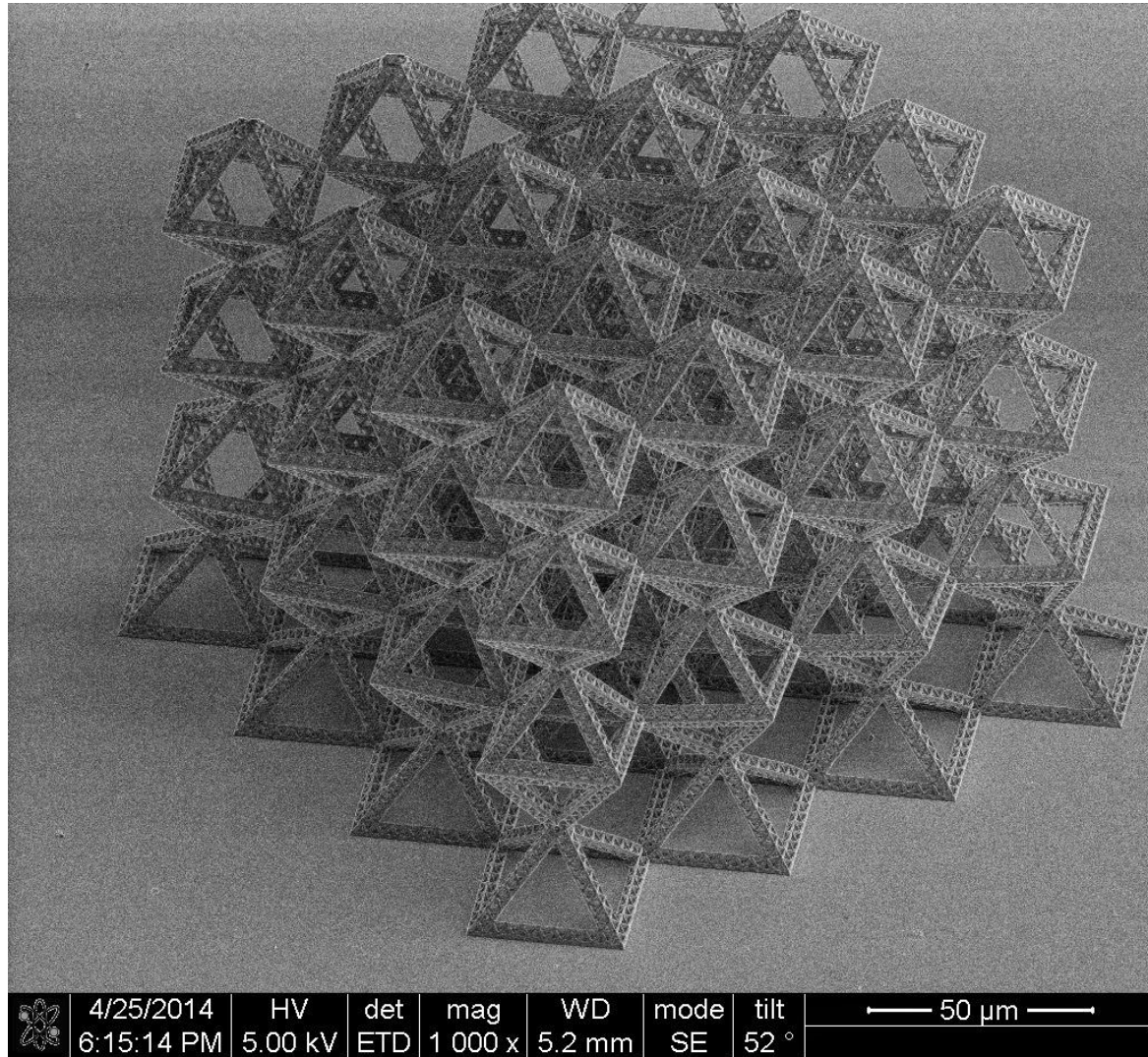
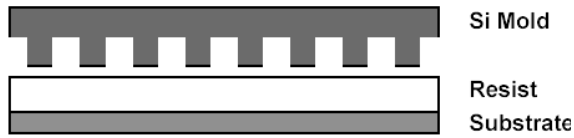


# Current Microfabrication and Nanofabrication Technologies



# Nanoimprinting Lithography (NIL)

## NIL Process



(1) Press in mold



(2) Heat up mold and substrate



(3) Mold separation after cooling



(4) O<sub>2</sub> RIE



**Nanonex NX-2000 Nanoimprinter**

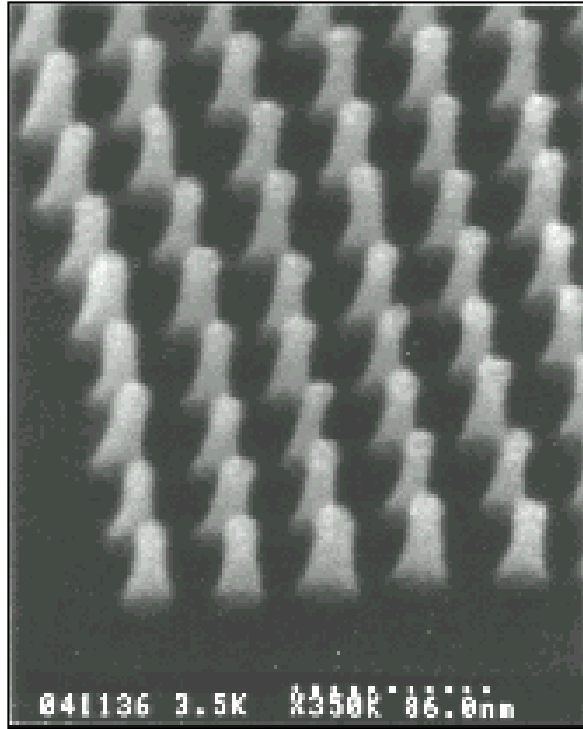
Up to 4" wafer

Sub-100 nm resolution

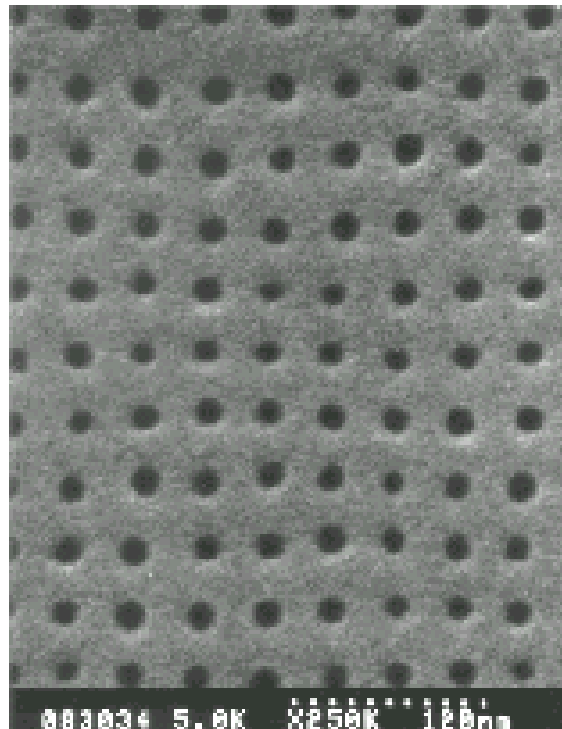
Up to 300°C, 600 psi, UV

- Sub-10nm feature size
- Large area (4-8 in.)
- High throughput
- Low cost

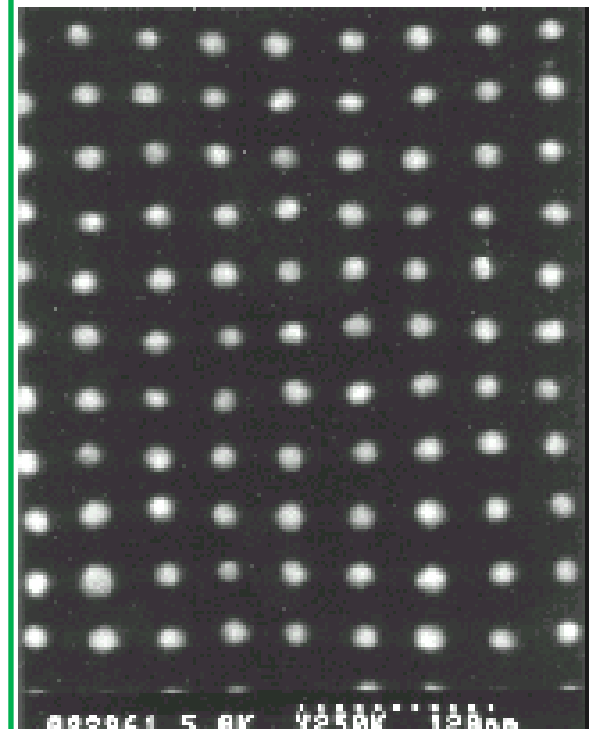
# Sub-10 nm Resolution of NIL



Imprint mold with  
10nm diameter pillars



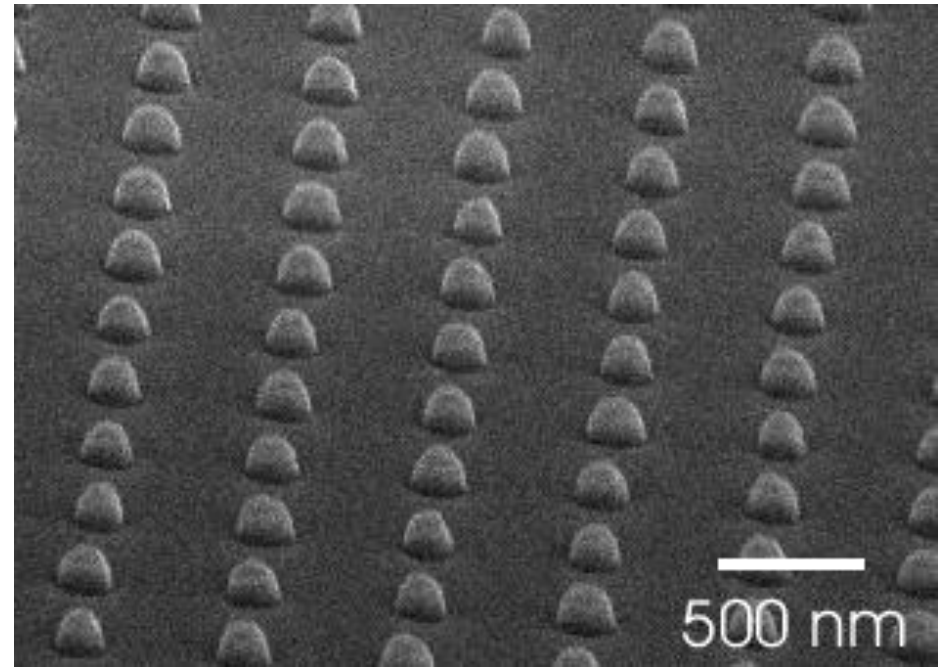
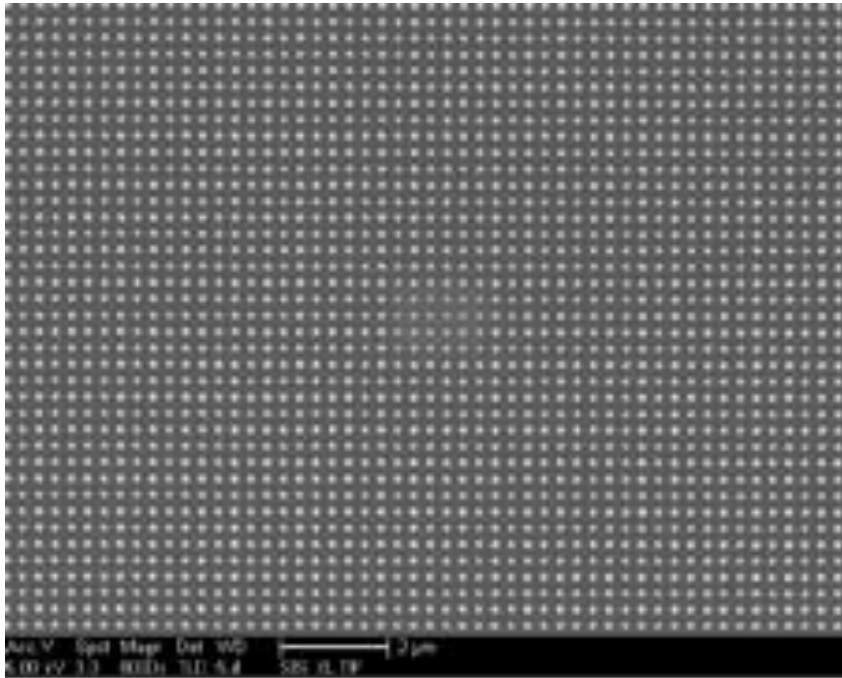
10nm diameter holes  
imprinted in PMMA



