Super-hydrophobic Surfaces

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Acknowledgements

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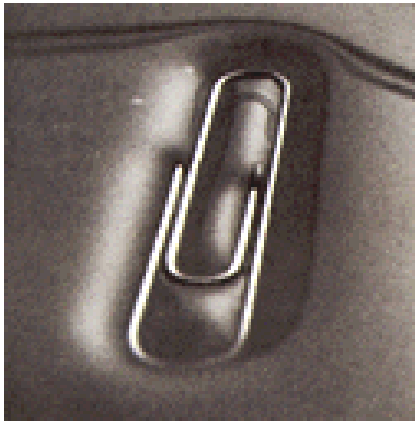
Sinking and Falling?

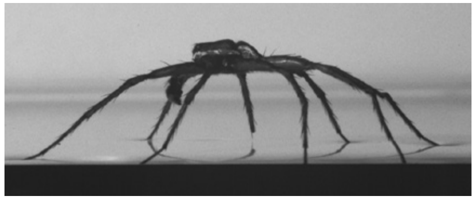
Water-on-Solids

- Liquids sometimes form drops, and sometimes spread over a surface and wet it. Why does this happen?
- Why are raindrops never a metre wide?
- Why don’t they run down the window?

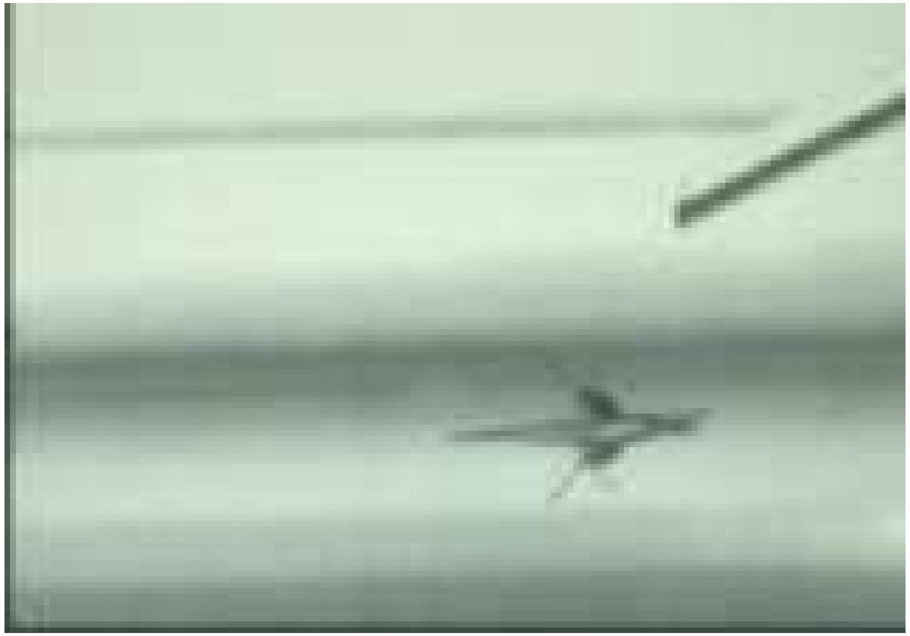
Solids-on-Water

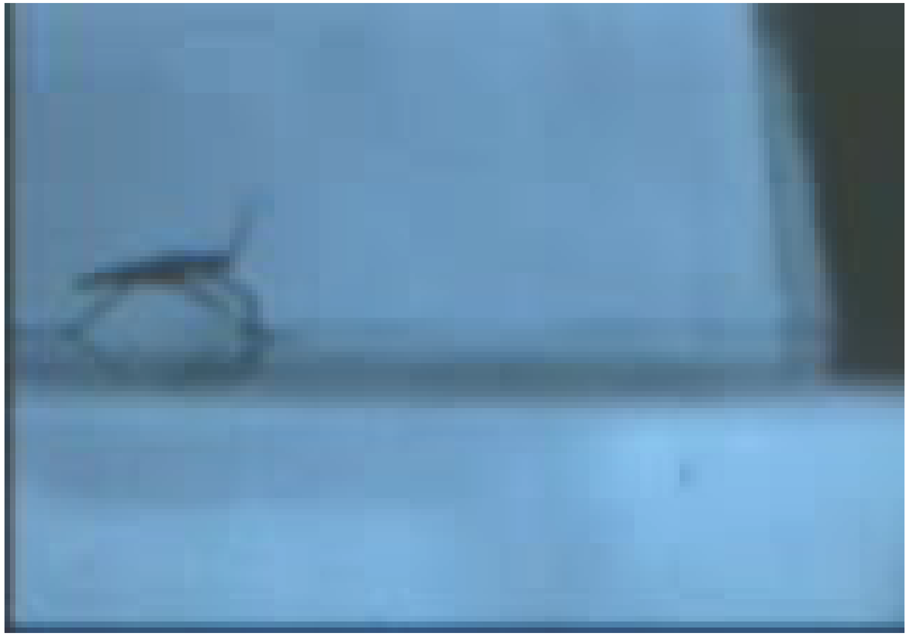
- How can pond skaters, and even fishing spiders walk-on-water? Why does this happen?
- How can metal objects “float” on water?





Movies: Pond Skaters





Movie of Infant

Movie of Adult

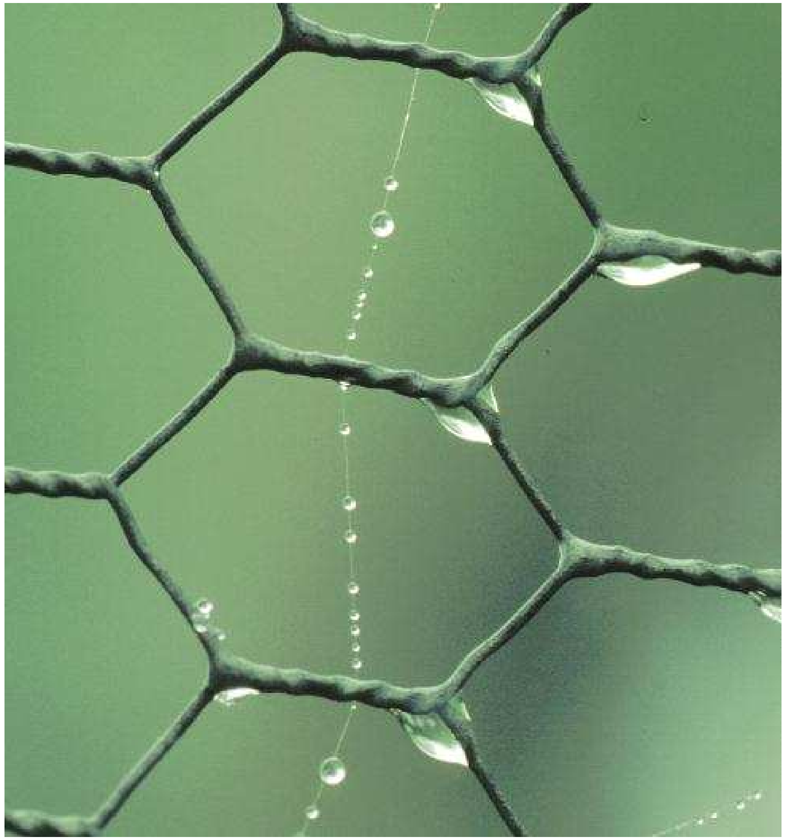
Surface Tension

Molecules at the Surface

- Have fewer neighbours
- Have higher energy than ones inside the liquid

Liquid Surface

- Behaves as if it is in a state of tension
- Tend to minimize its area in any situation
- For a free blob, the smallest area is obtained with a sphere



Surface Tension v Gravity

- Surface tension forces scale with length
- Gravity forces scale with length^3
- Small sizes $\Rightarrow$ Surface tension wins

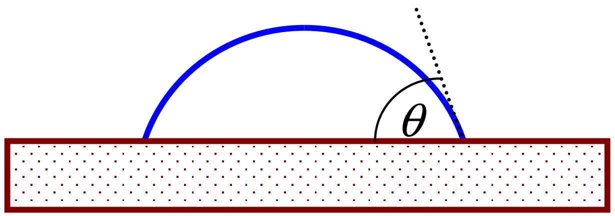
Acknowledgement www.brantacan.co.uk

Water Repellency (Hydrophobicity)

