CBM²
PRECISION MEDICINE

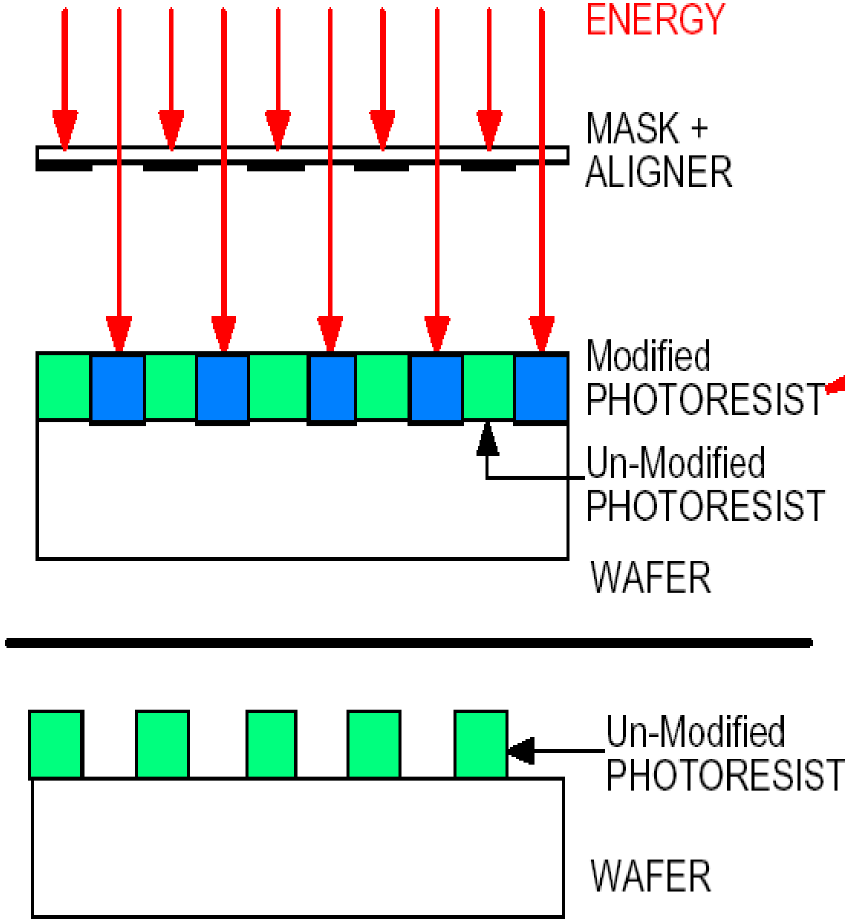
Etching and Thin Film Deposition

Prof. Steven Soper

NIH
NIBIB

THE UNIVERSITY OF KANSAS

What Happens After We Do Photolithography?