10nm diameter metal  
dots fabricated by NIL



# Metallic Nanodot Arrays

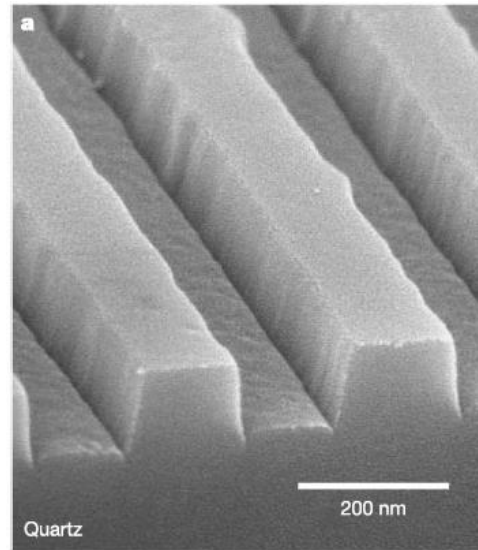
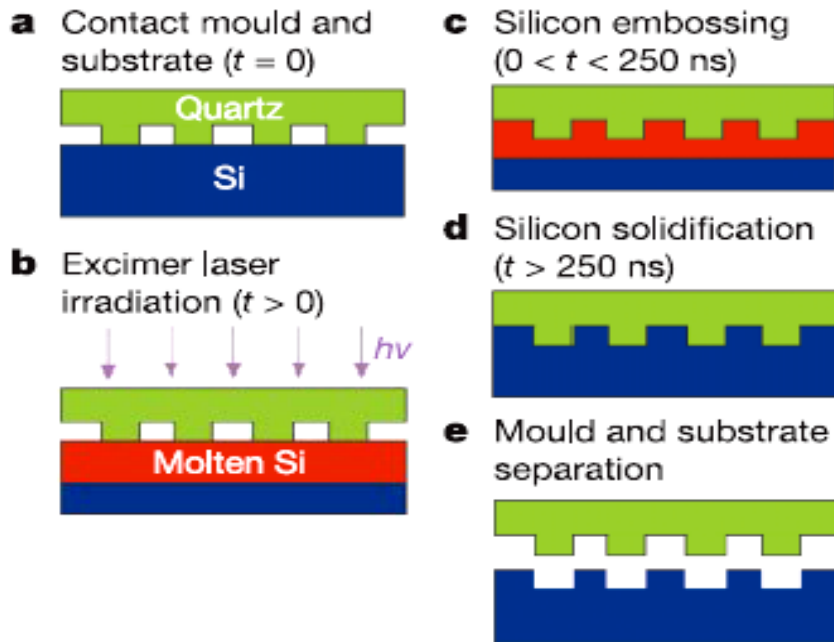


Nanodots localize magnetic or electrical fields at very small scales. Applications for nanodots could include high-density information storage devices.

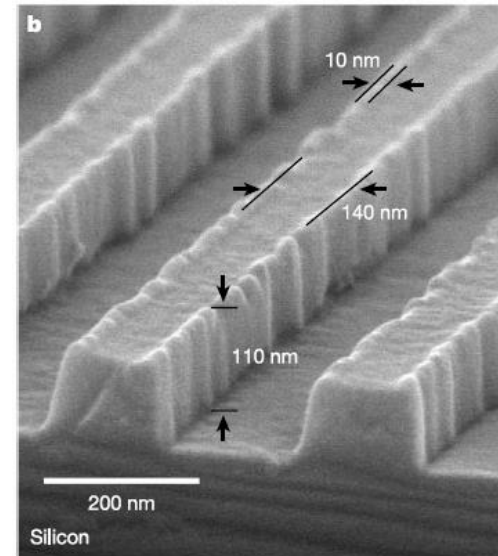


# Laser-Assisted-Direct-Printing (LADI) in Silicon

## LADI Process



Quartz mold



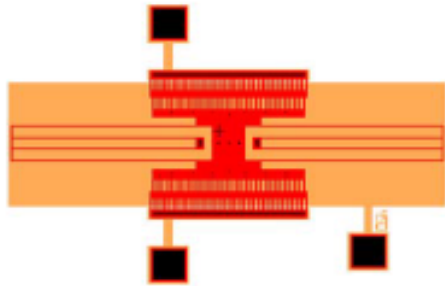
Imprinted Si

- Fast speed
- Direct patterning semiconductors
- Complex structures (e.g. lens) in Si
- With sub-10 nm resolution

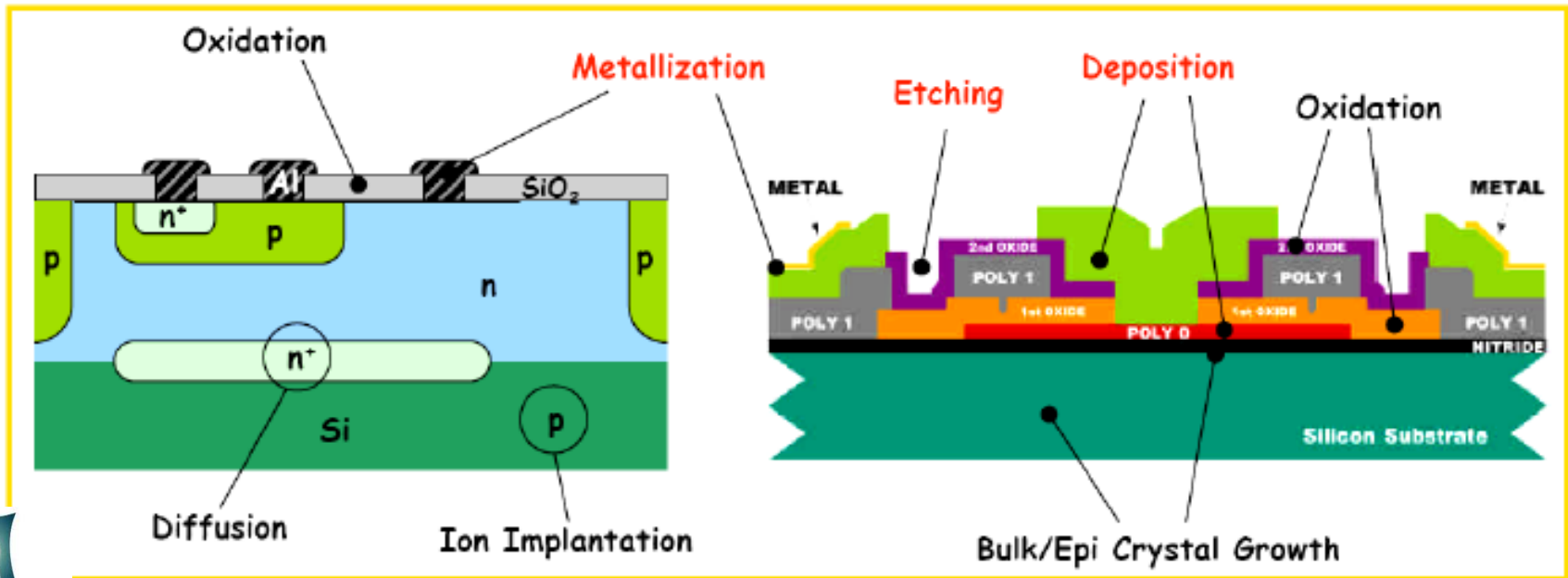
Chou, S. et al., *Nature*, (2002)

# The Big Picture

Technology CAD



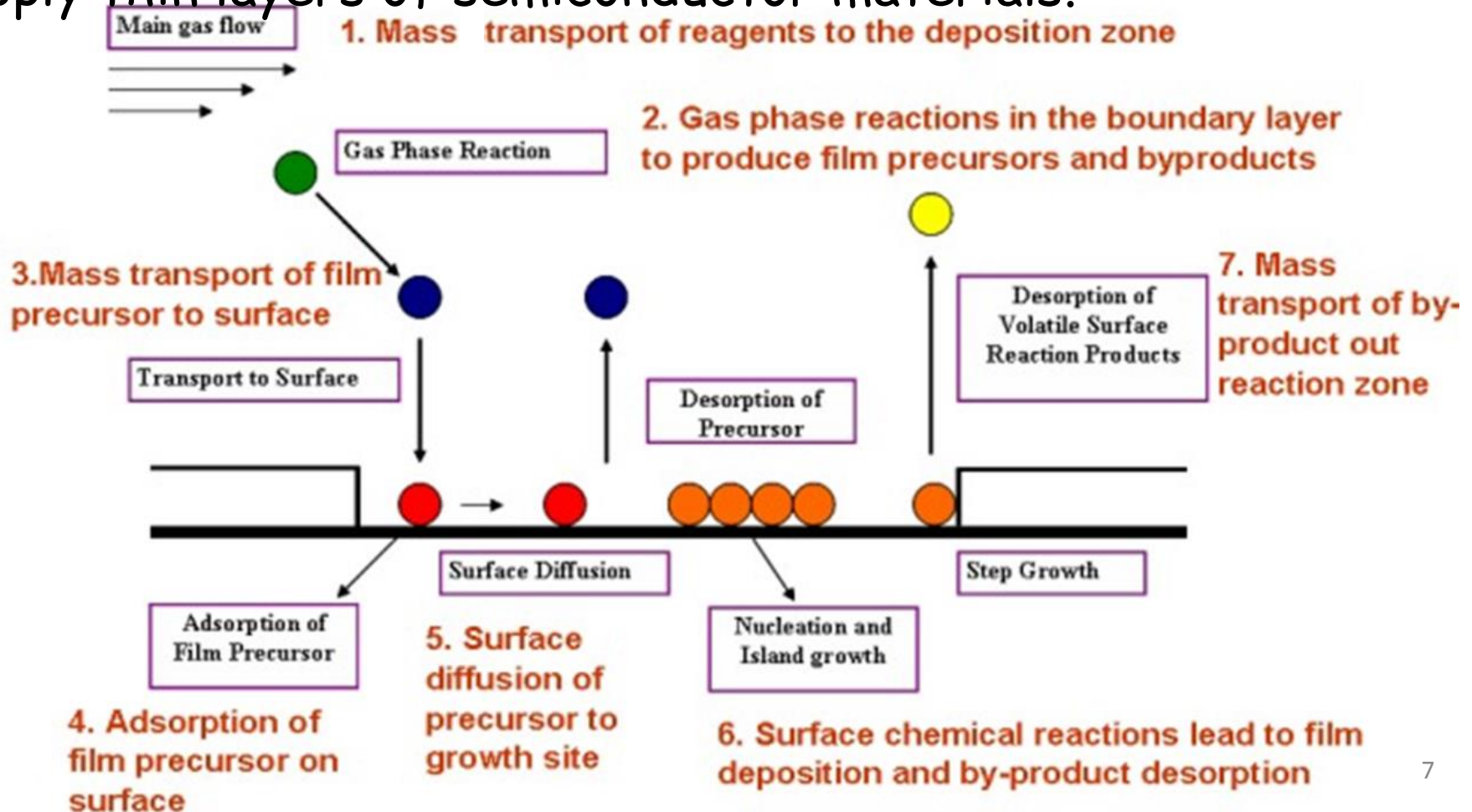
Microlithography



# Chemical Vapor Deposition Mechanism

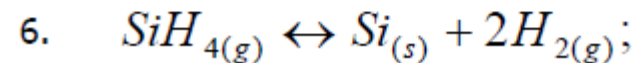
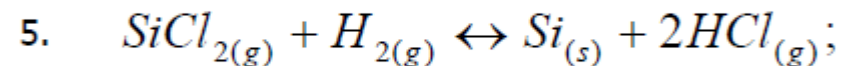
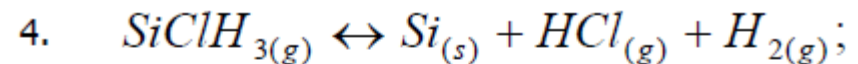
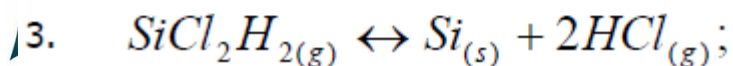
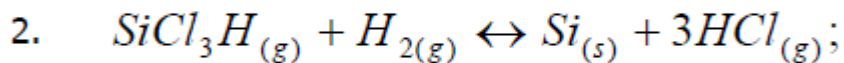
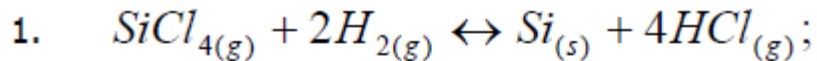
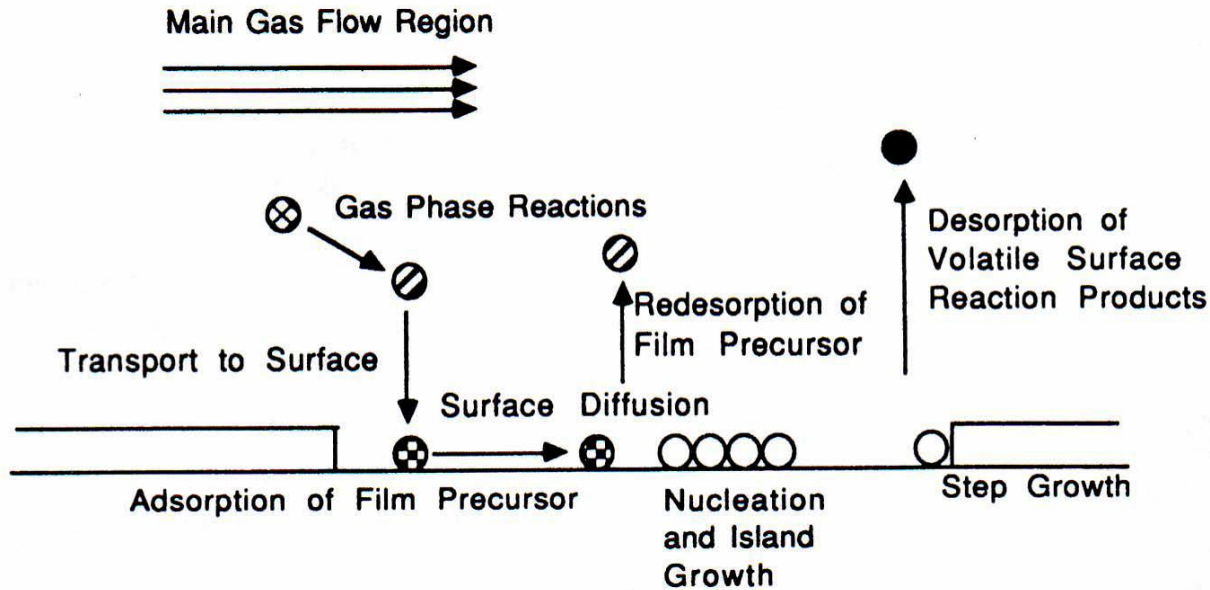
## Chemical Vapor Deposition (CVD) :

Apply thin layers of semiconductor materials.