Surface Chemistry

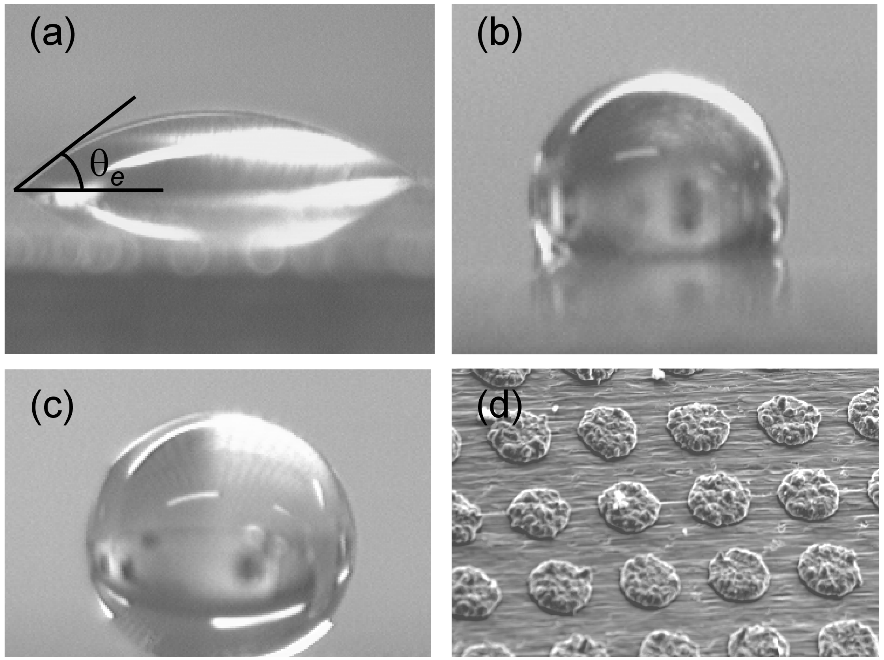
- Terminal group determines whether surface is water hating
- Hydrophobic terminal groups are Fluorine (F) and Methyl (CH_3)

Contact Angles



- Characterises hydrophobicity
- Water-on-Teflon gives ~ 115°
- The best that *chemistry* can do

Physical Enhancement



- (a) is water-on-copper
- (b) is water-on-fluorine coated Cu
- (c) is a super-hydrophobic surface
- (d) "chocolate-chip-cookie" surface

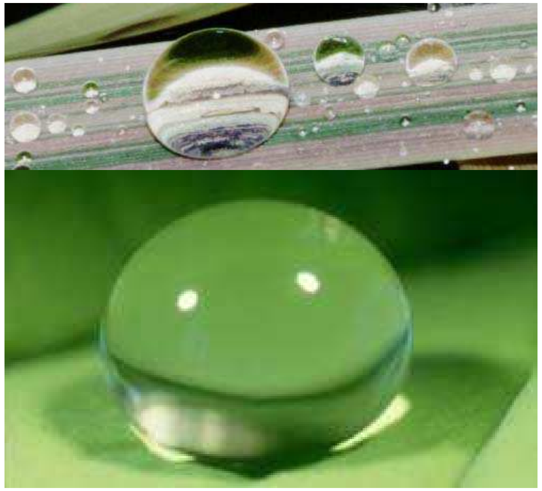
Super-hydrophobicity is contact angles larger than 150°

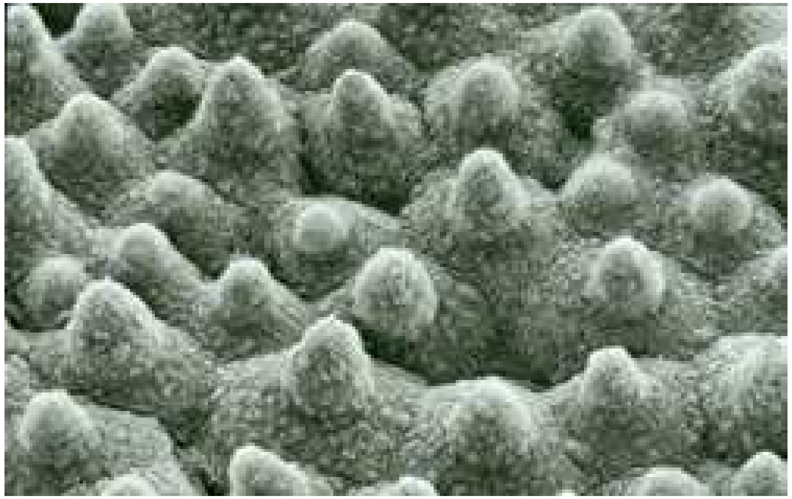
The Sacred Lotus Leaf

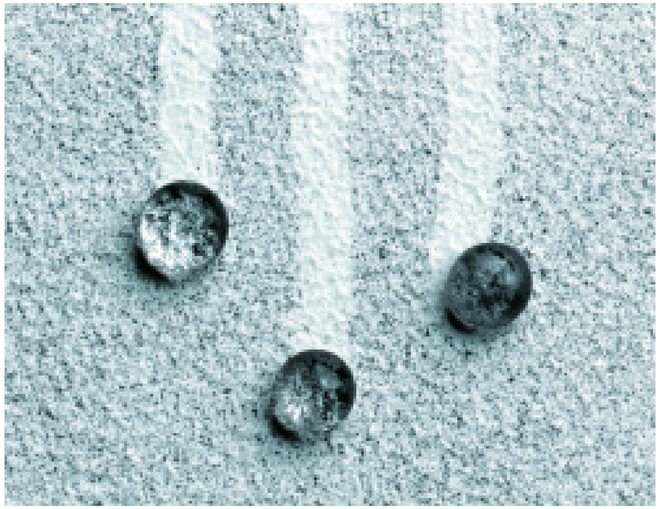
Plants

- Many leaves are super-hydrophobic
- The Lotus plant is known for its purity
- Super-hydrophobic leaves are self-cleaning under the action of rain

