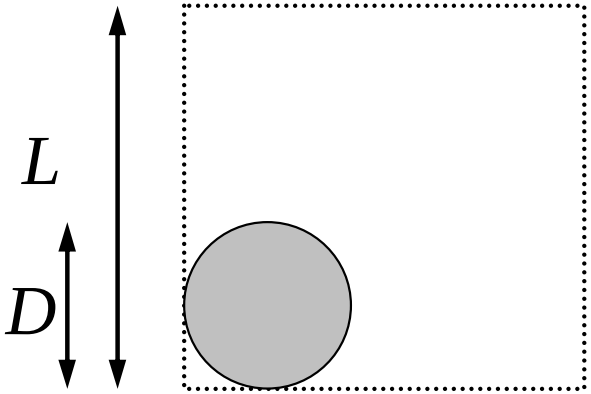
Cassie = Wenzel

$$\cos\theta_e^s = \frac{\varphi_s - 1}{r - \varphi_s} \quad \text{or} \quad r = \frac{-1 + \varphi_s\left(\cos\theta_e^s + 1\right)}{\cos\theta_e^s}$$

Texture Example

Circular Pillars

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



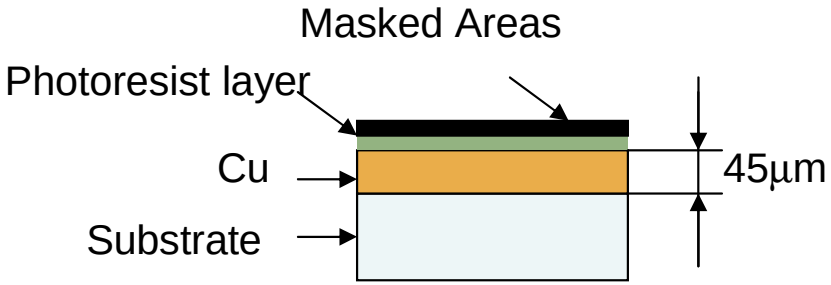
$$\varphi_s = \frac{\pi D^2}{4L^2} \qquad r = 1 + \frac{\pi}{4}\left(\frac{h}{D}\right)$$

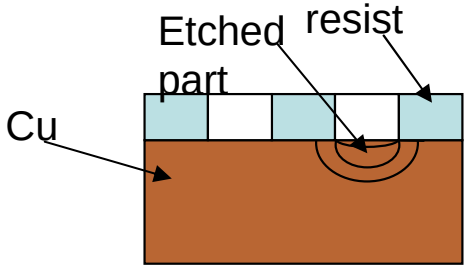
Example

L=2D	φ_s=0.196	θ_e^s=115°	θ_e^c=152°
D=15 µm	*h*=21 µm		before θ_e^w=152°
D=5 µm	*h*=21/3=7 µm		before θ_e^w=152°

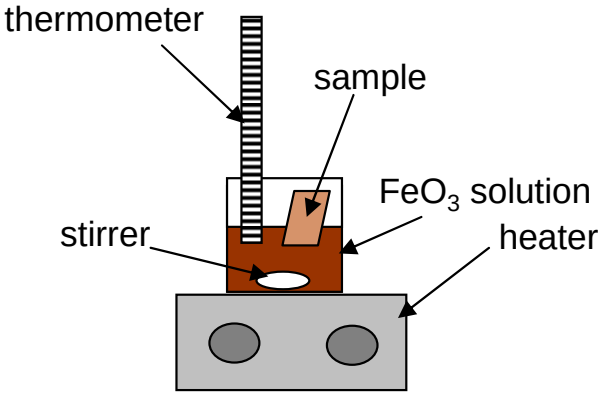
Etching of Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