# Transport and Reaction Processes of CVD

## CVD of Si in a Si-Cl-H system

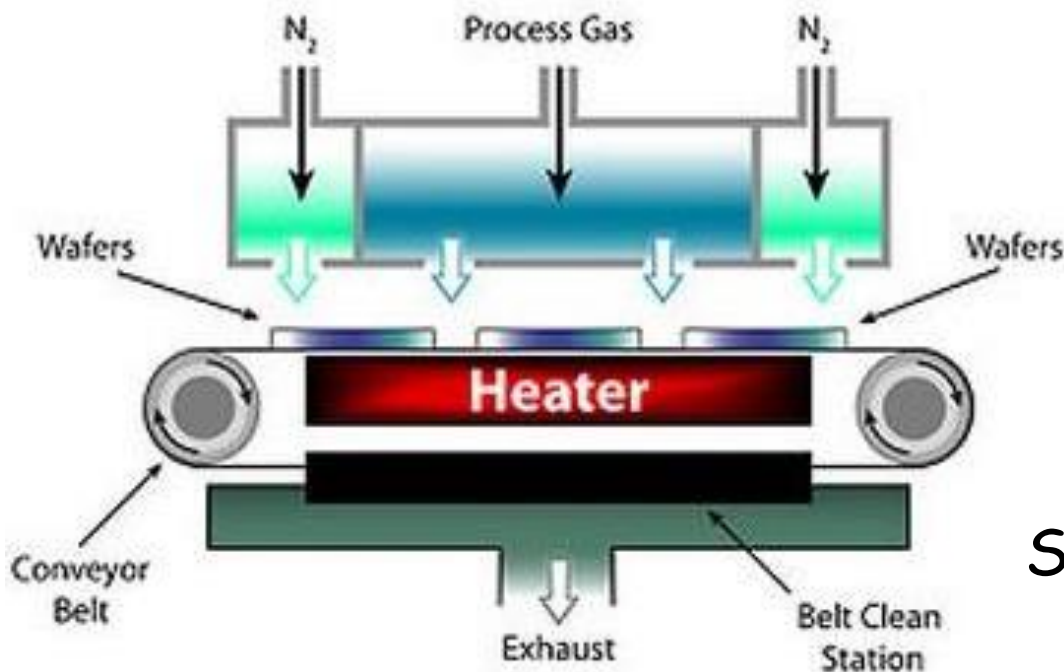




# Chemical Vapor Deposition Techniques 1

## Atmospheric Pressure Chemical Vapor Deposition (APCVD)

- Dielectrics and metals
- Atmospheric pressure or partial pressure in  $N_2$
- **Low film purity**
- Temperature of 600-1150°C

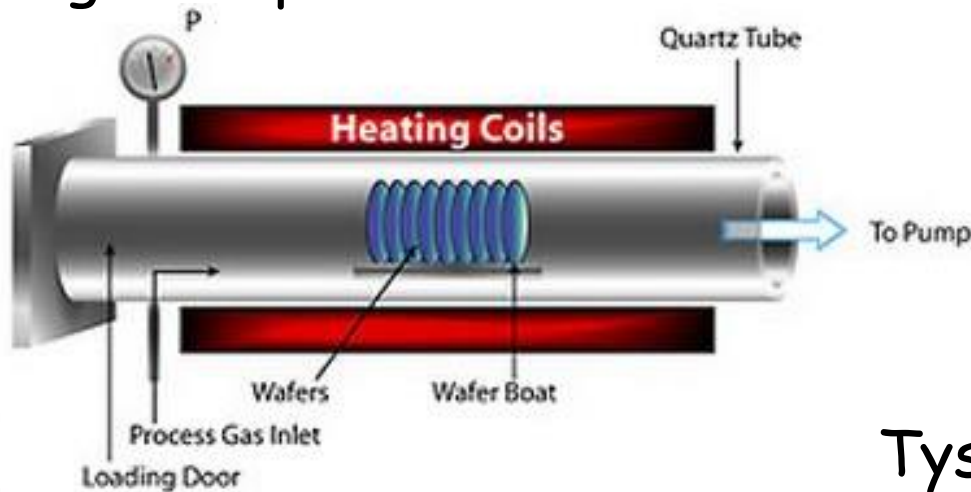


SierraTherm APCVD Furnaces

# Chemical Vapor Deposition Techniques 2

## Low-Pressure Chemical Vapor Deposition (LPCVD)

- Dielectrics and metals
- Performed at reduced pressure or "rough vacuum"
- $10^{-3}$  to  $10^{-5}$  Torr (1 atm = 760 Torr)
- **High purity**
- High temperature



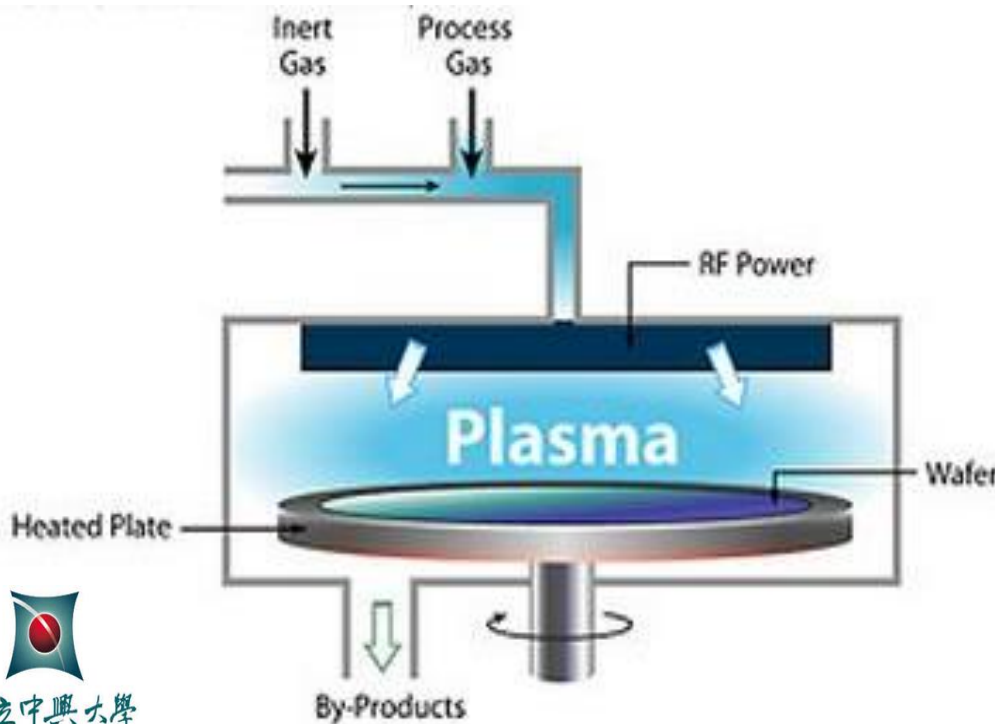
Tystar LPCVD Tube Furnaces



# Chemical Vapor Deposition Techniques 3

## Plasma Enhanced Chemical Vapor Deposition (PECVD)

- Dielectrics only
- 'High' vacuum ( $10^{-6}$  Torr)
- 300-400°C



Plasma-Therm 790 PECVD



# Chemical Vapor Deposition Techniques

## APCVD:

### Advantages:

- Relatively low operating cost since no vacuum needed

### Disadvantages:

- Uniformity of deposited layer compromised at higher temperatures and pressures
- Gas flow dynamics hard to control at high pressures

## LPCVD:

### Advantages:

- Lower reaction temperatures than APCVD reactors
- Good step coverage and uniformity
- Less dependence on gas flow dynamics

### Disadvantages:

- More expensive than APCVD reactors
- Downstream depletion can occur in horizontal designs

## PECVD:

### Advantages:

- Combination of vacuum pressures and lower temperature produces better uniformity in the deposited layer.
- Reactor can be used in other microelectronic production process steps.

### Disadvantages:

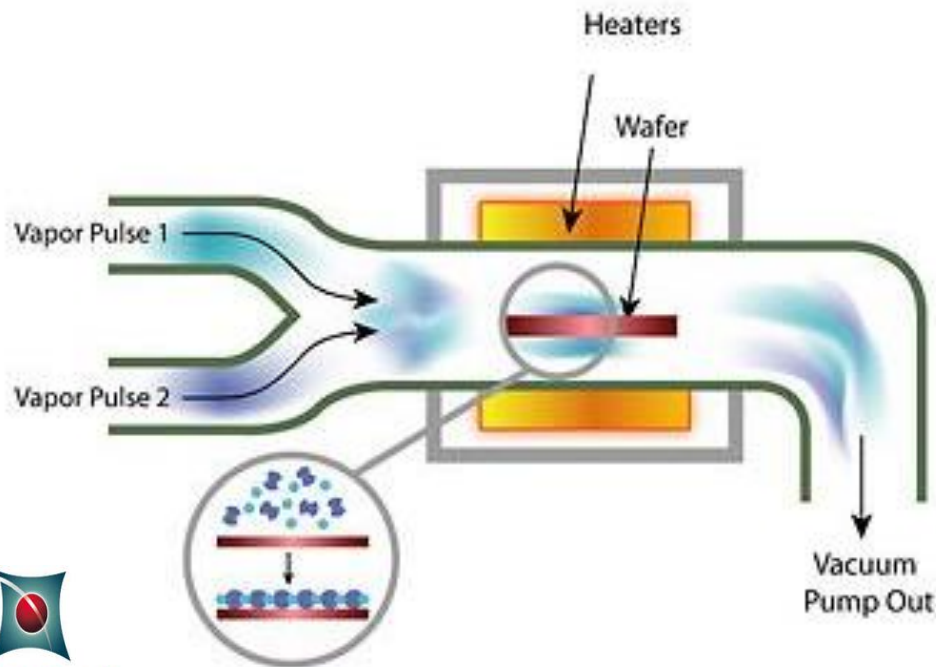
- More process variables to be controlled compared to other CVD reactors.
- Cost of operation is increased with increased number of components.