ENERGY

MASK +
ALIGNER

Modified
PHOTORESIST

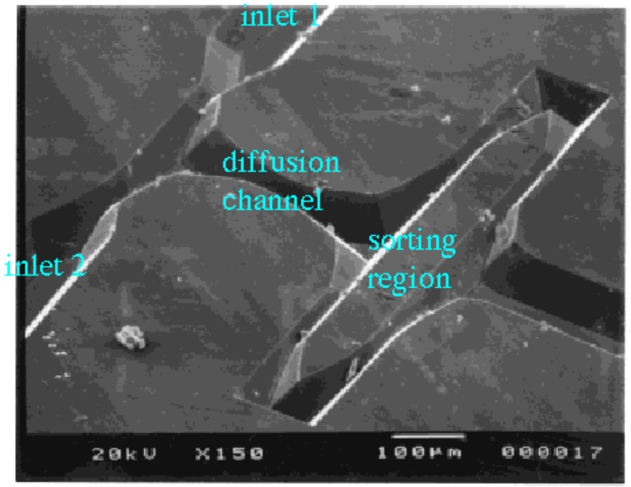
Un-Modified
PHOTORESIST

WAFER

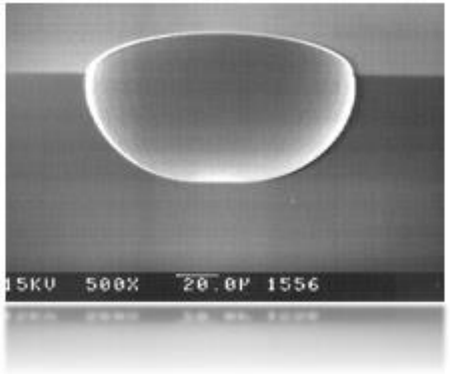
Un-Modified
PHOTORESIST

WAFER

Modified PHOTORESIST
removed after development

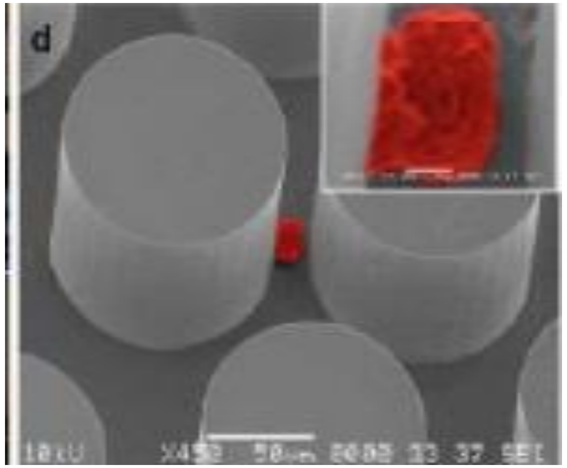


Wet Etching
(anisotropic)



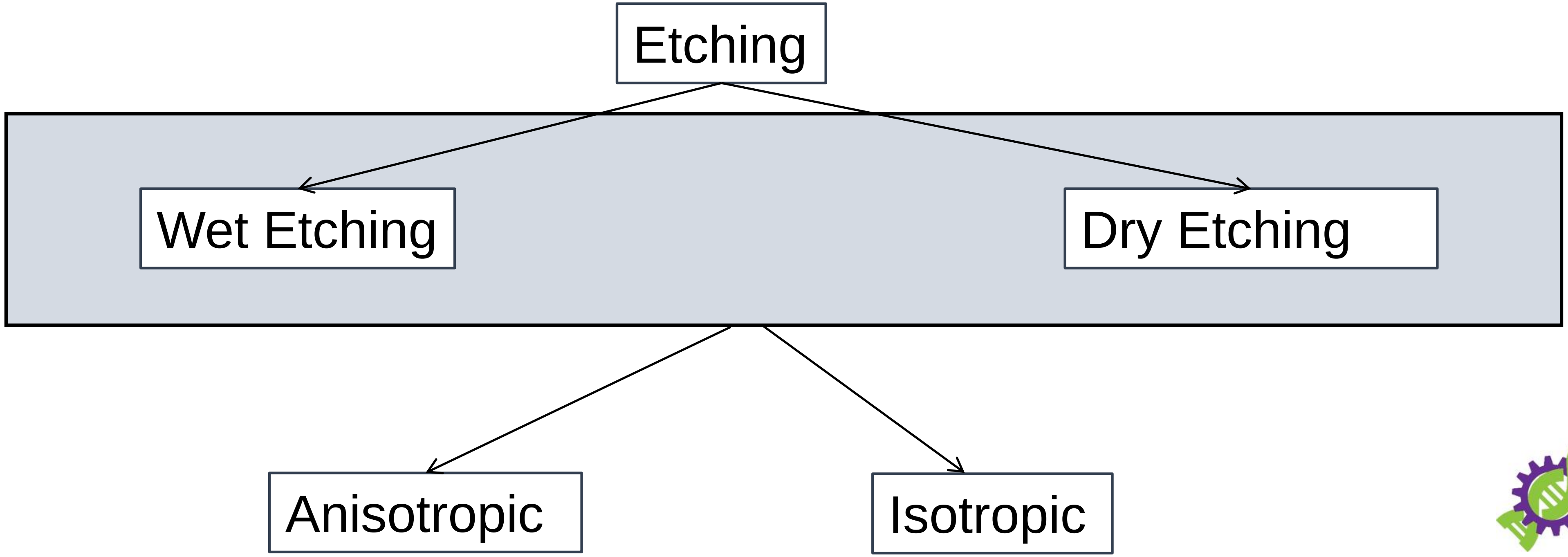
Wet Etching
(isotropic)