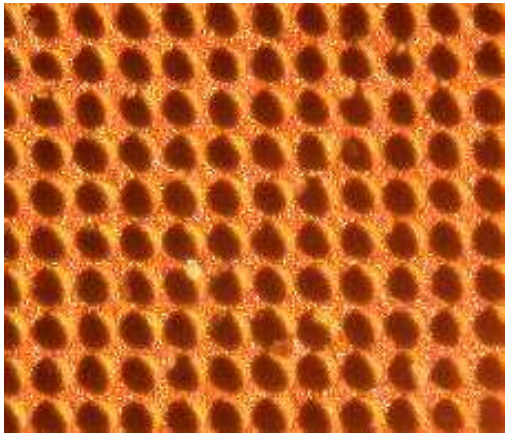




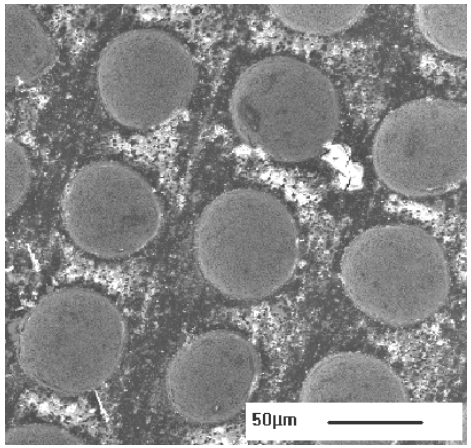
hole growth



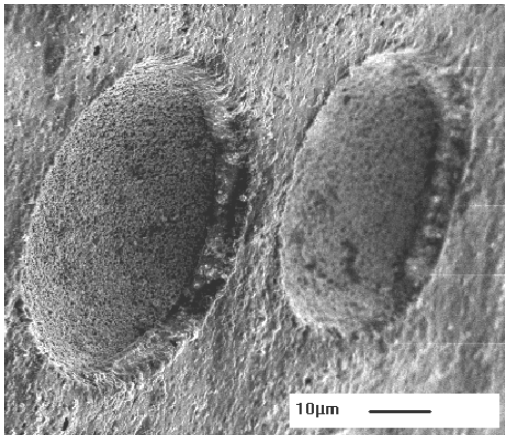
Setup of the copper etching



Copper sample etched through a 30 µm pattern

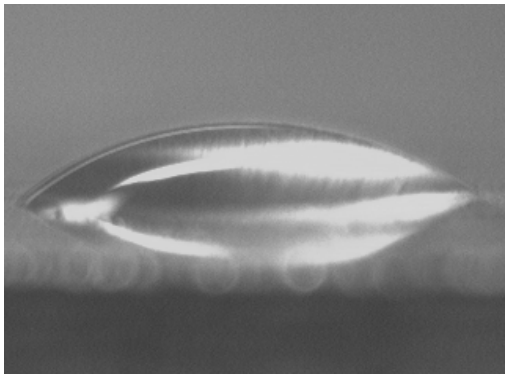


SEM picture of the pattern of the etched copper surface

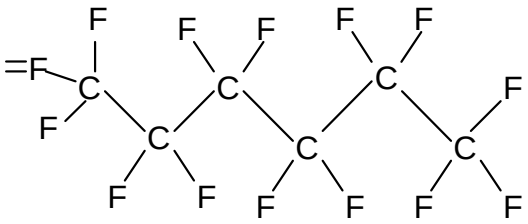


SEM picture of an etched hole in copper sample

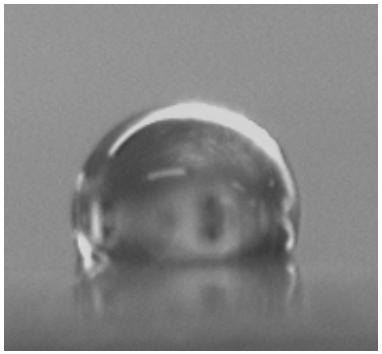
Hydrophobised Etched Copper Surfaces



Simple Cu surface



Grangers' molecular chain



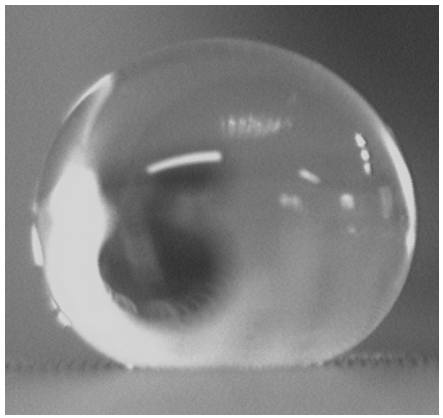
Hydrophobic surface

30 μm and 40 μm Patterns

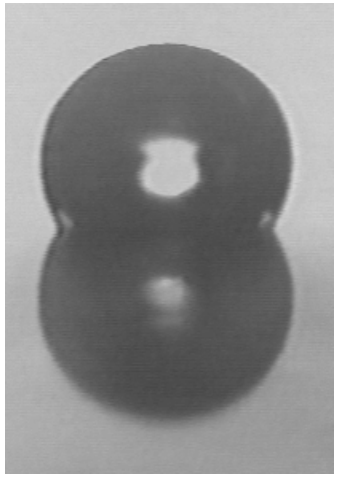
Typically 152º to 158º

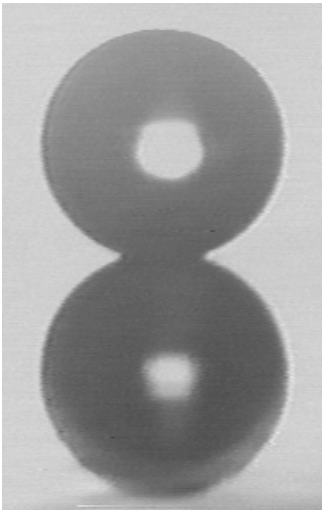