Drops on Leaves | SEM of a Lotus Leaf | Self-Cleaning

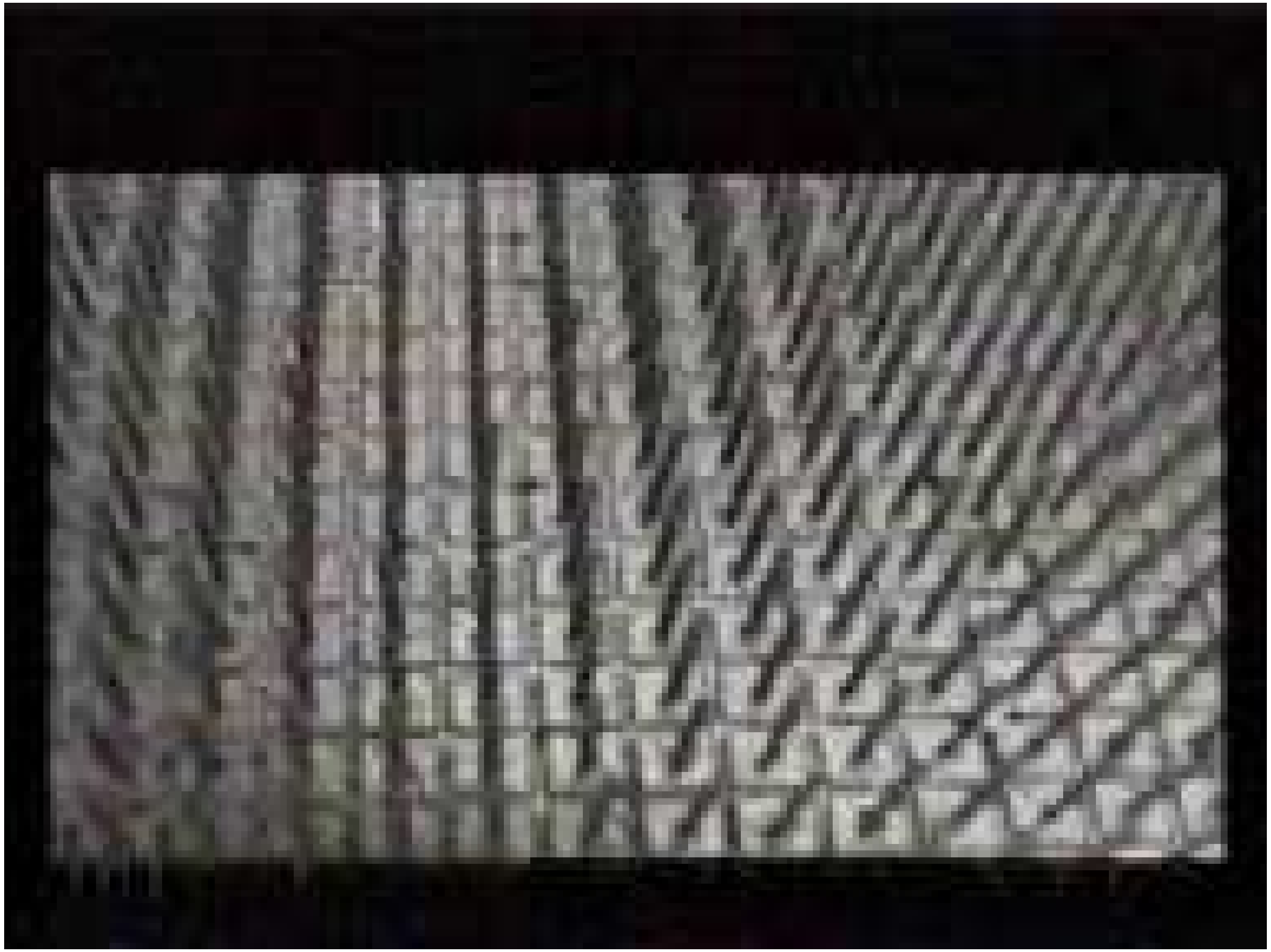






Acknowledgement Neinhuis and Barthlott

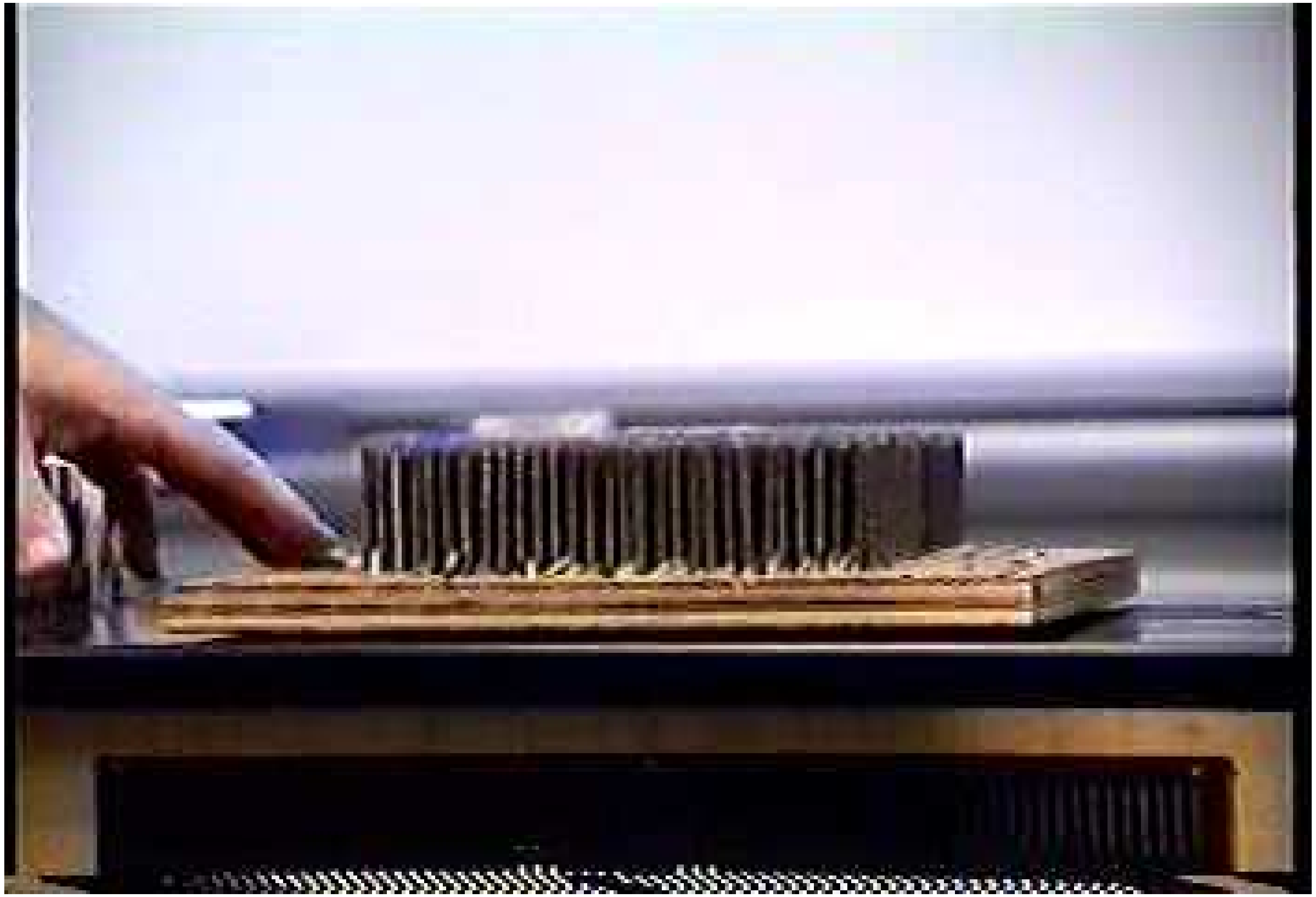
A “Bed of Nails” Effect



Movie of Professor on a Bed of Nails

Acknowledgement Mahanakorn University Physics

A “Bed of Nails” Effect



Balloon on a Bed of Nails

Acknowledgement Wake Forest University

Two Forms of Super-hydrophobicity

Wenzel's Equation

- Based on roughness, *r*

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

Consequences

- Causes larger/smaller contact angles when θ_e^s > or < 90º
- Creates a "Sticky" surface – drops don't easily move

Cassie-Baxter Equation

- Based on composite air-solid surface, φ_s (Lotus effect)

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

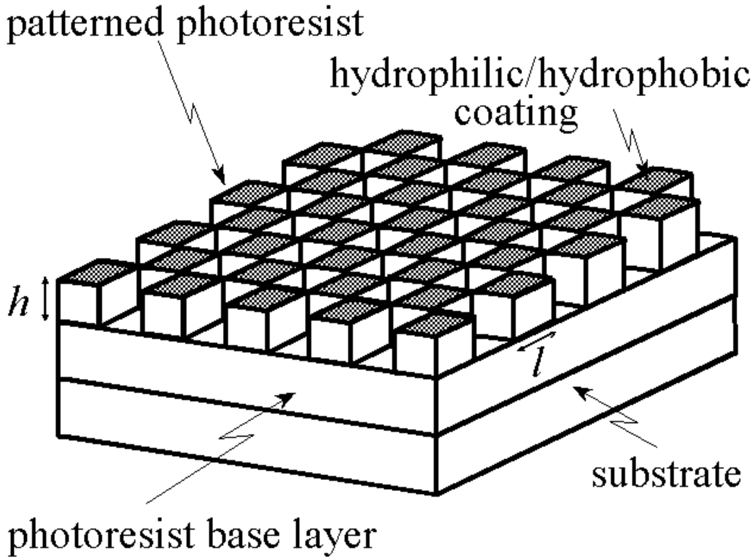
Consequences

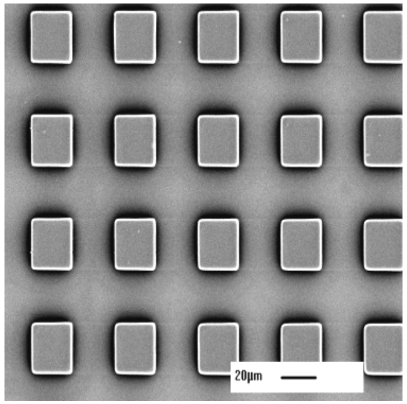
- Easier to get 150+º than with Wenzel
- Creates a "Slippy" surface – drops easily move