# Chemical Vapor Deposition Techniques 4

## Atomic Layer Deposition (ALD)

- Depositing one atomic layer at a time
- Highly uniform
- Process can be thermal or plasma-enhanced

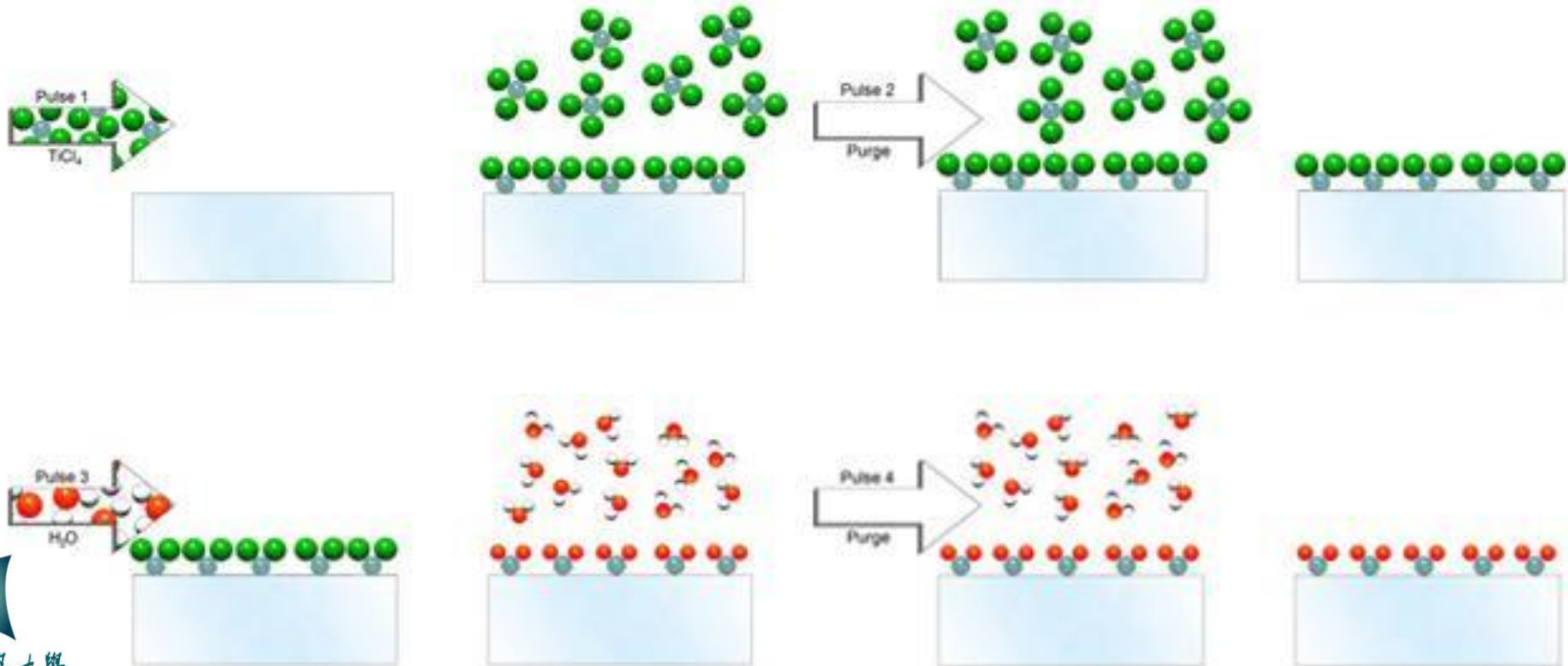


NanoTech ALD 13



# ALD Mechanism

1. Pulse of precursor is exposed to the surface.
2. Purge of excess unreacted precursor using inert gas.
3. Pulse of a second precursor followed by a surface reaction.
4. Purge of gaseous reaction by-products.



# Physical (Vapor) Deposition Mechanism

## Physical vapor deposition (PVD):

Deposit thin films by the condensation of a vaporized material onto substrate surface.

- Assure low contamination
- Large mean free path at low pressures

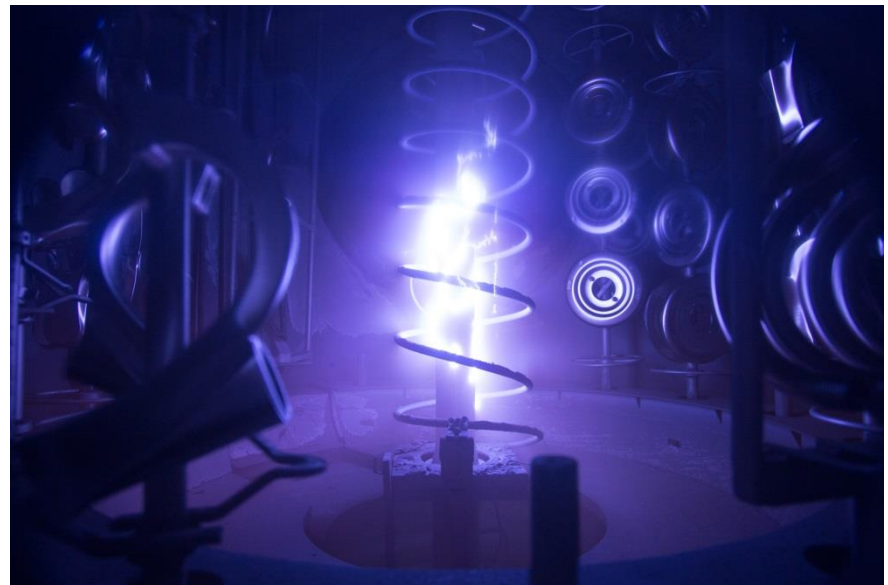
Source (Solid/Liquid)



Gas Phase



Solid Phase

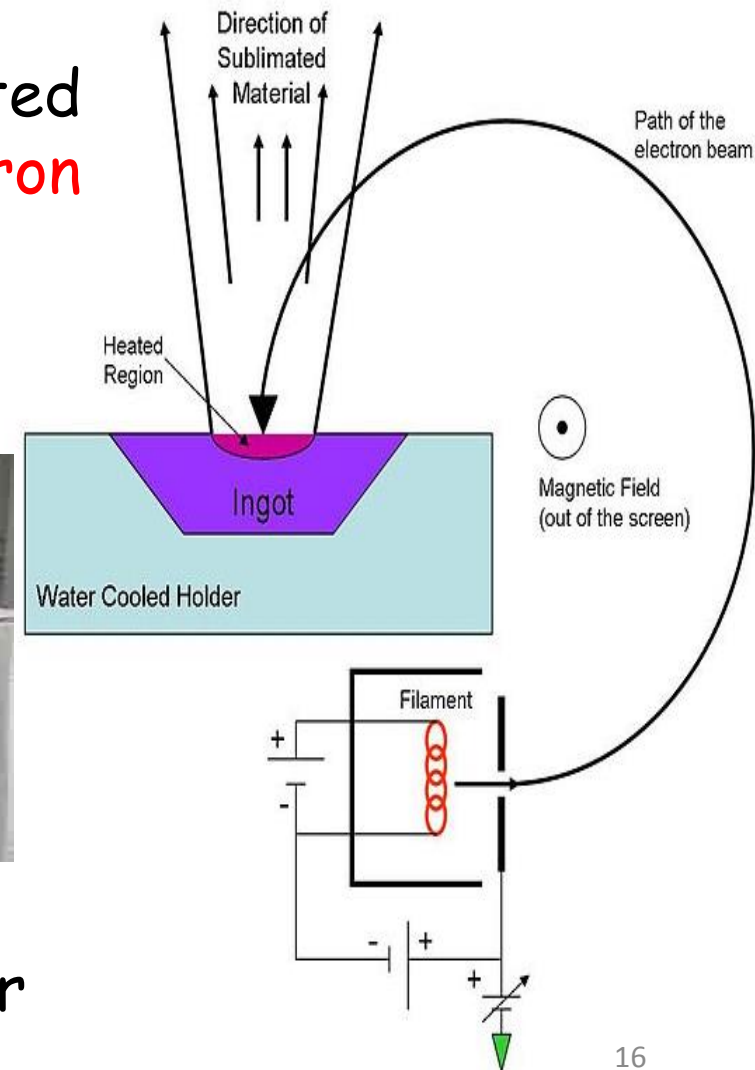


# Physical Deposition Techniques 1

## Evaporator Deposition:

The deposited materials are evaporated or sublimated, either by an **electron beam** or a **heated source**.

- Mainly metals
- High vacuum ( $10^{-6}$  Torr)



Edwards E306A

Denton DV-502A

thermal evaporator

e-beam evaporator

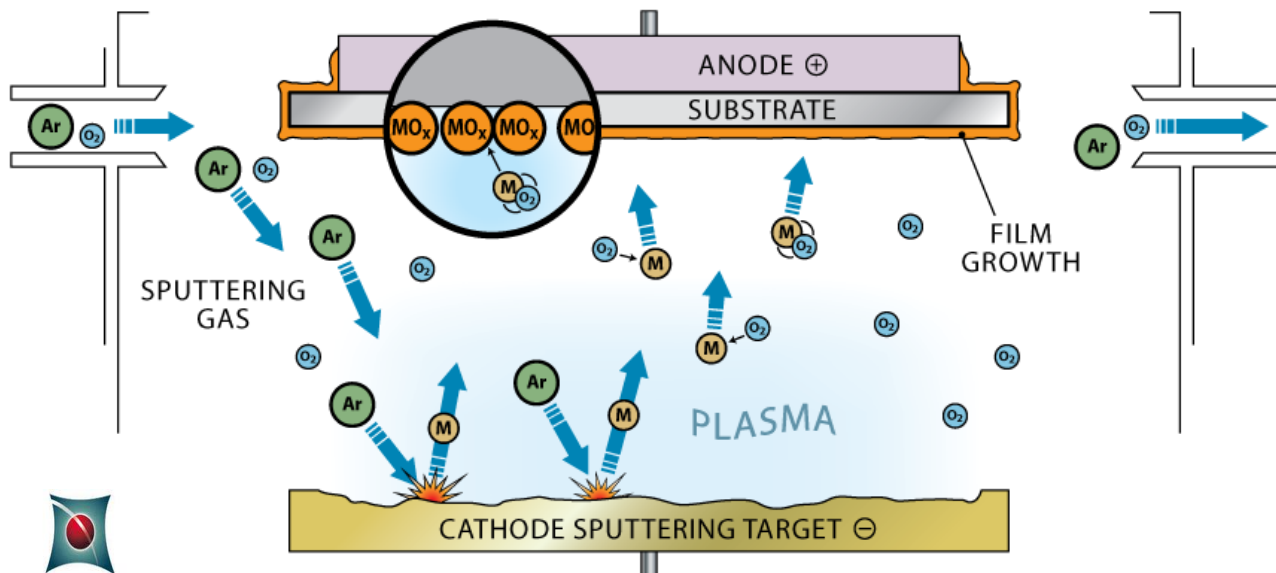


# Physical Deposition Techniques 2

## Sputter Deposition:

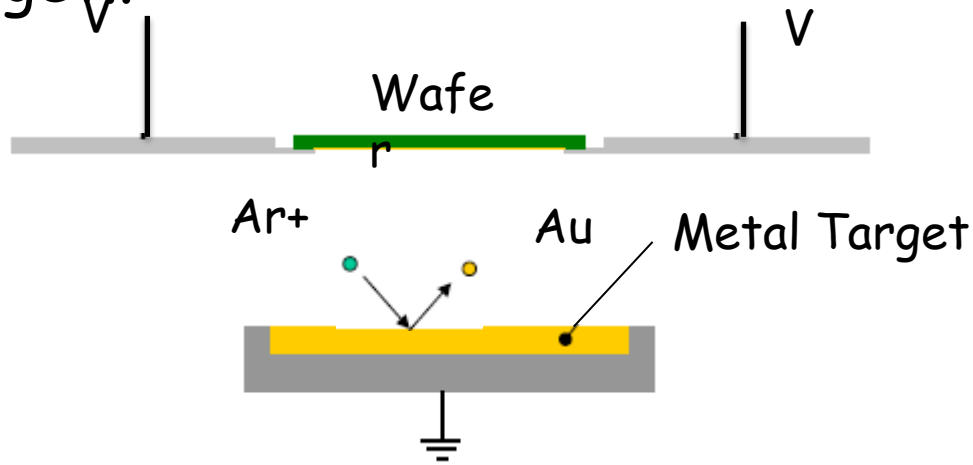
Sputtering involves the collisions of ions ( $\text{Ar}^+$ ) with target material, leading to the ejection of target atoms that are collected on a substrate.

- Metals and dielectrics
- High vacuum ( $10^{-6}$  Torr)



# Sputtering Process

A high electric field ionizes argon atoms and accelerates them into a metal target.



- Forms very uniform films
- Excellent step coverage (distributed angles of impact)
- Sputtering allows easy deposition of alloys (Al-Cu-Si)
- Wafer heating less than 300°C
- Sputtering of dielectrics uses both DC and RF fields

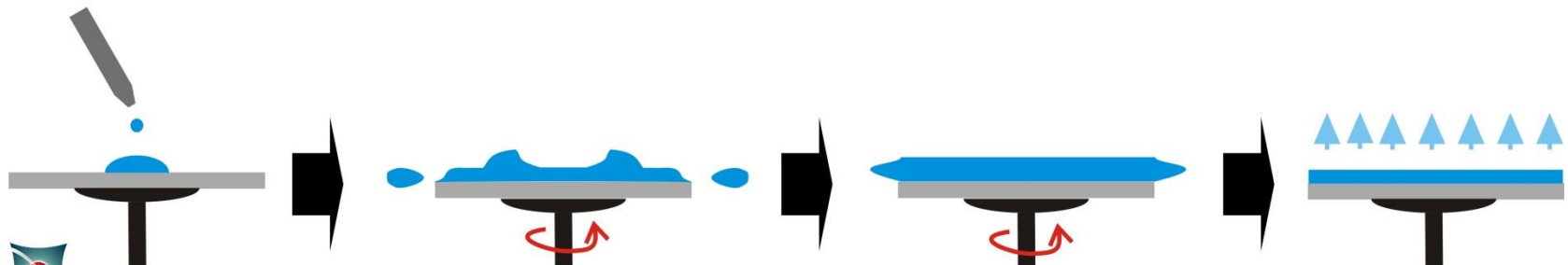


# Physical Deposition Techniques 3

## Spin-on Deposition:

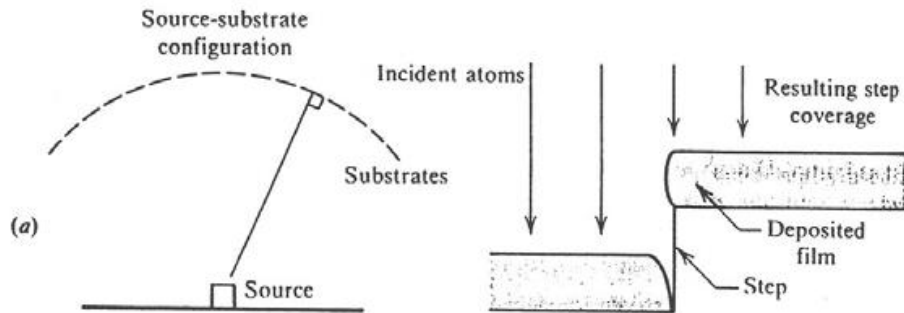
Coat the substrate with material which is originally in the **liquid form**. Liquid is dispensed onto the substrate surface and the substrate is rapidly rotated (during spinning, liquid is uniformly distributed on the surface by centrifugal forces), material is then solidified.