But have achieved far higher

- over-etch to create peaks



40μm pattern with Grangers





Acknowledgement

Gregoire Chabrol

Electroplated Copper Surfaces

- Copper acid bath

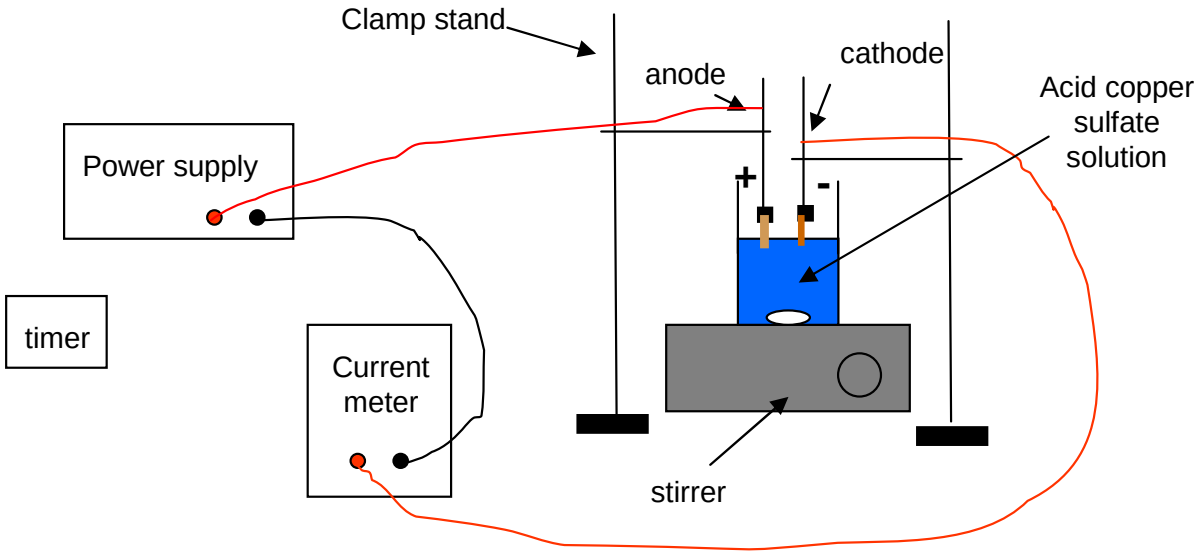
  Copper sulphate ($CuSO_4$) and sulphuric acid (H_2SO_4)

Current density

Slightly rough to highly rough (Fractal)

Masking

Mask and grow pillars in Cu on Cu

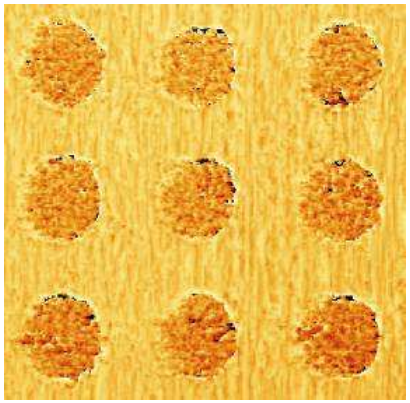


Setup for the copper plating

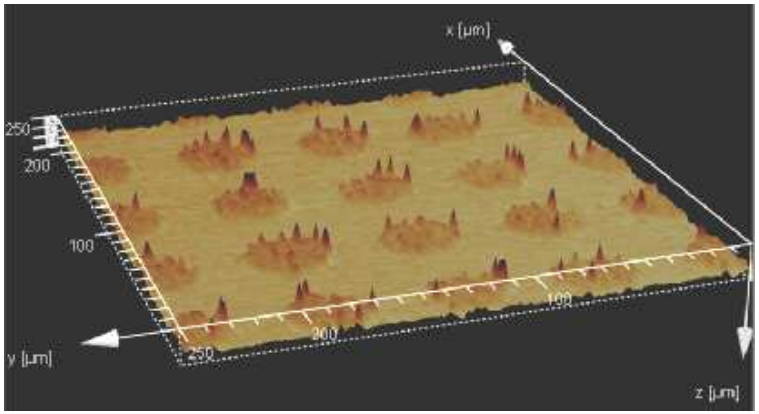
Electroplated Textured Surfaces

- Electroplating through a mask

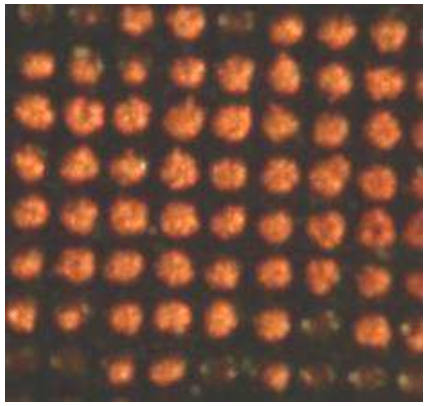
Base Cu electroplated surface



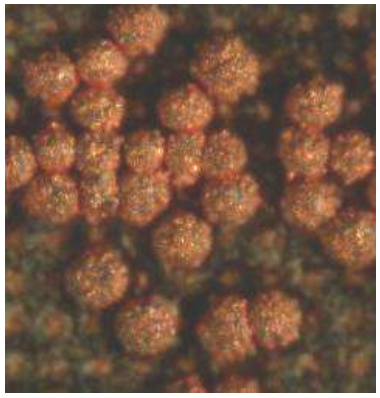
Confocal image of a 30µm textured electroplated Cu