NTU Work

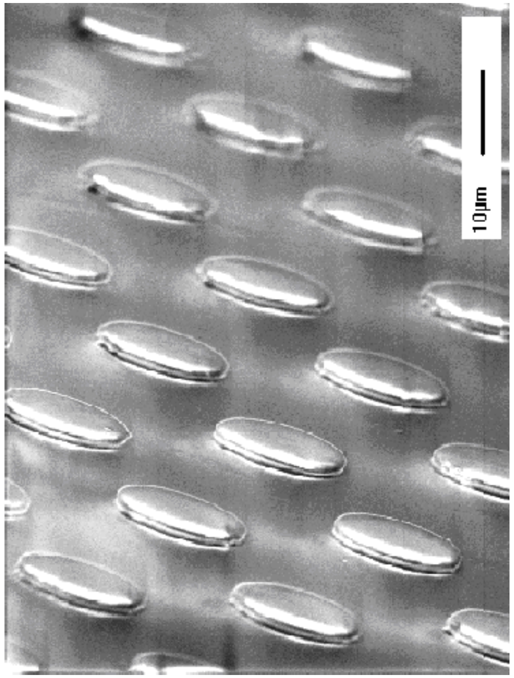
Lithographic Structures

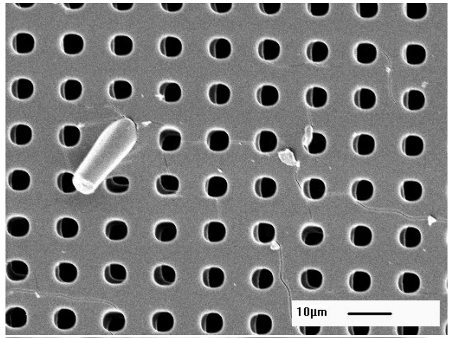
Principles

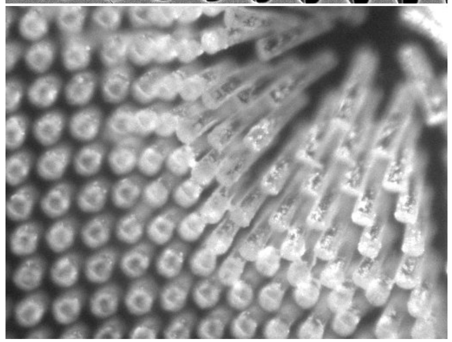


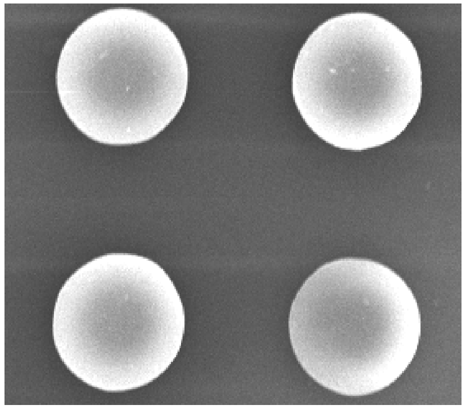


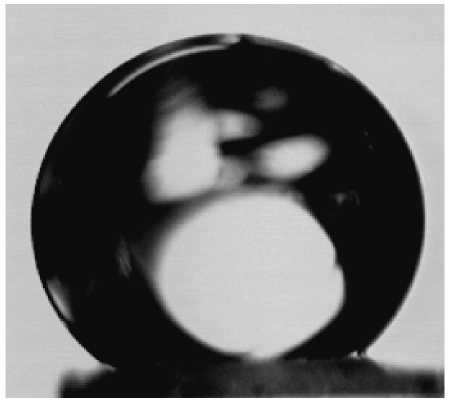
Practice







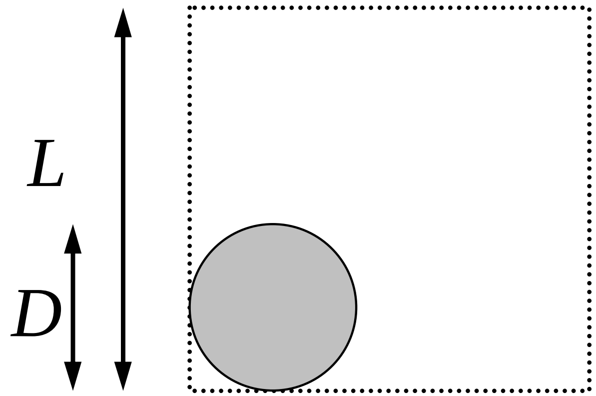




Texture Example

Circular Pillars

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



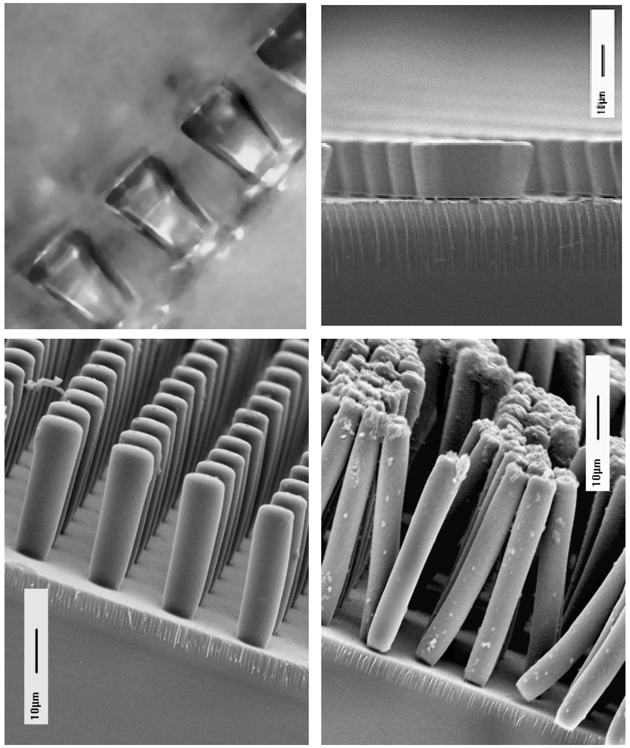
$$\varphi_s = \frac{\pi D^2}{4L^2} \qquad r = 1 + \frac{\pi}{4}\left(\frac{h}{D}\right)$$

Example

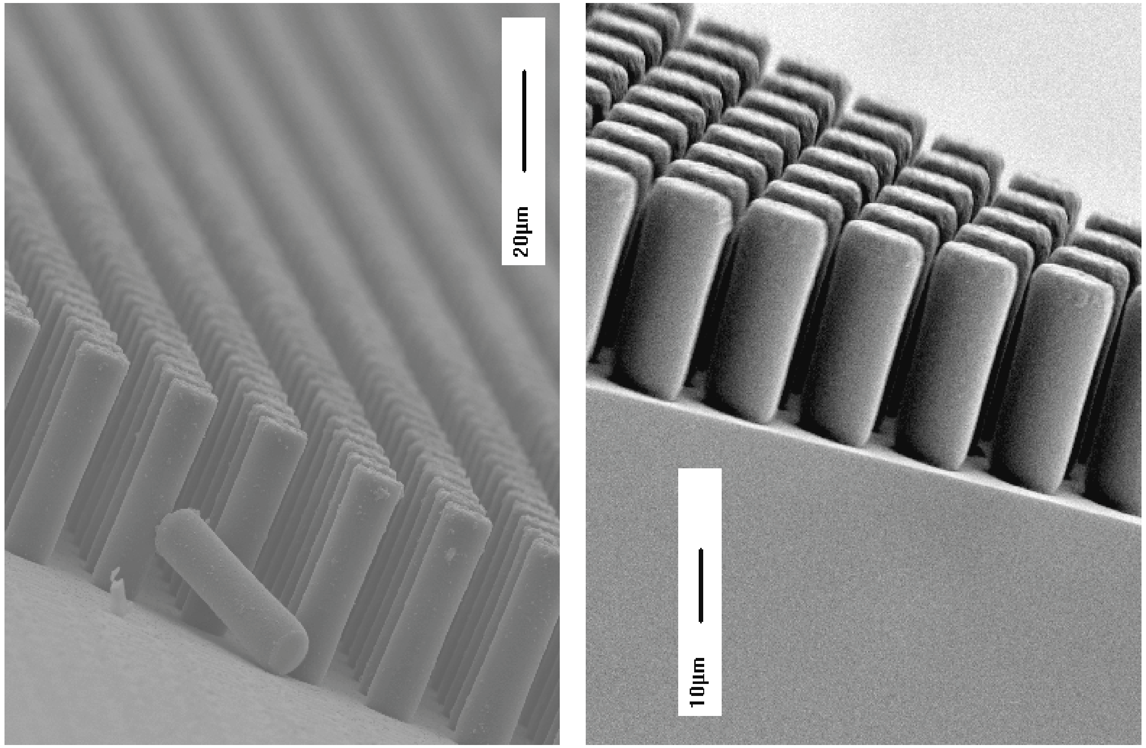
L=2D	φ_s=0.196	θ_e^s=115^o	θ_e^c=152^o
D=15 μm	*h*=21 μm	before θ_e^w=152^o	
D=5 μm	*h*=21/3=7 μm	before θ_e^w=152^o	

SU-8 Photoresist Pillars

Problems



Solutions



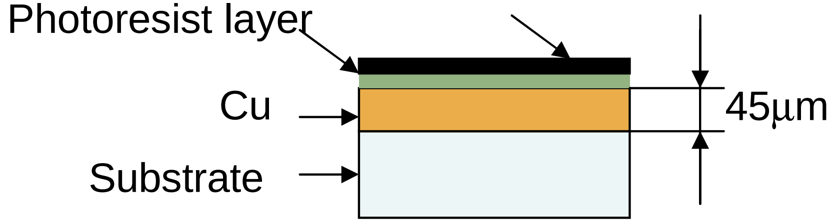
- SU-8 Photoresist

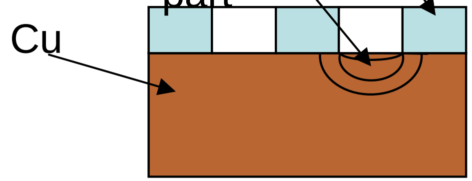
  Tall structures to 45-75 μm, smooth and straight walls