- Glass dielectrics
- Performed at atmosphere
- 100-1000°C

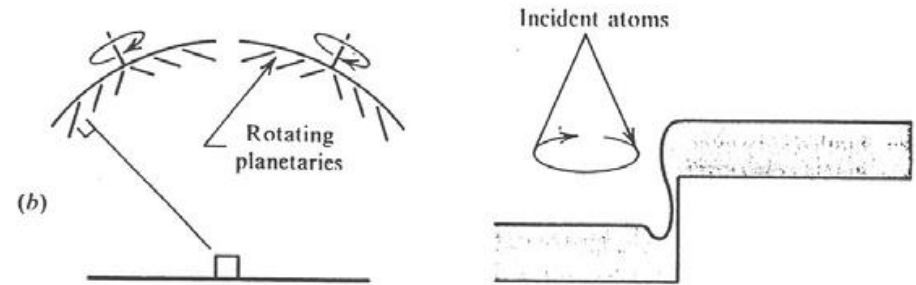


# Step Coverage in PVD

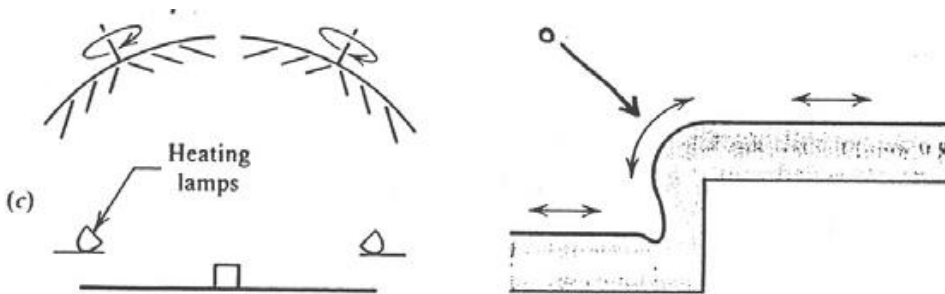
## Factors governing step coverage in evaporation:



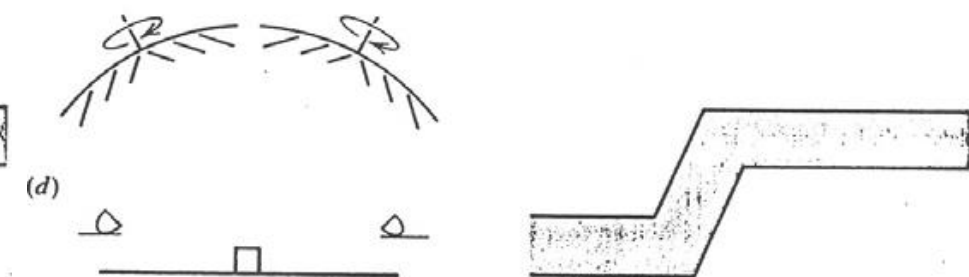
Perpendicular step on perpendicular substrate.  
No coverage.



Rotating planetaries with substrate inclination.  
Improved coverage.



Same as (b) with substrate heating.  
Further improved coverage.  
(Heat raises the surface mobility of atoms and improves step coverage)



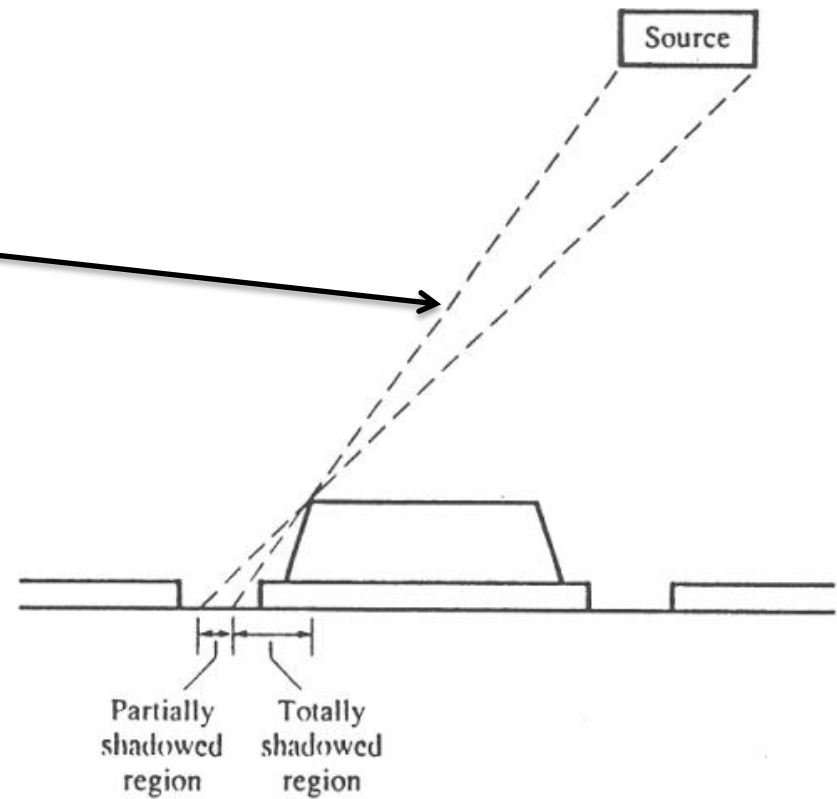
Reduced slope of step, plus rotation and heating.  
No thinning over step.

# Shadowed Deposition

Material deposition is highly dependent on the orientation angle of the samples due to the large mean free path of the depositing atoms.

Large mean free path ( $\lambda$ ) allows a direct path from source to substrate.

Great for lift-off process



# Film Etching

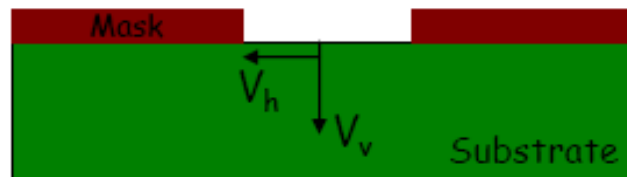
## Materials of interest:

- Conductors: Al, Cu, Au, Cr
- Dielectrics: SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, Polyimide
- Semiconductors: Si, GaAs

Etches are characterized by the **verticality** and **anisotropy**.

- If  $V_h$  is the horizontal etch rate and  $V_v$  is the vertical etch rate, the anisotropy can be given by:

$$A = 1 - \frac{V_h}{V_v}$$



- $A=1$  for fully anisotropic etches ( $V_h = 0$ )
- $A=0$  for fully isotropic etches ( $V_v = 0$ )

Etches can be performed using **chemical solutions (wet)** or **plasmas (dry)**.

# Isotropic Wet Etching

**Wet etching** of amorphous (polycrystalline) materials is usually **isotropic**, meaning no direction is favored.

- $\text{SiO}_2$ : buffered hydrofluoric acid (HF)
- $\text{Si}_3\text{N}_4$ : hot phosphoric acid (65-70 °C)
- Al: nitric/phosphoric/acetic acid (can't use if on GaAs!) or hydrochloric acid (HCl; OK on GaAs)
- PolySi: HF and nitric acid
- Cr: potassium permanganate
- Au: potassium iodide and iodine ( $\text{KI}/\text{I}_2$ )



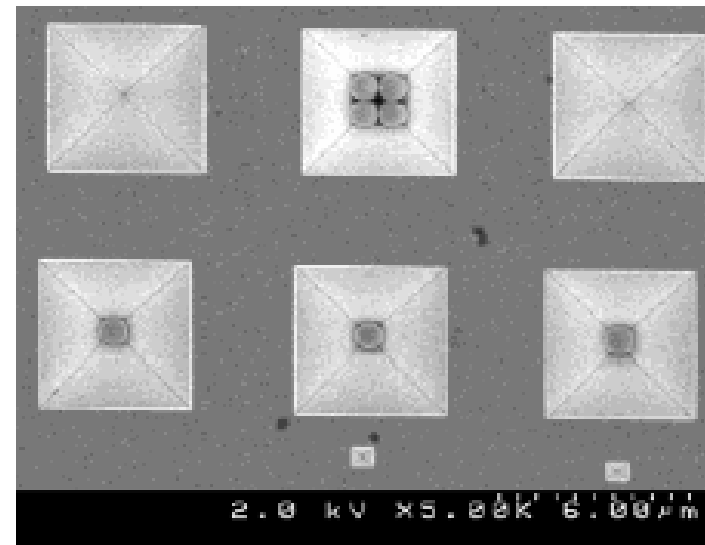
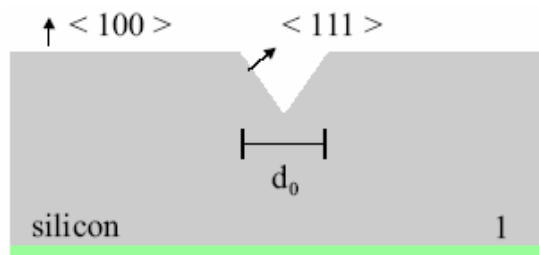
# Anisotropic Wet Etching

Wet etching of crystalline (single-crystal) materials is usually anisotropic, meaning some crystallographic directions are favored than others.

- Silicon - anisotropic etch: basis of silicon micromechanics.
- GaAs - anisotropic etch: bromine and methanol (highly exothermic!!) or hydrogen peroxide/sulfuric acid.



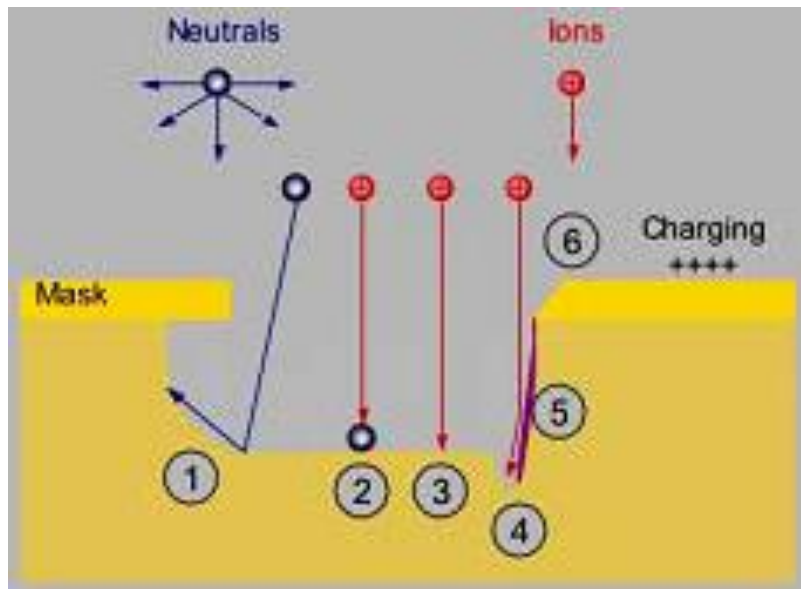
Single-crystal      Multi-crystal



Pyramid shaped pits in Si (100)



# Overview of Plasma Etch Mechanisms



## 1. Chemical etching:

Spontaneous, isotropic, very selective.

## 2. Ion enhanced etching:

Neutrals and ions involved, ion energy needed to stimulate chemical reaction or to remove reaction products. Anisotropic and selective.

## 3. Physical etching:

Anisotropic and non-selective.

## 4. Trenching:

Caused by ion deflection from sidewalls.

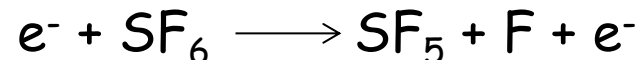
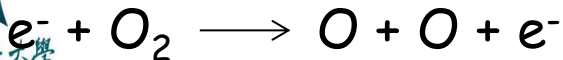
## 5. Sidewall passivation:

Deposition of non-volatile materials: Etch byproducts, surface reactions with gas or mask materials.

## 6. Mask erosion:

Caused by ion bombardment/sputtering.