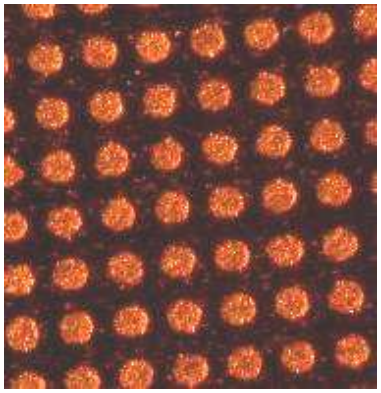
3D view of a electroplated copper sample



Deposition time too short



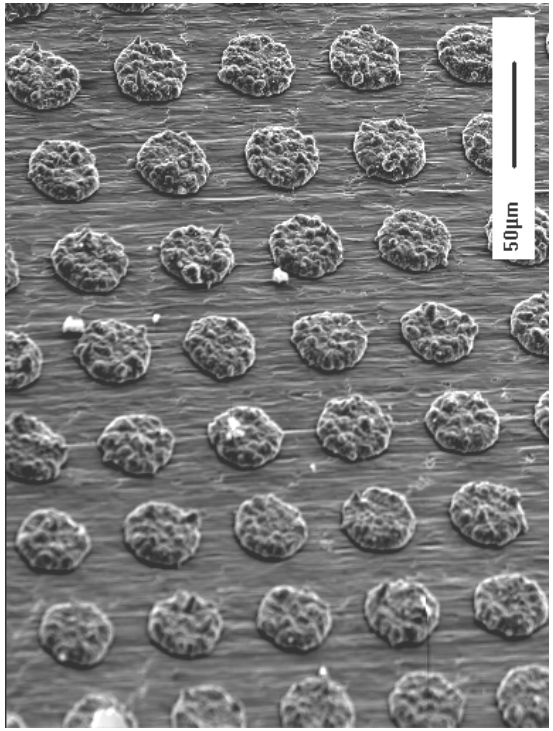
Deposition time too long - mushrooms touch