  Aspect ratios up to ~ 4

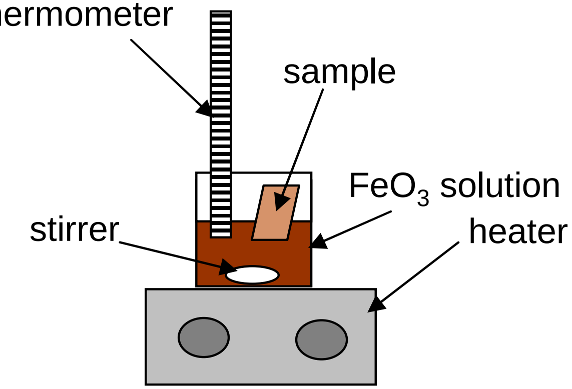
Etching of Copper Surfaces

- Etching using PCB Techniques – Simple and Effective

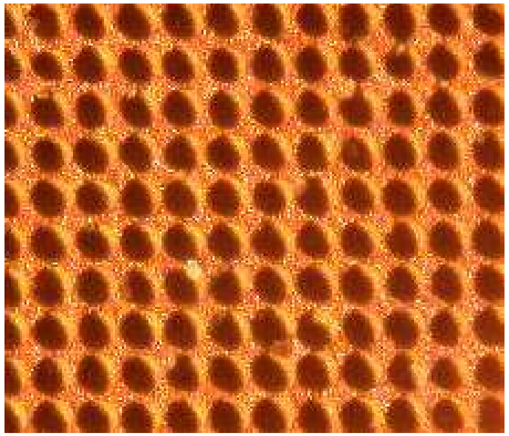




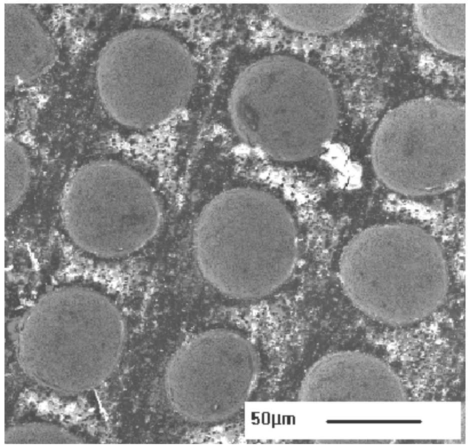
hole growth



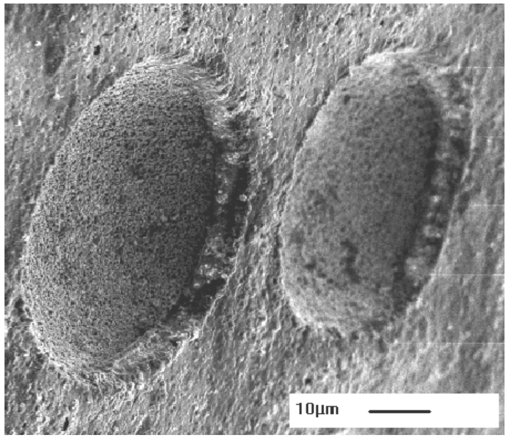
Setup of the copper etching



Copper sample etched through a 30 µm pattern

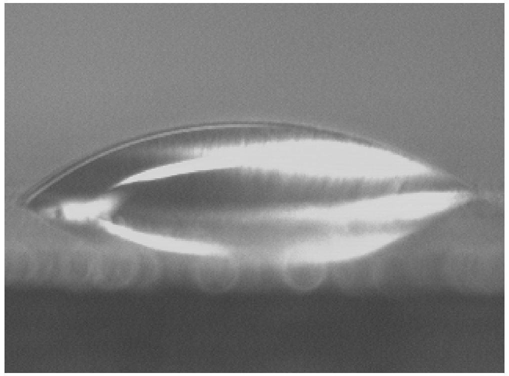


SEM picture of the pattern of the etched copper surface

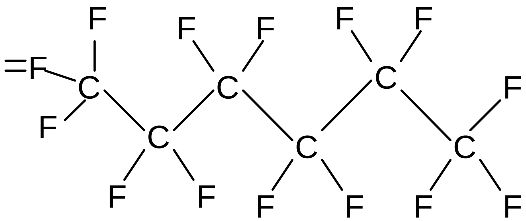


SEM picture of an etched hole in copper sample

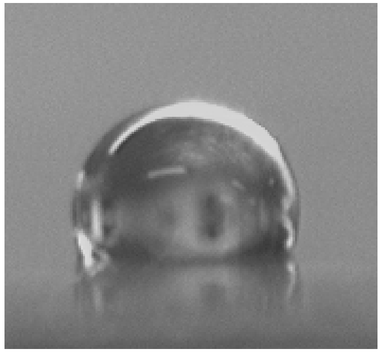
Hydrophobised Etched Copper Surfaces



Simple Cu surface



Grangers' molecular chain



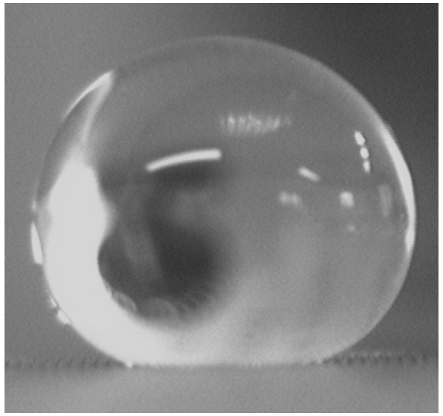
Hydrophobic surface

30 µm and 40 µm Patterns

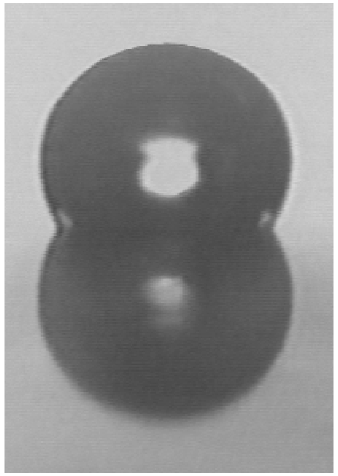
Typically 152º to 158º

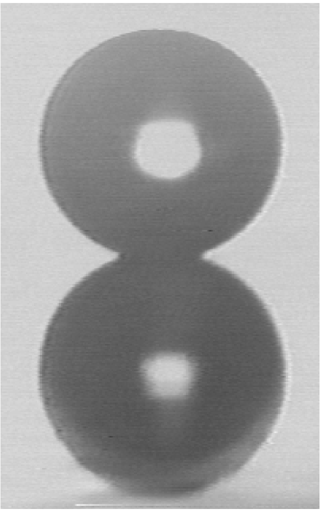
But have achieved far higher

- over-etch to create peaks



40µm pattern with Grangers





Acknowledgement

Gregoire Chabrol

Electroplated Copper Surfaces

- Copper acid bath

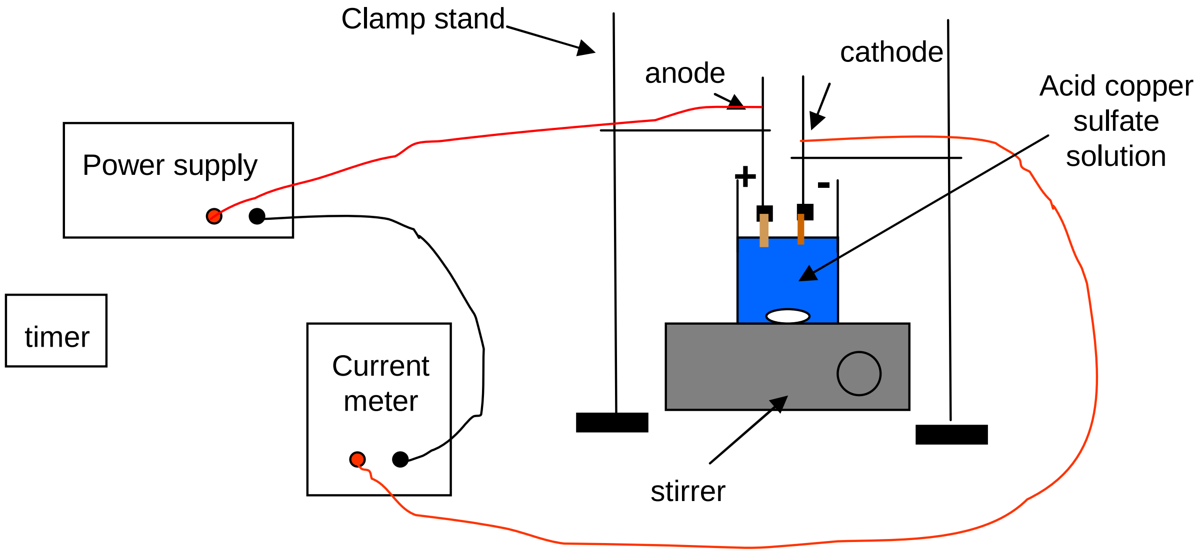
    Copper sulphate ($CuSO_4$) and sulphuric acid (H_2SO_4)

Current density

Slightly rough to highly rough (Fractal)

Masking

Mask and grow pillars in Cu on Cu

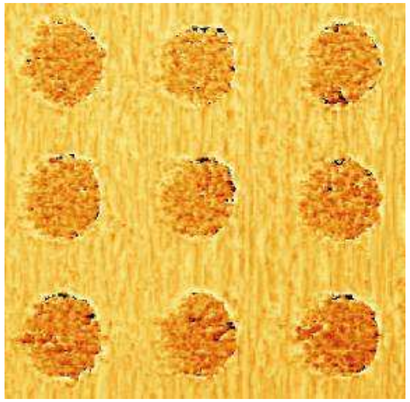


Setup for the copper plating

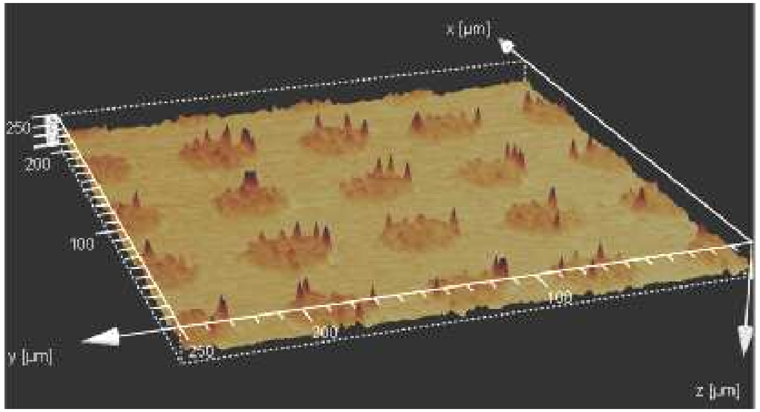
Electroplated Textured Surfaces

- Electroplating through a mask

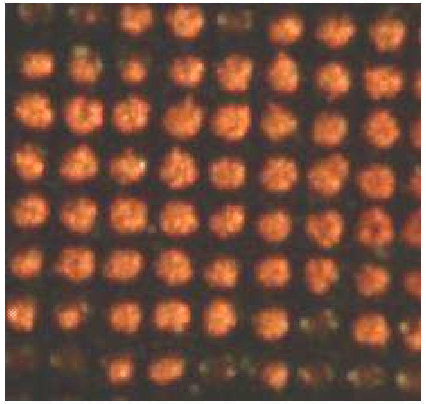
Base Cu electroplated surface



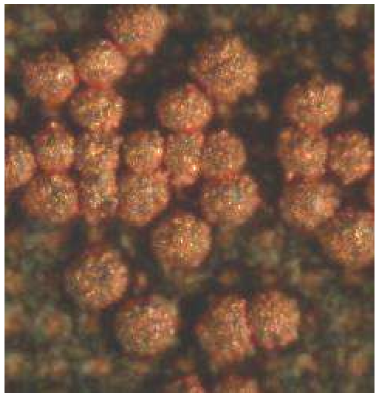
Confocal image of a 30μm textured electroplated Cu