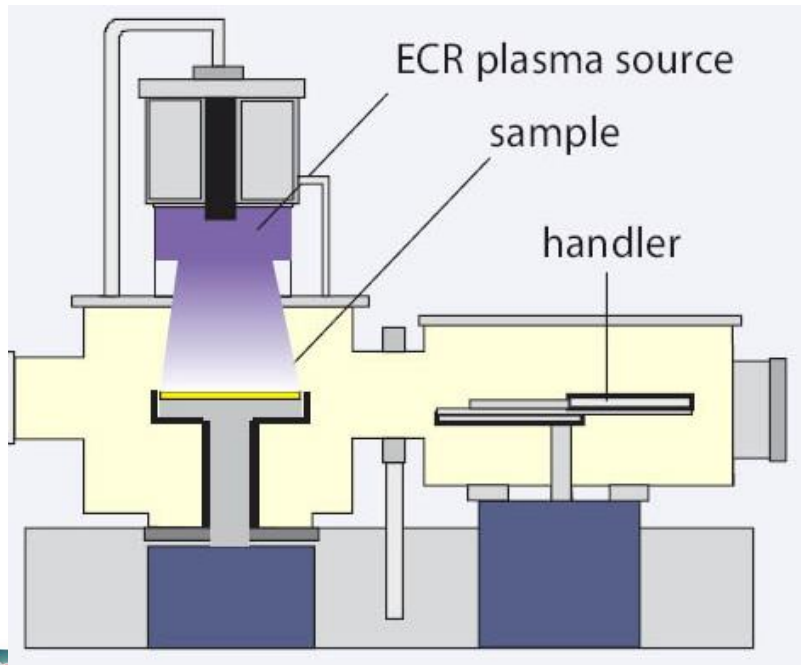
## Electron-Impact Dissociation:



# Dry Etching Techniques 1

## Reactive ion etching (RIE)

- **Isotropic**: barrel configuration (or high gas pressure)
- **Anisotropic**: parallel plate configuration



Nanotech reactive ion etcher<sup>26</sup>



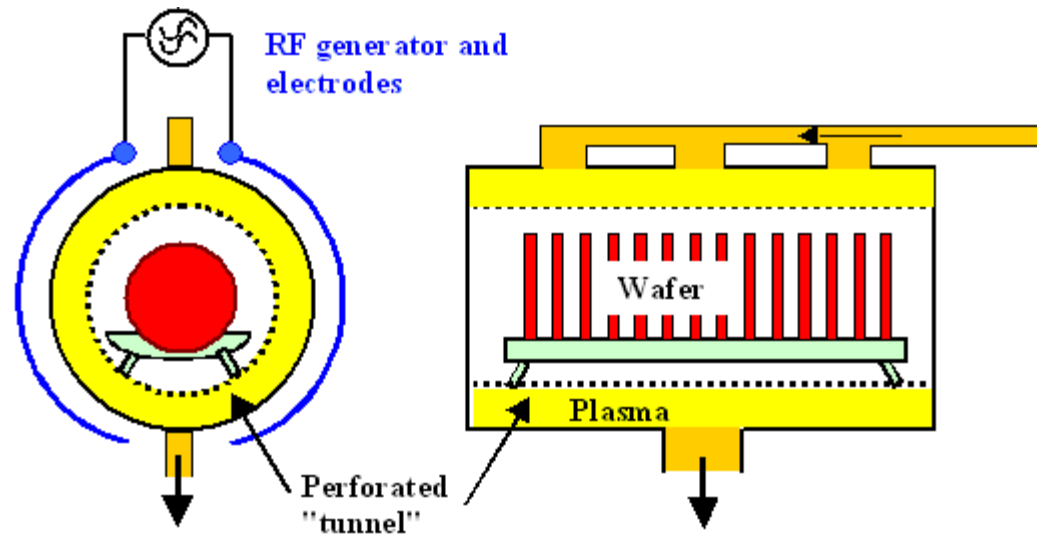
# Dry Etching Techniques 2 & 3

## Barrel etcher

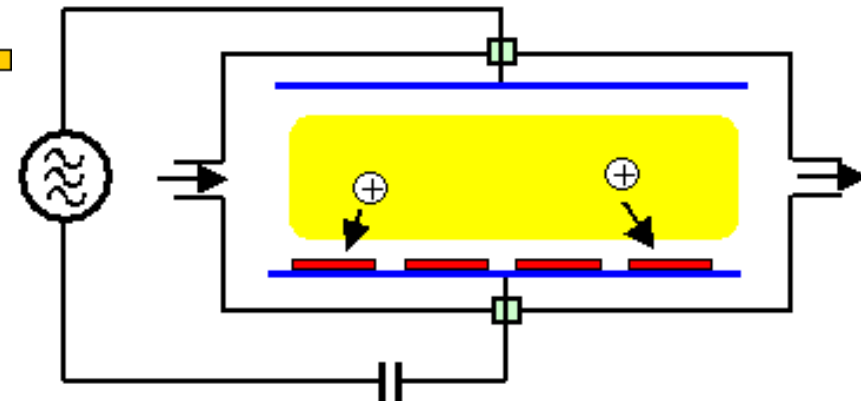
- Uniform stripping of films (e.g. resist)

## Parallel plate etcher

- High **anisotropy**



Barrel etcher



Parallel plate etcher

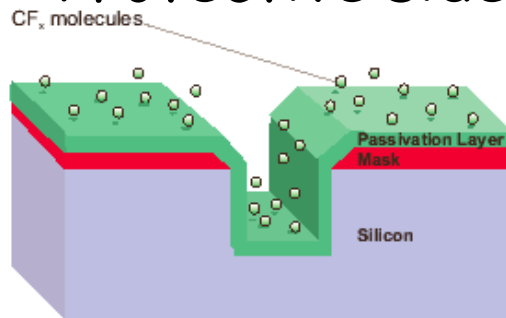


# Dry Etching Techniques 4

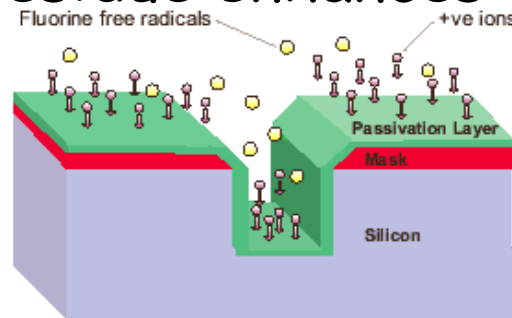
## Deep Reactive Ion Etch (DRIE)

Anisotropy arises from material processes as redeposition / passivation. Anisotropy enhanced by:

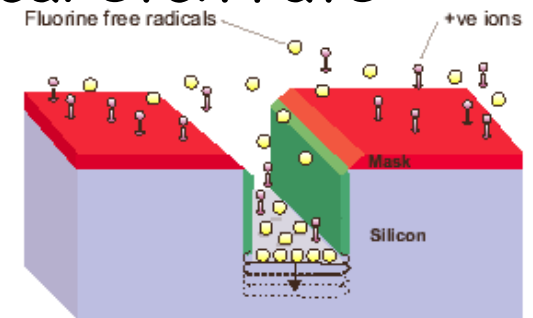
- Sputtering - physical removal of atoms
- Chemical reaction and heating due to bombardment
- Protective sidewall residue enhances vertical etch rate



**Passivation Step:** At the beginning of each cycle a  $C_4F_8$  based plasma is used to conformally deposit a few monolayers of PTFE-like fluorocarbon polymer across all surfaces exposed to the plasma.



**Etch Step 1:** The plasma gas is then switched to  $SF_6$  to create a plasma chemistry that isotropically etches silicon. Through the application of a d.c. bias to the platen, ions from the plasma bombard the surface of the wafer, removing the polymer. Increased ion energy in the vertical direction results in a much higher rate of removal of fluorocarbon polymer from surfaces parallel to the wafer surface.



**Etch Step 2:** Following selective polymer removal, the silicon surface at the base of the trench is exposed to reactive fluorine-based species that isotropically etch the unprotected silicon. The remaining fluorocarbon polymer protects the vertical walls of the trench from etching.



# Common Plasma Etchants

**Table 6-4 Plasma etchants for common microelectronic materials**

Material	Common etch gases†,‡	Dominant reactive species	Product vapor pressure (torr at 25°C)
Aluminum	Chlorine-containing	Cl, Cl <sub>2</sub>	AlCl <sub>3</sub> 7 × 10 <sup>-3</sup>
Copper	(Forms only low-pressure compounds)		CuCl <sub>2</sub> 5 × 10 <sup>-3</sup>
Molybdenum	Fluorine-containing	F	MoF <sub>6</sub> 530
Polymers of carbon	Oxygen	O	H <sub>2</sub> O 26
Silicon	Fluorine- or chlorine-containing	F, Cl, Cl <sub>2</sub>	CO, CO <sub>2</sub> > 1 atm SiF <sub>4</sub> > 1 atm SiCl <sub>4</sub> 240
SiO <sub>2</sub>	CF <sub>4</sub> , CHF <sub>3</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub>	CF <sub>x</sub>	SiF <sub>4</sub> > 1 atm CO, CO <sub>2</sub> > 1 atm
Tantalum	Fluorine-containing	F	TaF <sub>5</sub> 3
Titanium	Fluorine- or chlorine-containing	F, Cl, Cl <sub>2</sub>	TiF <sub>4</sub> sublimates at low pressure TiF <sub>3</sub> < 10 <sup>-3</sup> TiCl <sub>4</sub> 16
Tungsten	Fluorine-containing	F	WF <sub>6</sub> 1000

† Common chlorine-containing gases are BCl<sub>3</sub>, CCl<sub>4</sub>, Cl<sub>2</sub>, and SiCl<sub>4</sub>.

‡ Common fluorine-containing gases are CF<sub>4</sub>, SF<sub>4</sub>, and SF<sub>6</sub>.

Source: Reference 27. Reprinted with permission of *Solid State Technology*, published by Technical Publishing, a company of Dun and Bradstreet.