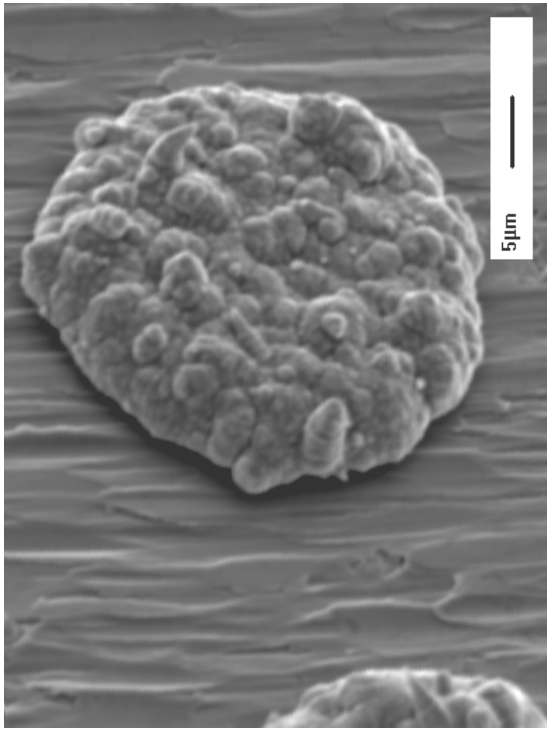


Deposition time OK

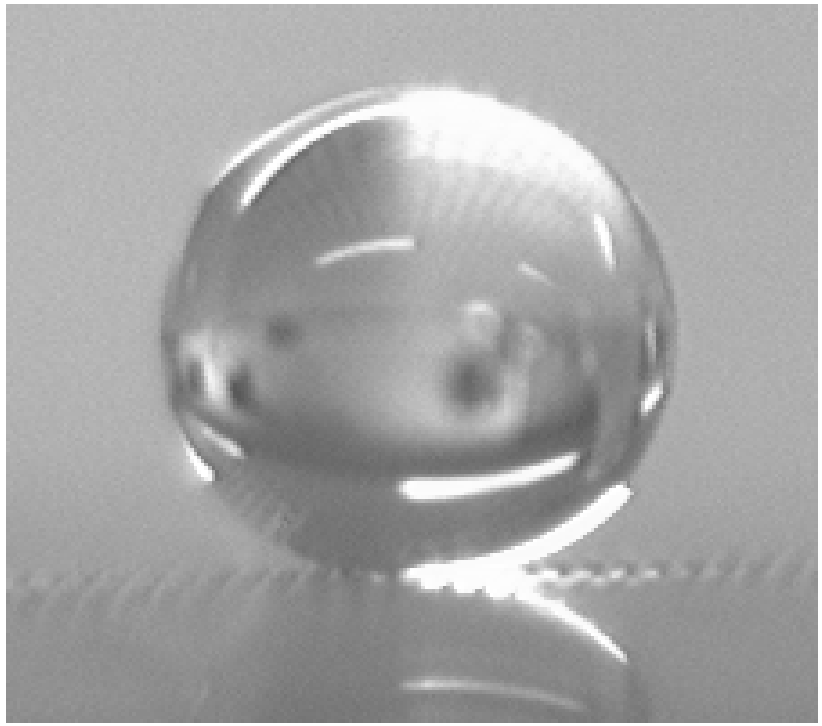
Electrodeposited Surfaces

"Chocolate Chip Cookies"





Water Drop



Contact angles of 160-180^{o}

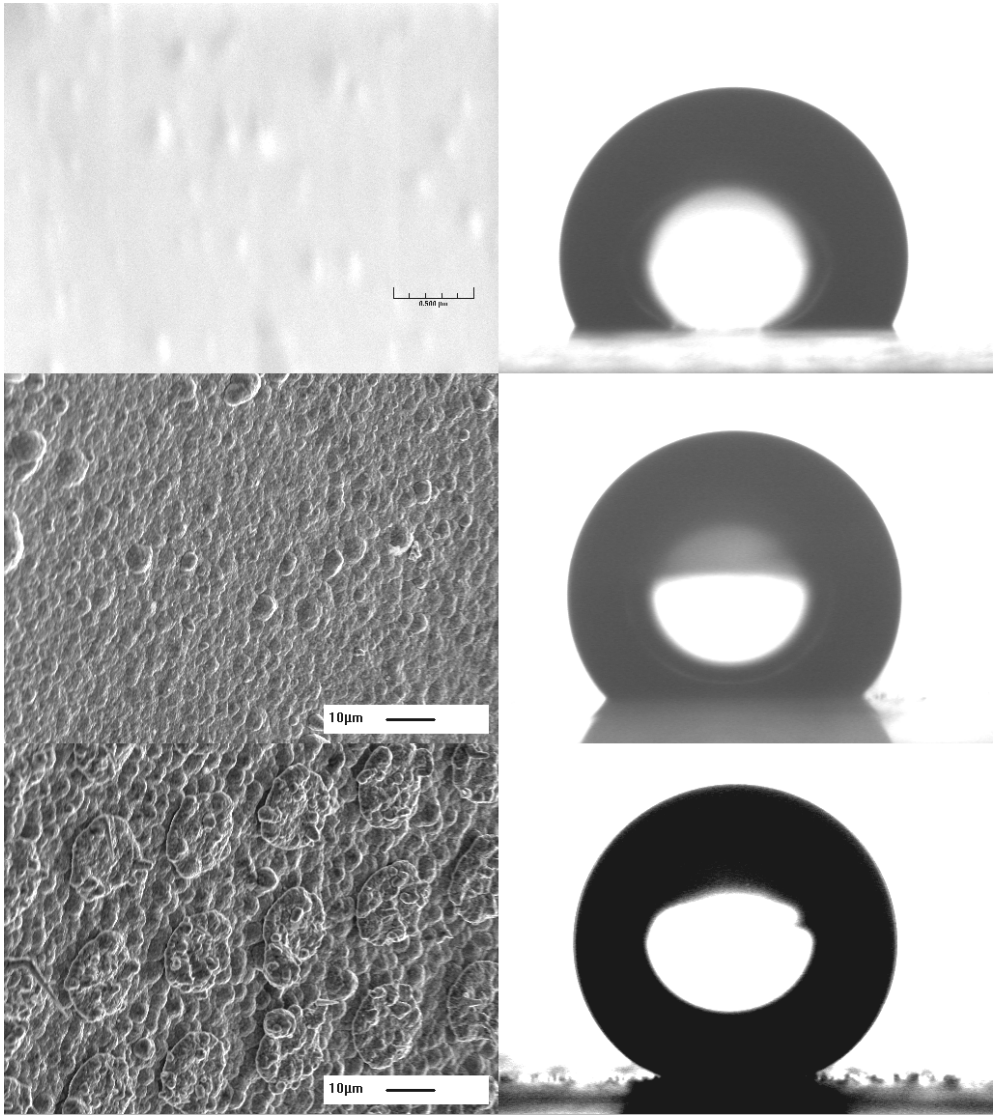
Electroplating can achieve 180^{o} even without texturing