Dry Etching



Etching

- Pattern transfer by chemical/physical removal of material from substrate where pattern is defined by a protective layer (photoresist, oxide, metal)
- Subtractive/Top-down process in which bulk material is removed to create smaller structures



Etching Metrics

Etch Rate

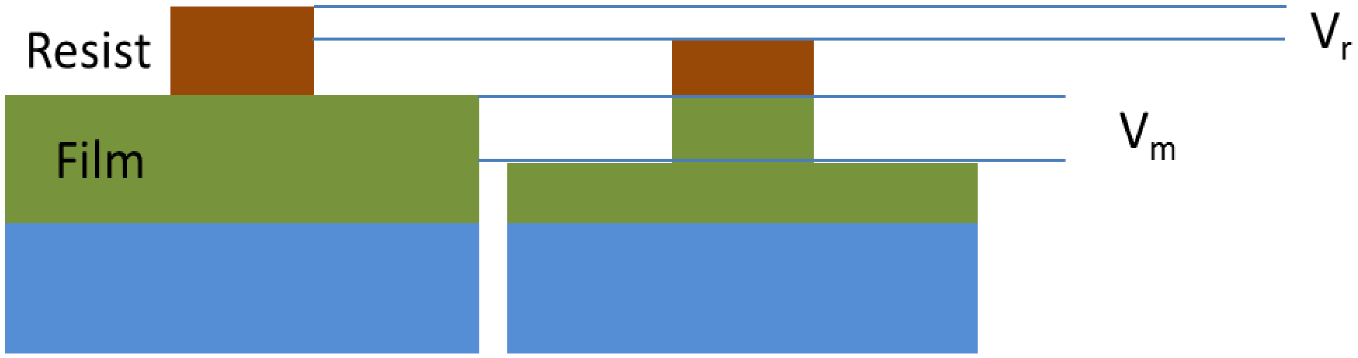
- Etched depth per unit time
- If it’s too high, difficult to control

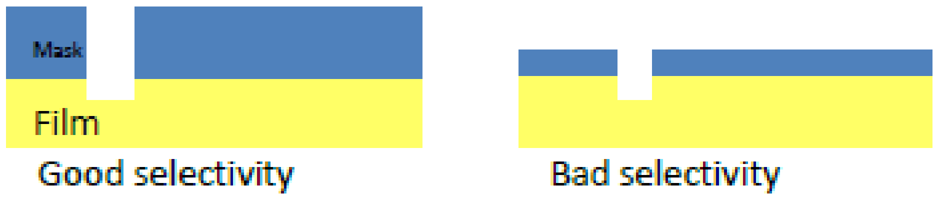
Uniformity – Percentage variation of etch across the wafer

Selectivity

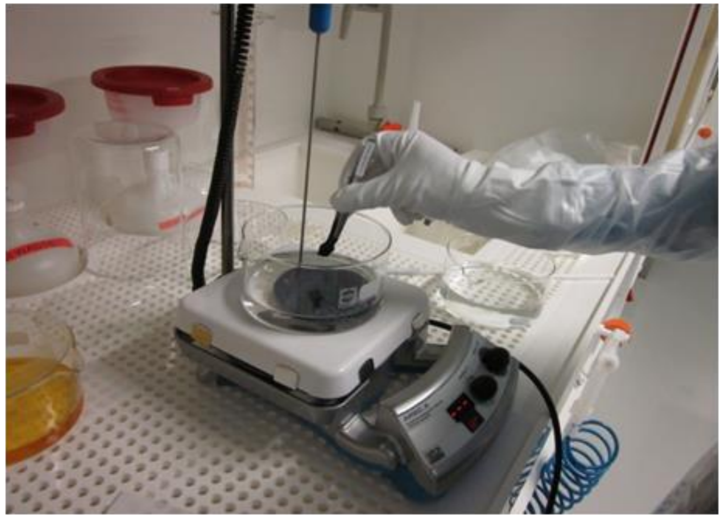
- Ratio of etching rate between different materials, usually the higher the better
- Generally, chemical etching has higher selectivity, physical etching (sputtering, ion milling) has low selectivity

$$\text{Etch selectivity} = \frac{\text{Etch rate of material we want to remove } (V_m)}{\text{Etch rate of masking material } (V_r)}$$