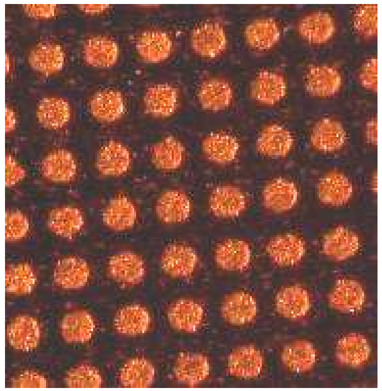
3D view of a electroplated copper sample



Deposition time too short



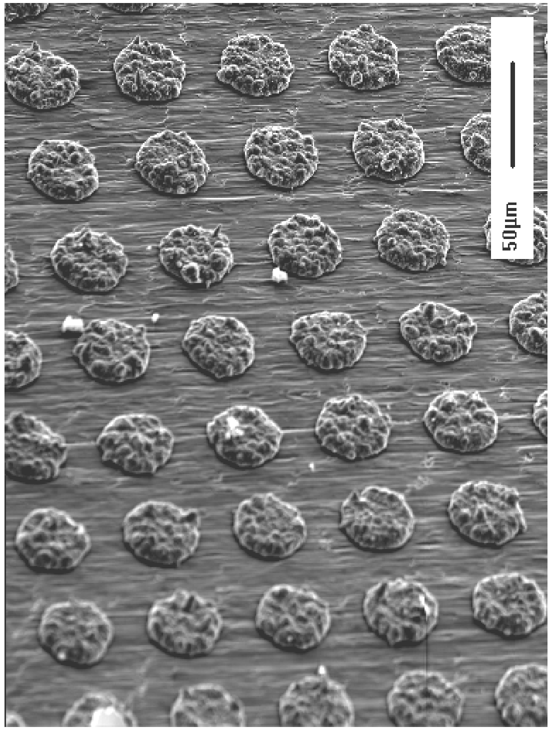
Deposition time too long - mushrooms touch

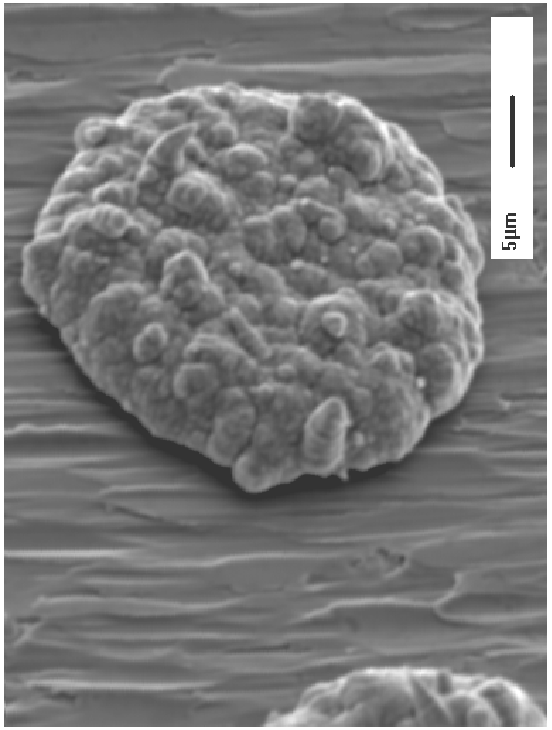


Deposition time OK

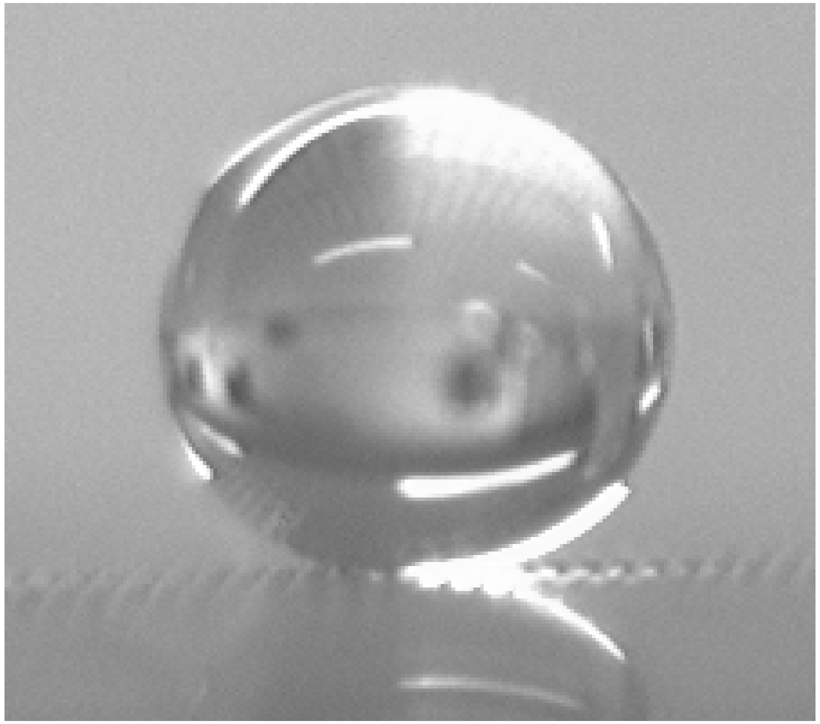
Electrodeposited Surfaces

“Chocolate Chip Cookies”





Water Drop



Contact angles of 160-180º

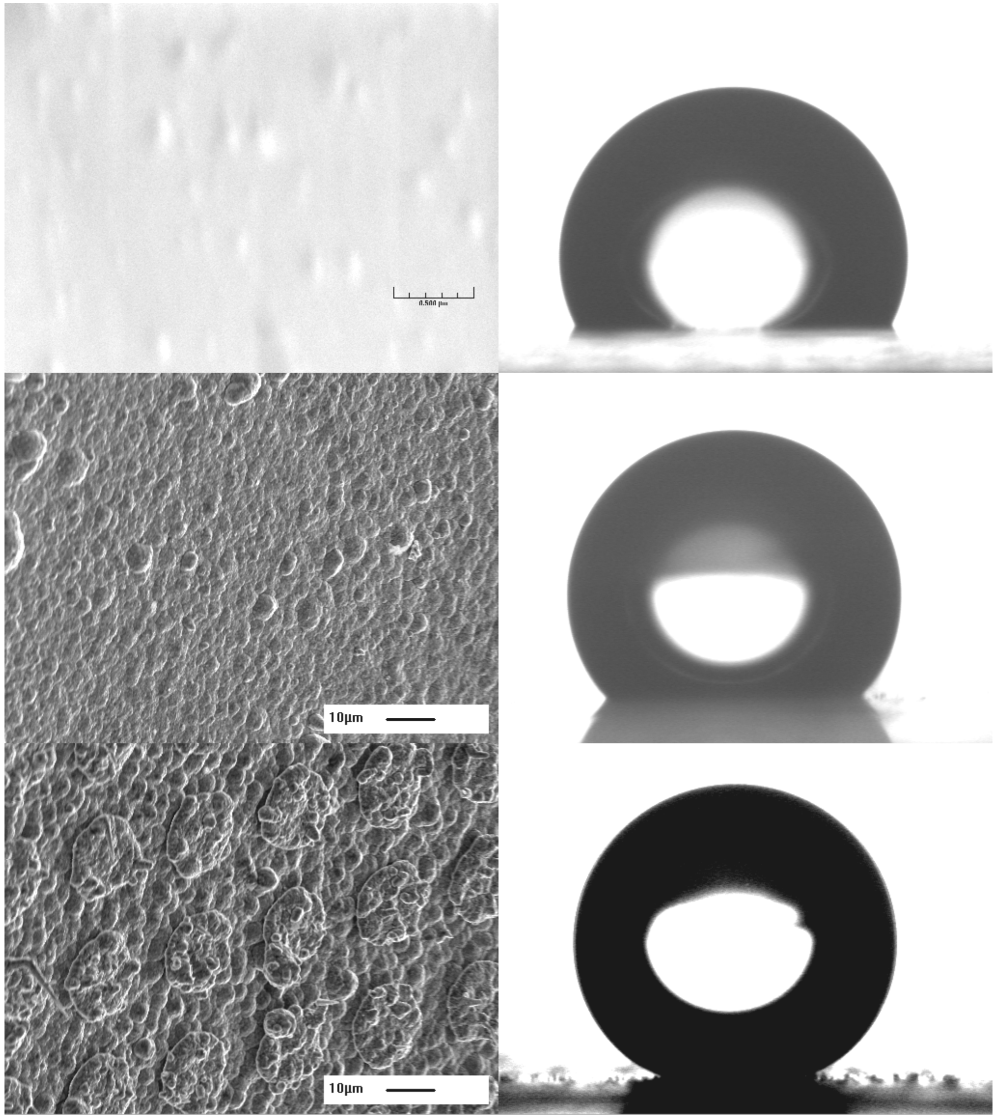
Electroplating can achieve 180º even without texturing