– use current to obtain a fractally rough surface

Combining Slight Roughness and Texture

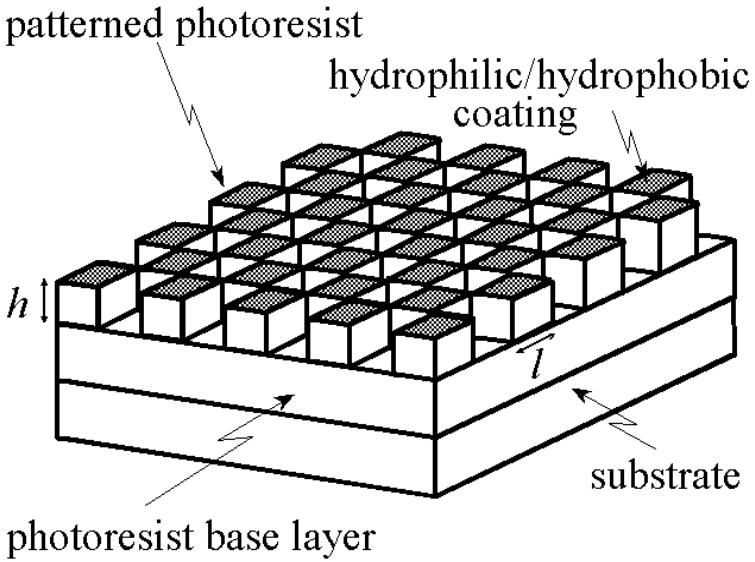
- Smooth and Hydrophobised 115°
- Slightly Rough and Hydrophobised 136°
- Slightly Rough, Textured and Hydrophobised 160°