# Superhydrophobic/Self-Cleaning Coatings



**Hydrophilic**



**Hydrophobic**



# What does "Superhydrophobicity" mean?

## Hydrophilic Surface:

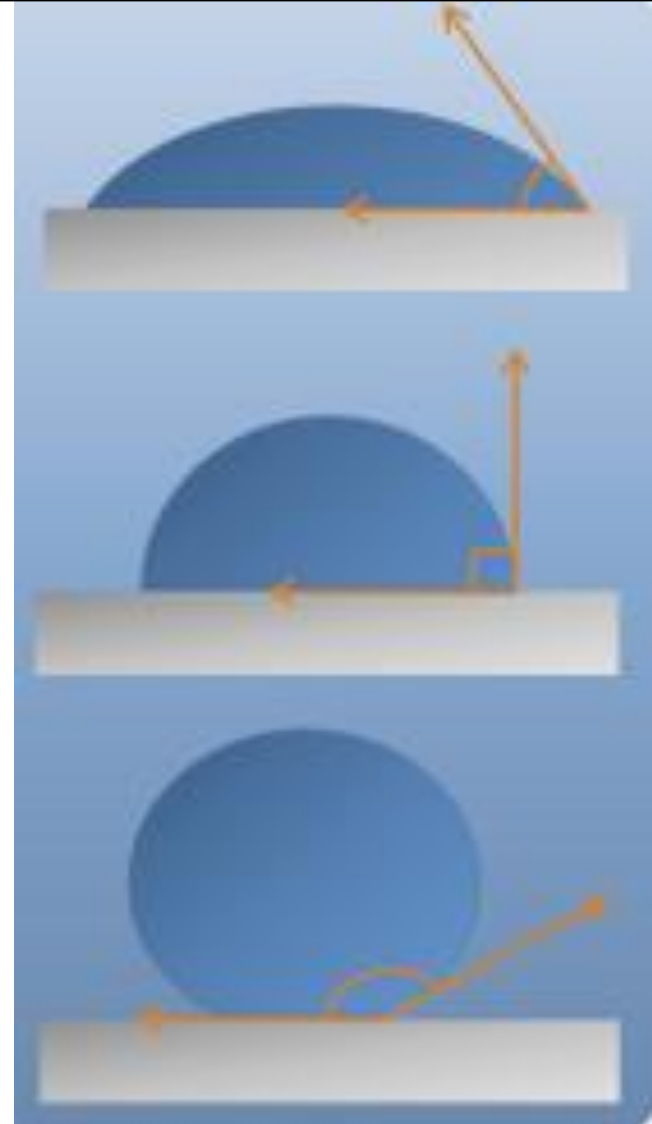
Water Contact Angle  $< 90^\circ$

## Hydrophobic Surface:

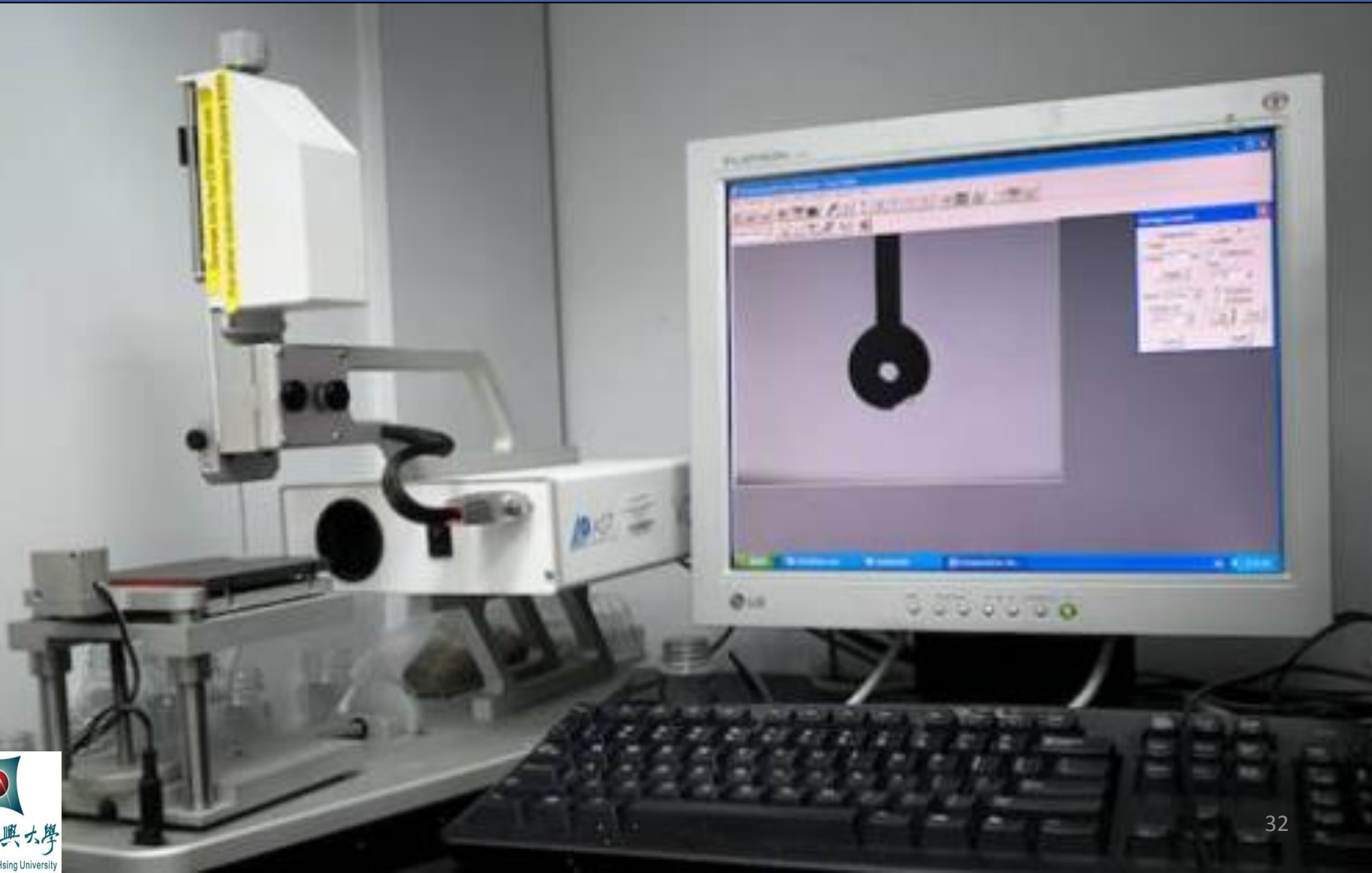
Water Contact Angle  $> 90^\circ$

## Superhydrophobic Surface:

Water Contact Angle  $> 150^\circ$



# Water Contact Angle Measurement





# Measure Water Contact Angle

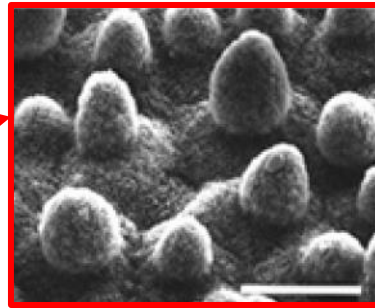
Angles: (140.40°, 140.50°)



# Superhydrophobic Surface



**Lotus Effect:** Water Contact Angle  $> 150^\circ$

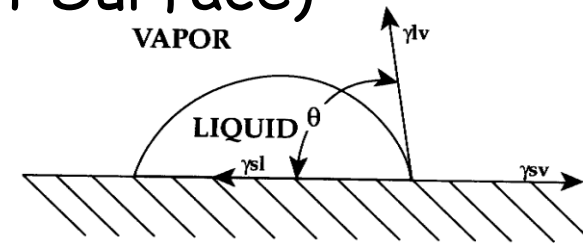


**Factors affect lotus effect:**

- Hydrophobic surface
- High surface roughness

**Young's Law:** (Hydrophobic/ Hydrophilic Flat Surface)

$$\cos \theta_y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

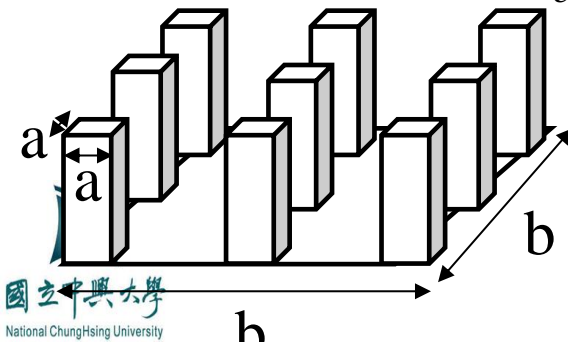
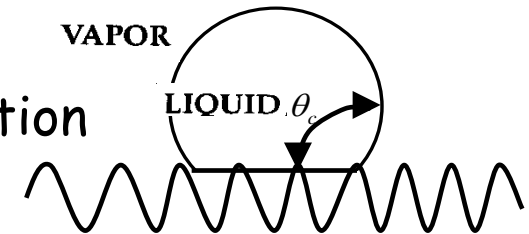


**Cassie's Law:** (Hydrophobic Rough Surface)

$$\cos \theta_c = f \cdot (\cos \theta_y + 1) - 1$$

$f$ : Solid Projected Area Fraction

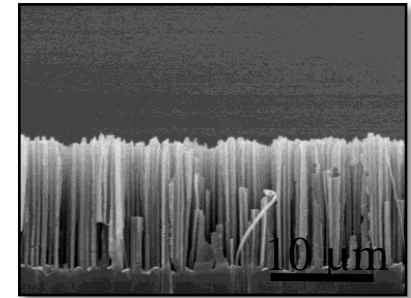
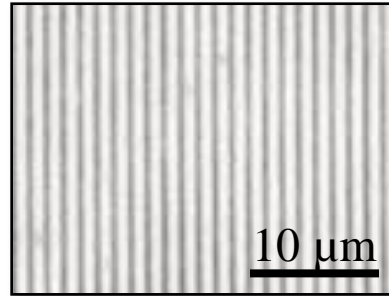
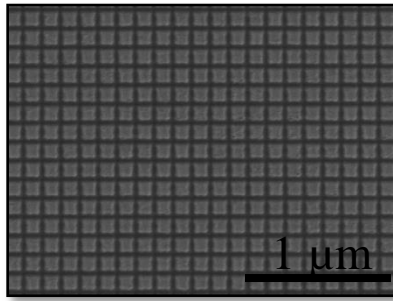
$$f = \frac{9a^2}{b^2}$$



# Superhydrophobic Coating Technologies

## Top-Down Method

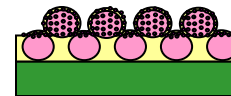
Focus Ion Beam Etching    Lithographic Patterning    Reactive Ion Etching



Principe, E L. et al, *Microscopy & Microanalysis* (2005)

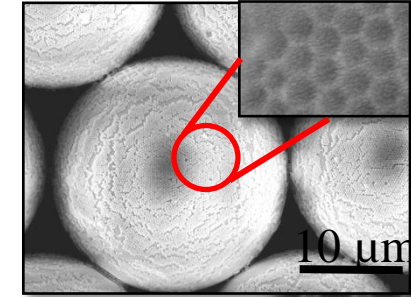
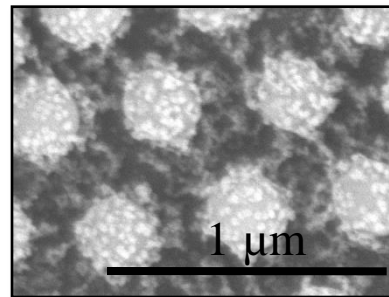
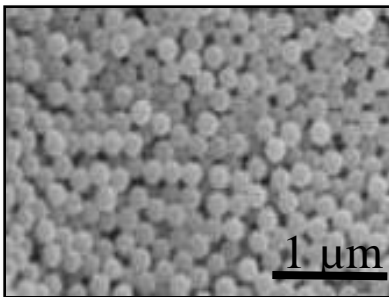
Mazur, E. et al, *Langmuir* (2006)

Yang, H. et al, Submitted (2014)



## Bottom-Up Method

Multilayer Deposition Method    Spin-coating Tech.    Langmuir-Blodgett Method



Yang, H. et al, *J. Colloid Inter. Sci.* (2008)

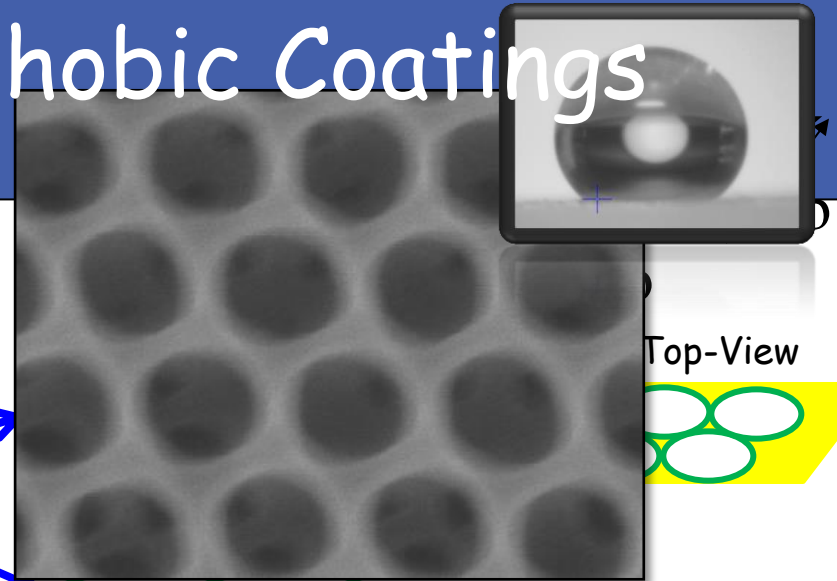
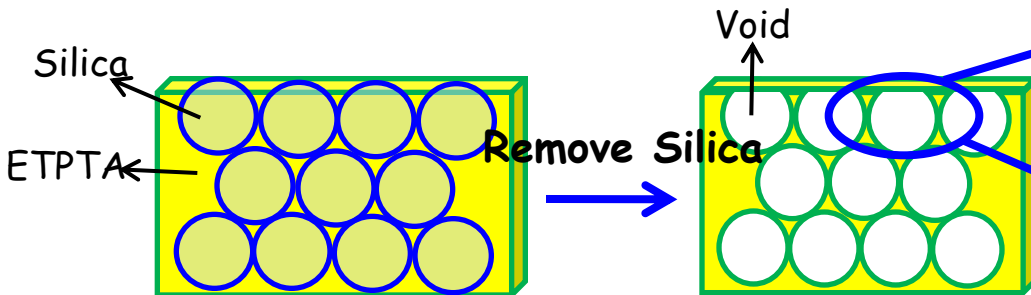
Yang, H. et al, *J. Colloid Inter. Sci.* (2010)

Yang, H. et al, Submitted (2014)

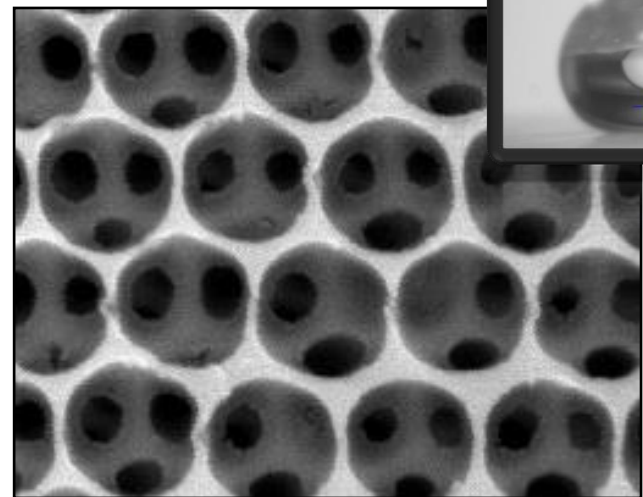
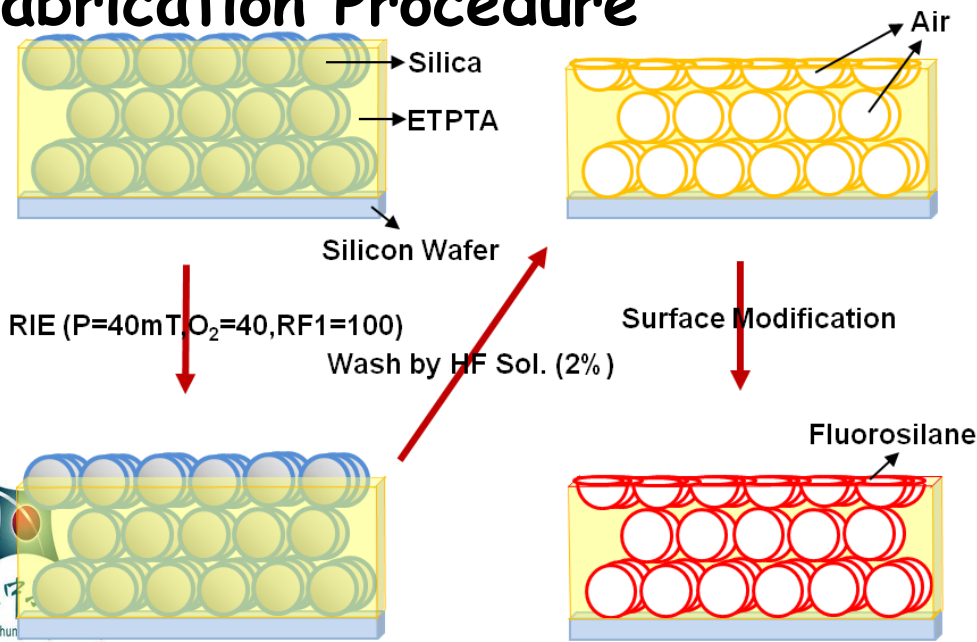
# Porous Superhydrophobic Coatings