– use current to obtain a fractally rough surface

Combining Slight Roughness and Texture

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

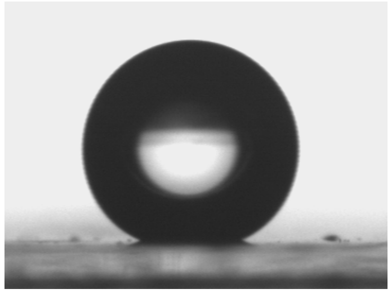
Two Length Scales is extremely effective



Drops on SU-8 Photoresist Pillars

- SU-8 Photoresist

  Flat and bare 84^{o}, flat and hydrophobised 115^{o}, tall and 5 µm pattern 155^{o}



- Super-wetting

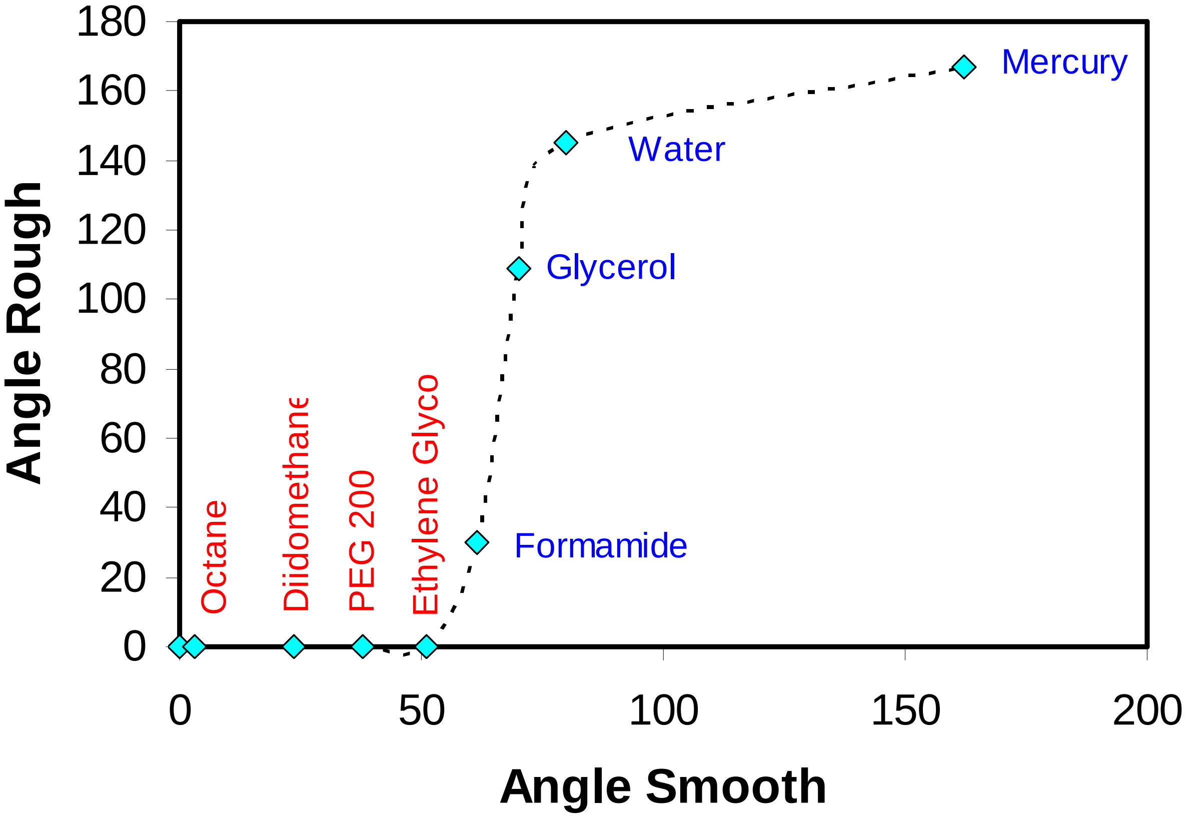
  SU-8 photoresist

  D =15 µm, *L* = 2*D*

  h = 43 µm

- Dynamics

  Oils spread much faster on super-hydrophobic surfaces

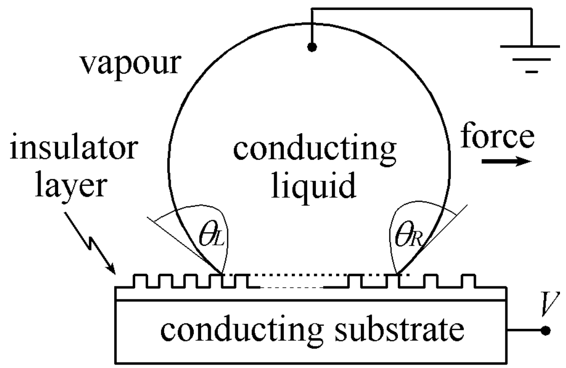


Non-NTU Work on Droplet Motion

Electrowetting

Driving Force

- Difference in angles on opposite sides of drop generates a driving force
- E.g. Tilting a super-hydrophobic a “slippy” super-hydrophobic surface drop moves once hysteresis overcome



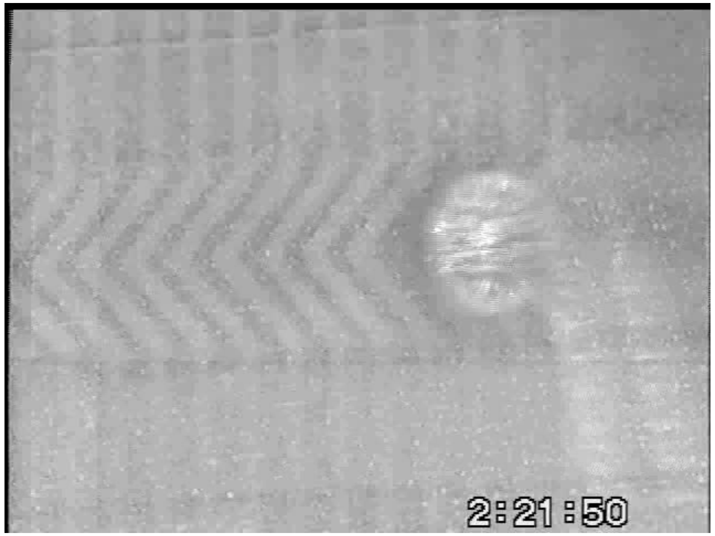
Voltage Induced Motion

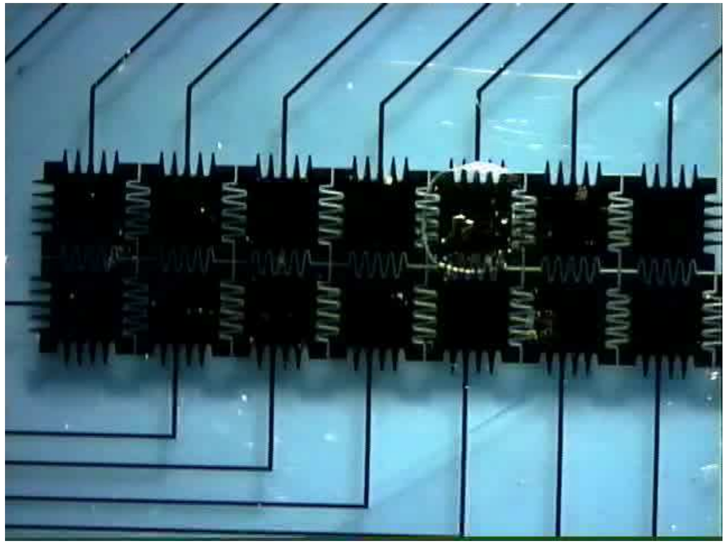
- Charging solid-liquid interface alters angle
- Selective control of charging generates differences in angles