Two Length Scales is extremely effective

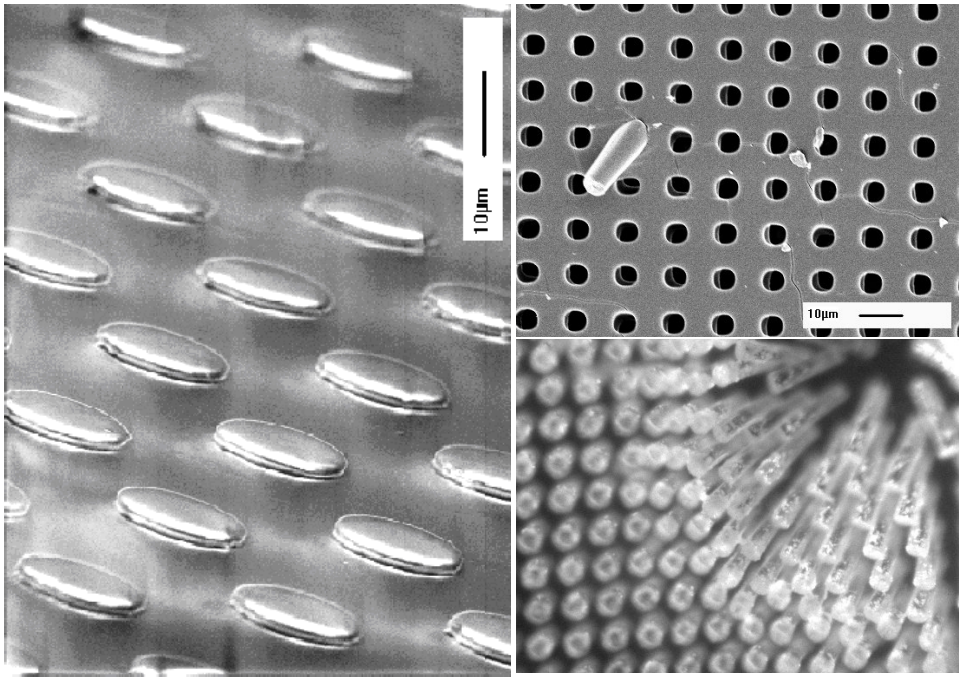


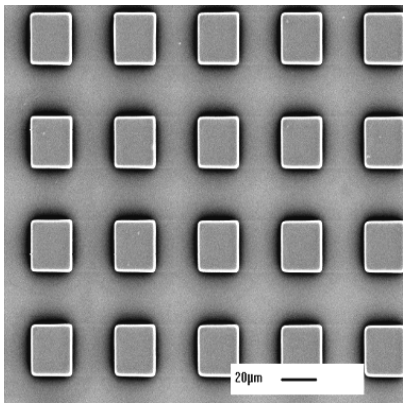
Lithographic Structures

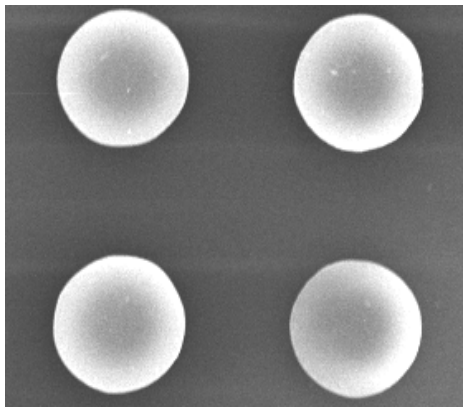
Principles

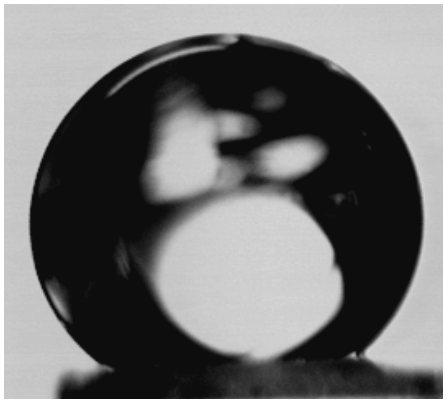


Practice



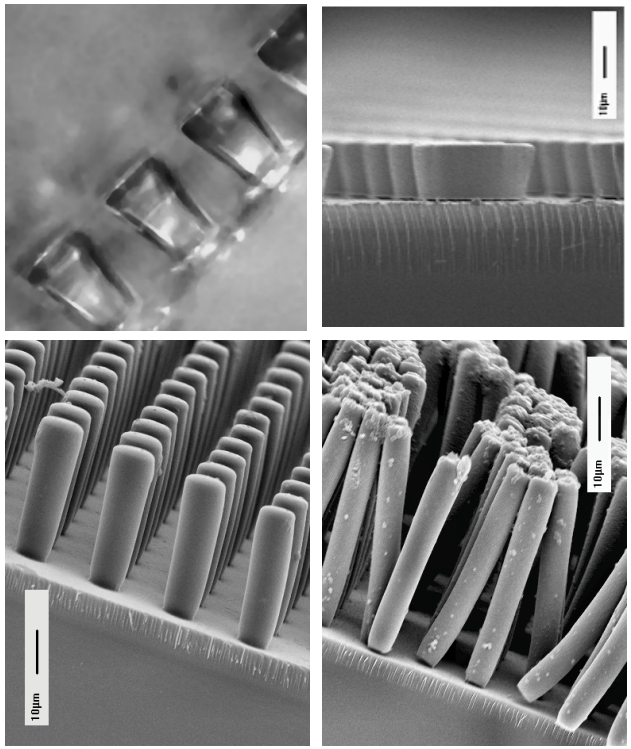




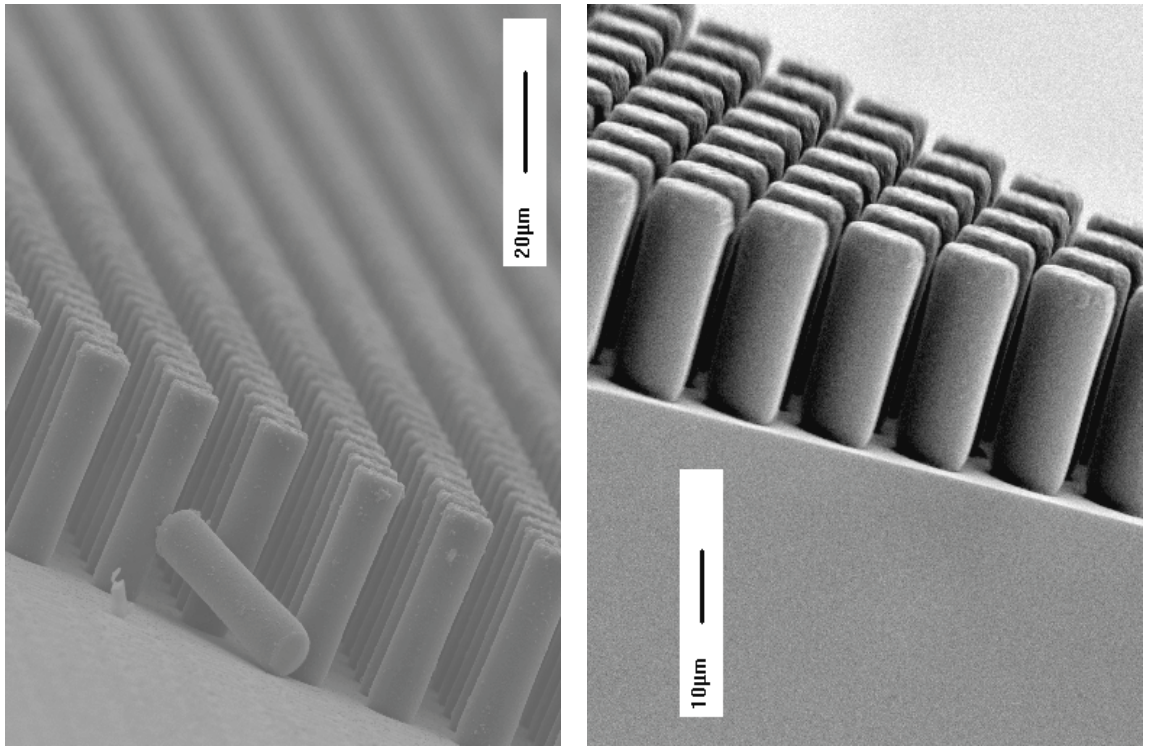


SU-8 Photoresist Pillars

Problems



Solutions



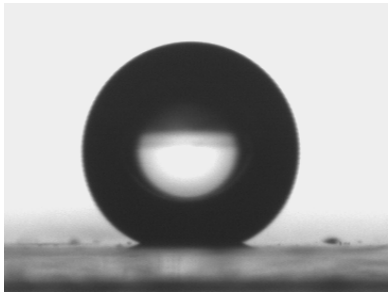