## Cassie's Law

$$\cos \theta_c = f \cdot (\cos \theta_Y + 1) - 1$$

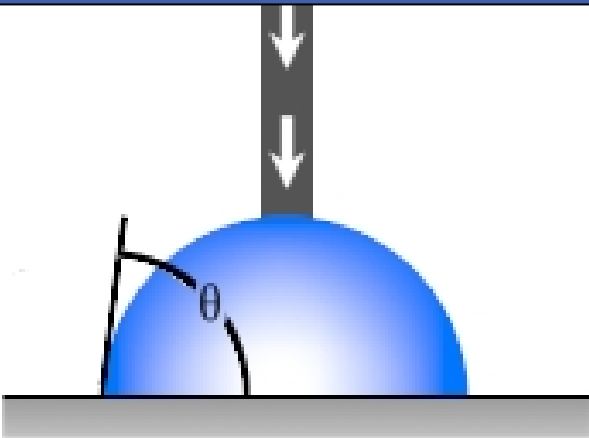


## Fabrication Procedure

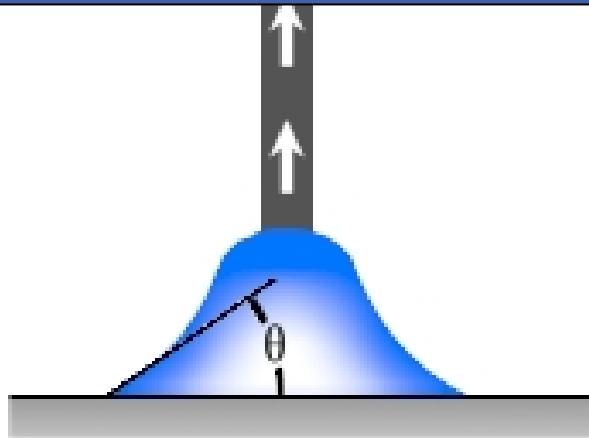


Yang, H. et al, *Langmuir* (2010)

# What does "Self-Cleaning" mean?



Advancing Angle

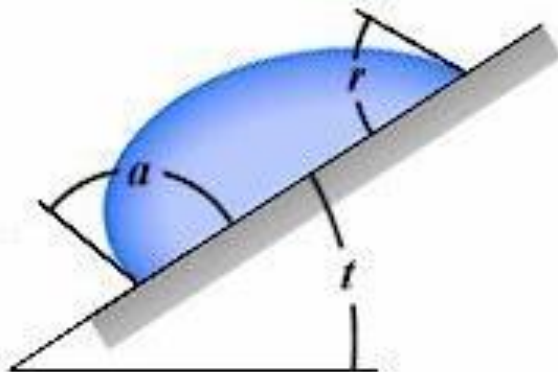


Receding Angle

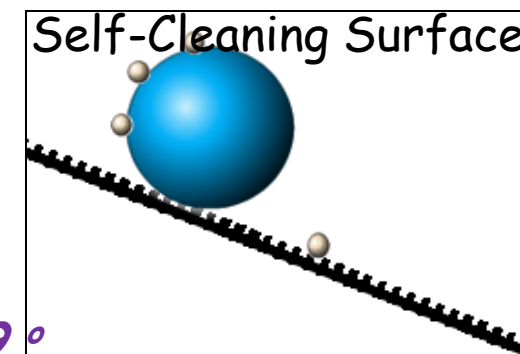
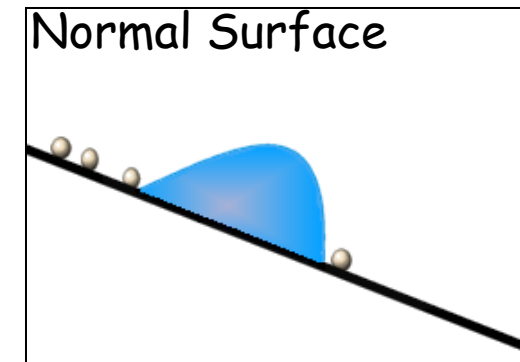
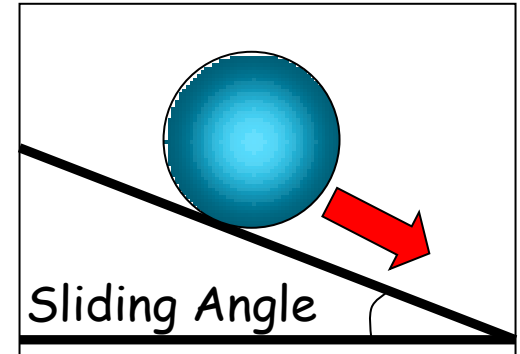
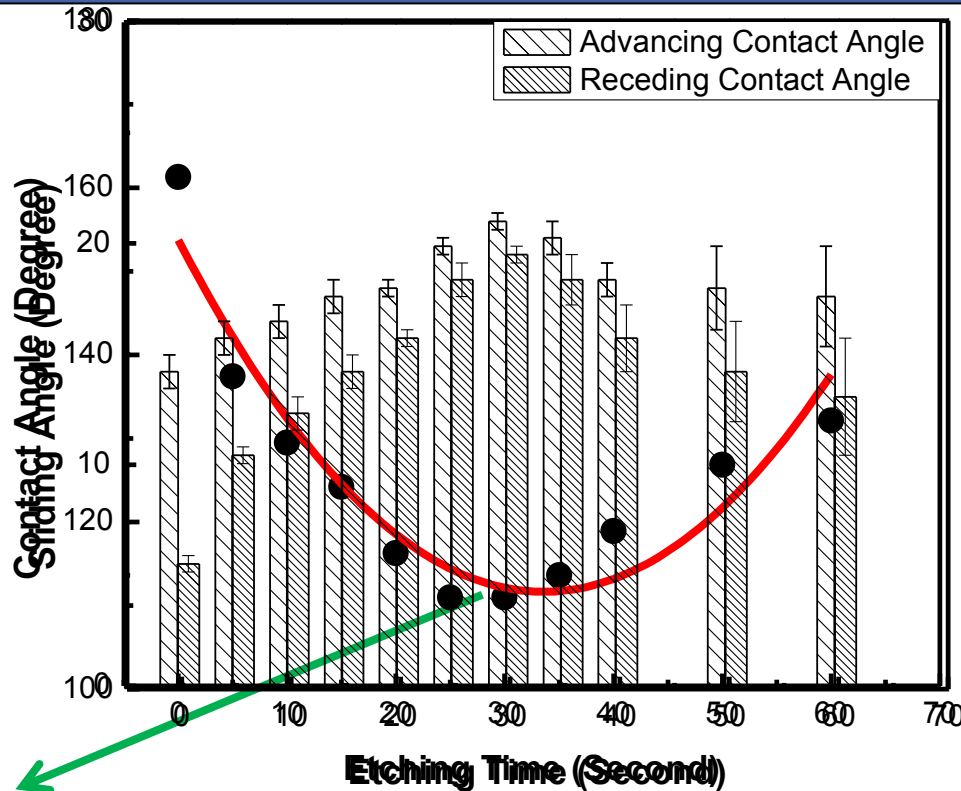


Sliding Angle

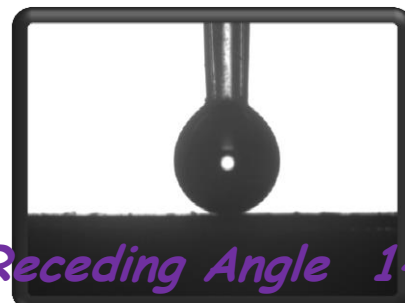
= Advancing Angle - Receding Angle



# Self-Cleaning Surface

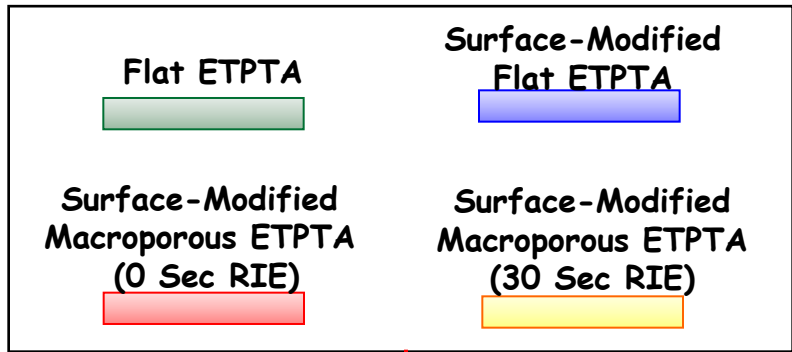
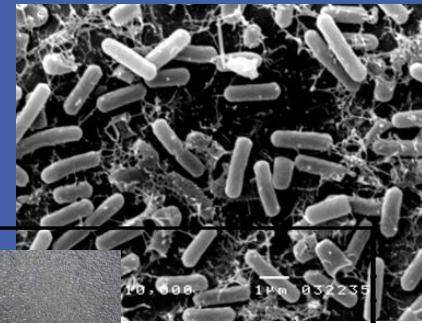


Sliding Angle = Advancing Angle - Receding Angle



Advancing Angle 154° Receding Angle 149°

# Self-Cleaning Property



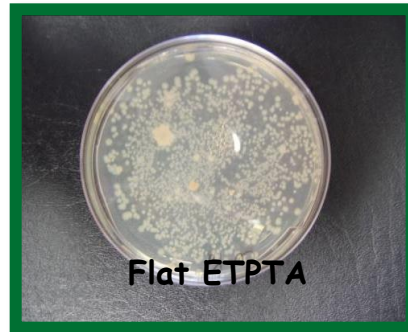
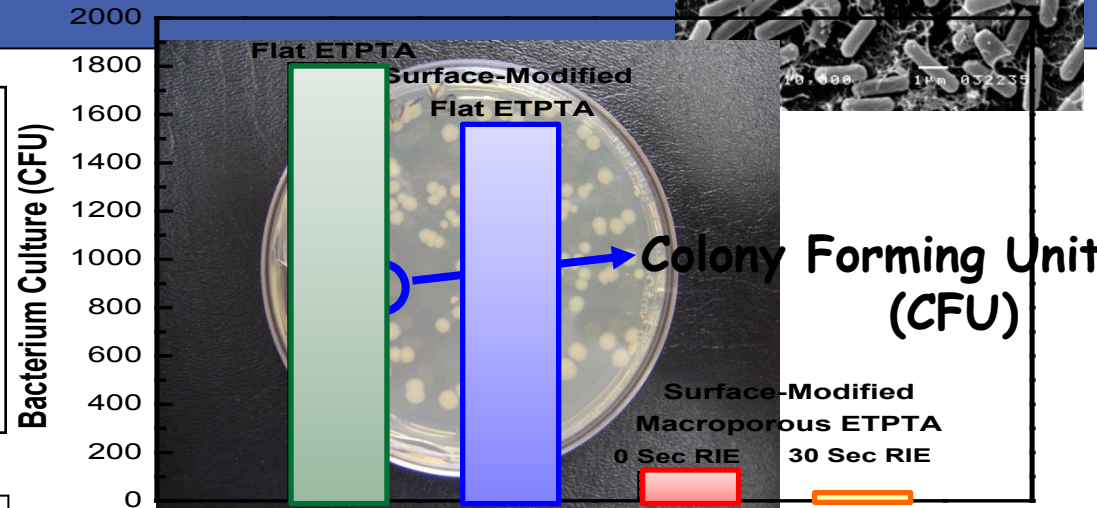
Spray Escherichia coli-ampicillin Solution

Offer an Inclining Angle of 5°

Submerge in LB Broth Medium Respectively

Culture at 37°C for 24 Hours Respectively

Account the CFU of E-coli in the LB Broth Agar Medium Respectively



# Applications of Self-Cleaning Surface