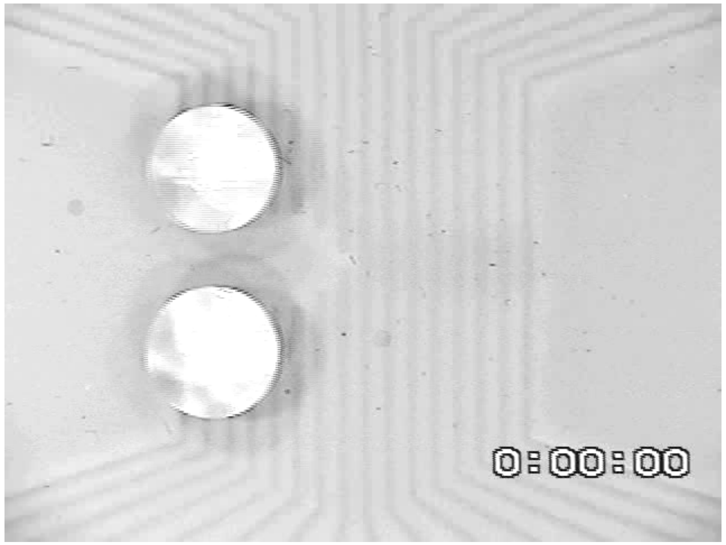
Dukes Video

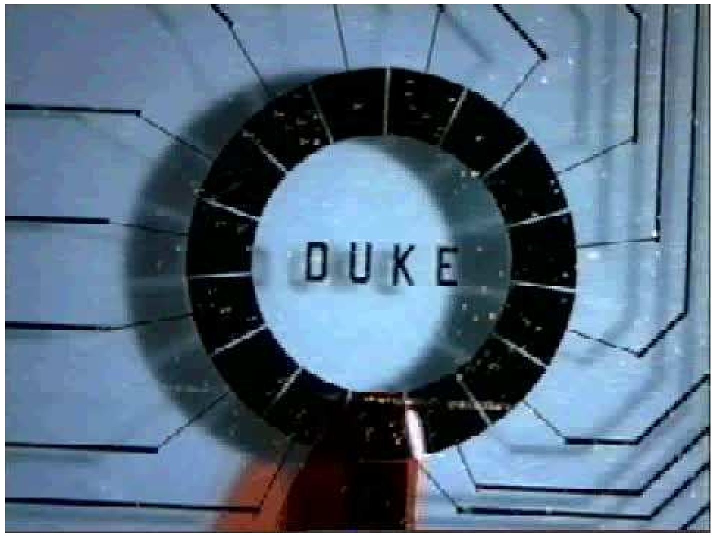
- Electrostatic reduction in both angles

Microfluidics (VTT and Nanolytics)









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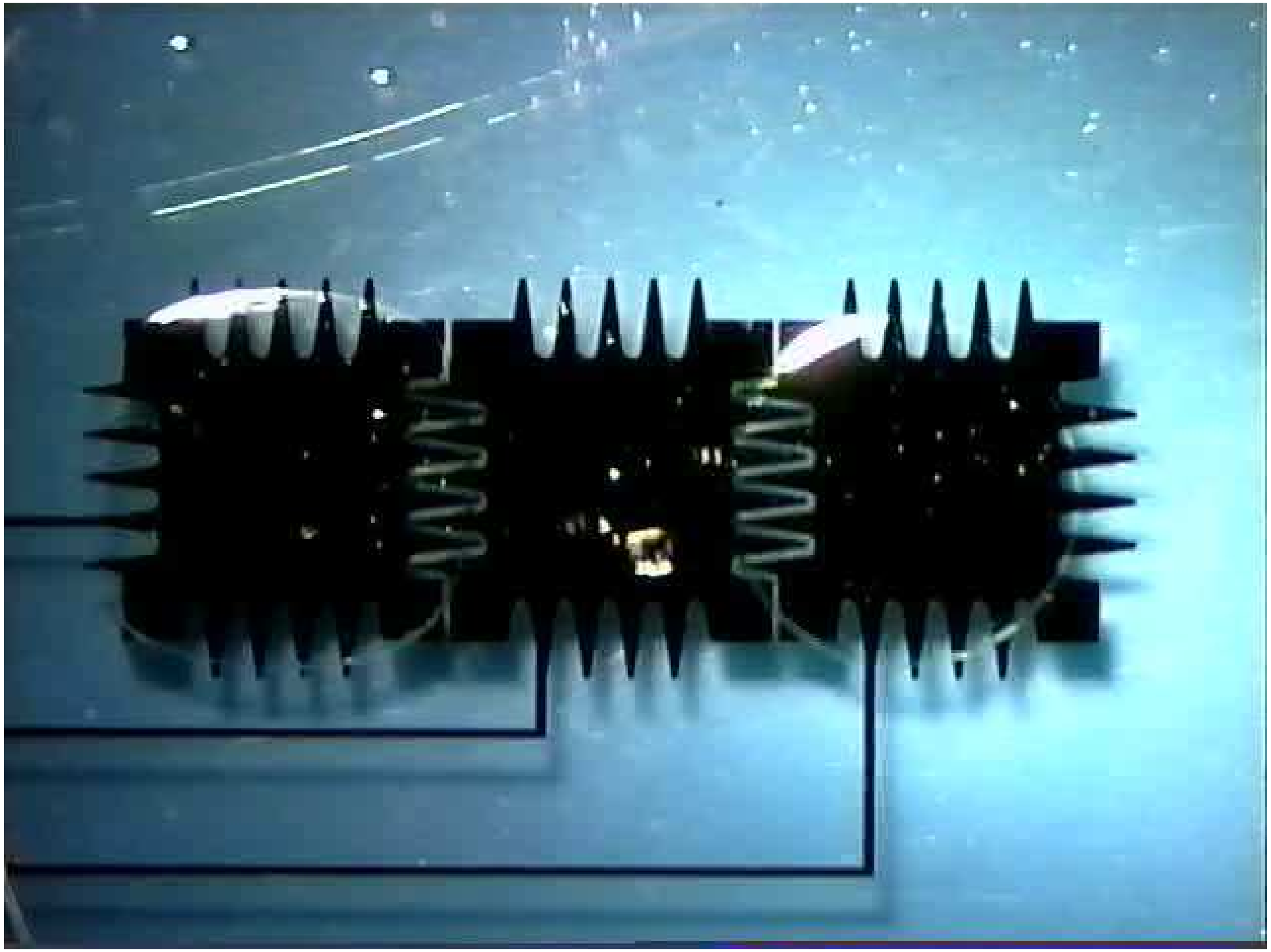

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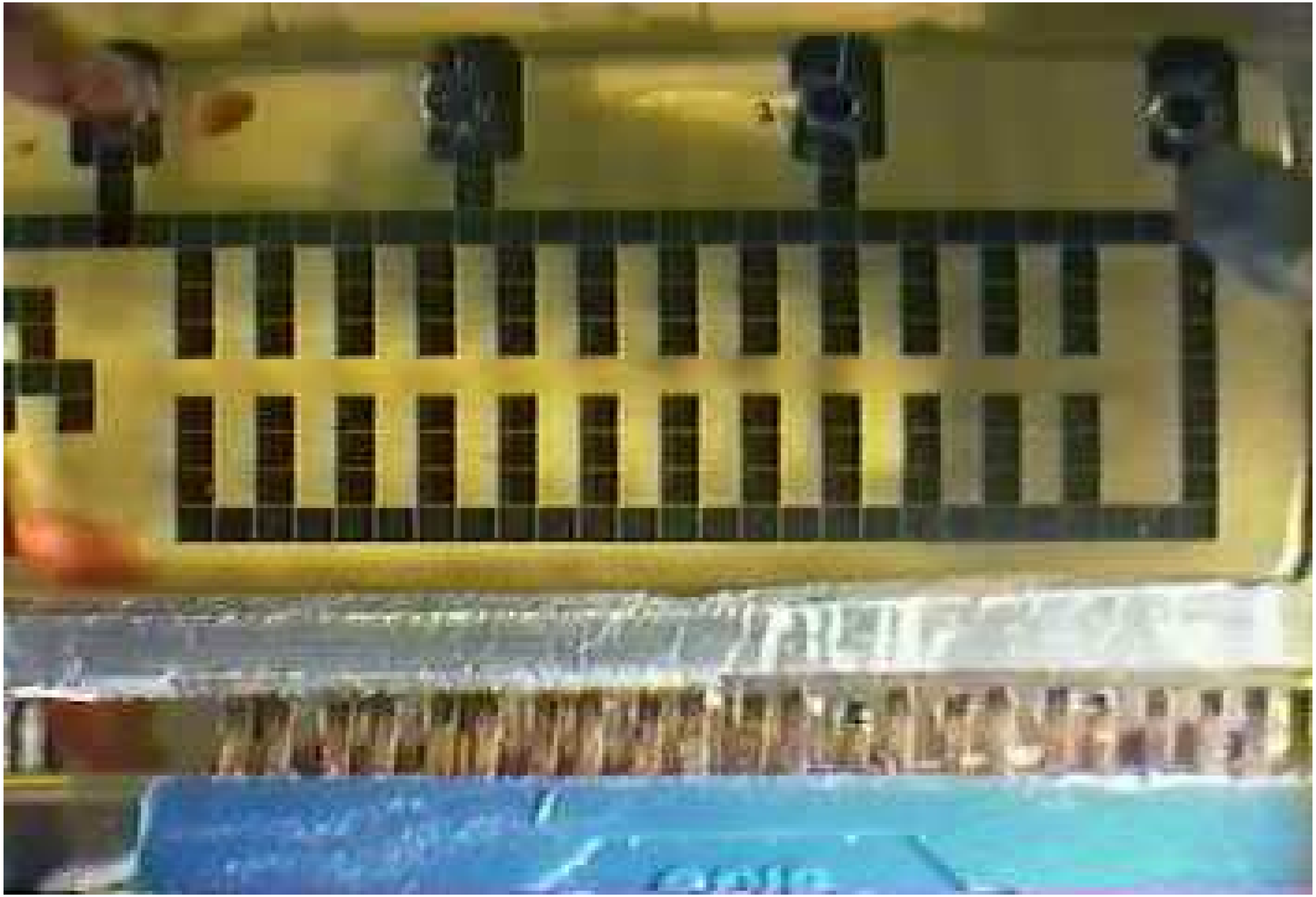

The End