- SU-8 Photoresist
  - Tall structures to 45-75 µm, smooth and straight walls
  - Aspect ratios up to ~ 4

Drops on SU-8 Photoresist Pillars

- SU-8 Photoresist

  Flat and bare 84°, flat and hydrophobised

  115°, tall and 5 μm pattern 155°

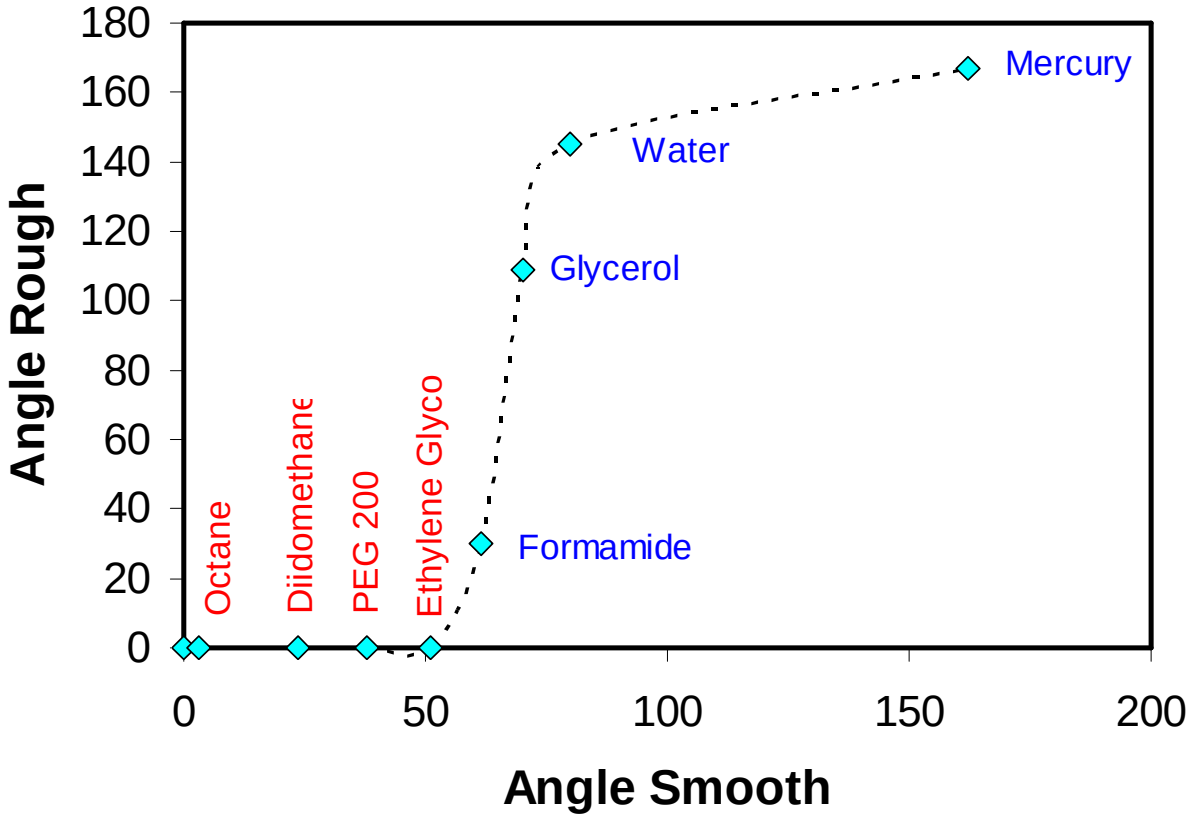


- Super-wetting

  SU-8 photoresist

  D =15 μm, *L* = 2*D*

  h = 43 μm



The End

Lithographic Pillars

Filleted and coated

Upright or not