Wet Etching and Dry Etching



Wet etching

- Substrate is placed in chemical solution and material is removed via chemical reaction
- Benchtop process

Dry etching

- Substrate is placed in chamber (typically gas in vacuum) .
- Etch species are accelerated towards surface to remove material via chemical and physical mechanisms
- More complex/expensive machinery than wet etching

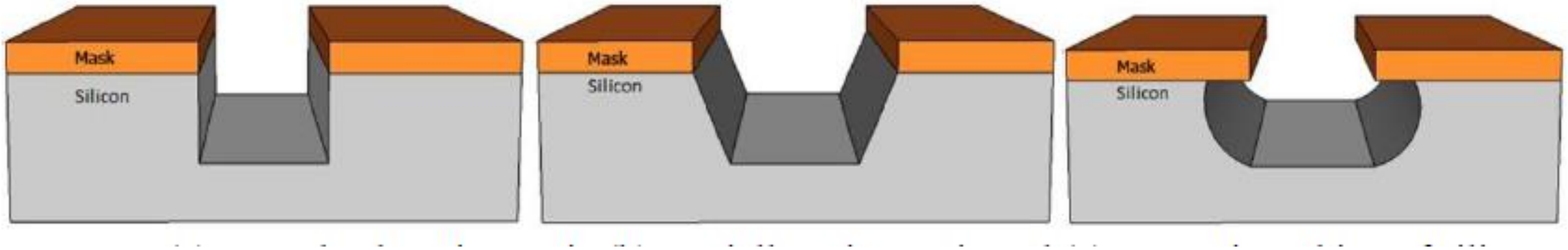
Types of Etching Processes

- **Anisotropic:**
  - Uniform etch rates in all directions (orientation dependent) A=1
  - Dry etching profiles are anisotropic
  - Best for making small gaps and vertical sidewalls
  - Typically more costly

$$Anistrophy, A = 1 - \frac{R_L}{R_v}$$

R_L – Lateral etch rate
R_V – Vertical etch rate

- **Isotropic:**
  - Different etch rates in vertical and lateral directions (orientation independent) i.e A=0
  - Wet etching profiles are isotropic except for etching crystalline material.
  - Best to use with large geometries, when sidewall slope does not matter, and to <u>undercut</u> the mask
  - Quick, easy, cheap



(a) (b) (c)

(a) Completely anisotropic (b) Partially anisotropic (c) Isotropic

"How to Make It and How to Use It", The University of Kansas, Lawrence, KS August 2019

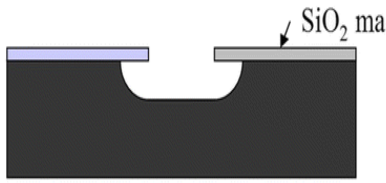
Wet Etching in Microfluidics - Silicon

Wet Etching of Silicon can be isotropic or anisotropic (orientation dependent) depending on the etchant used

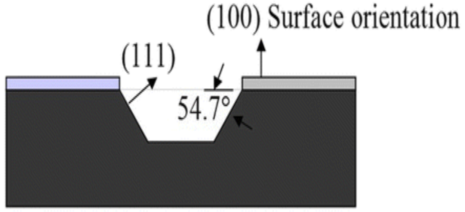
Isotropic

- Wet etching of Si recommended when dry process is not available
- Performed with HNA: HNO_3, HF, and acetic acid (up to 50 µm/min)
- HNO_3: oxidizes Si, HF: dissolves the generated oxide layer, acetic acid is diluent
- Best masking material for HNA: Si_3N_4 or SiO_2

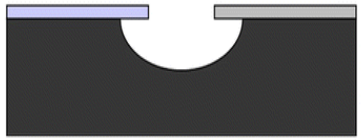
Isotropic wet etching with agitation



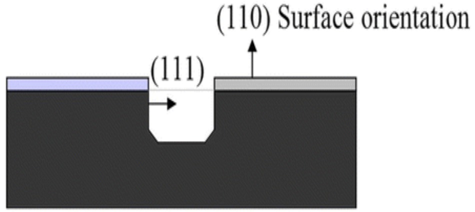
Anisotropic wet etching on (100) silicon



Isotropic wet etching without agitation

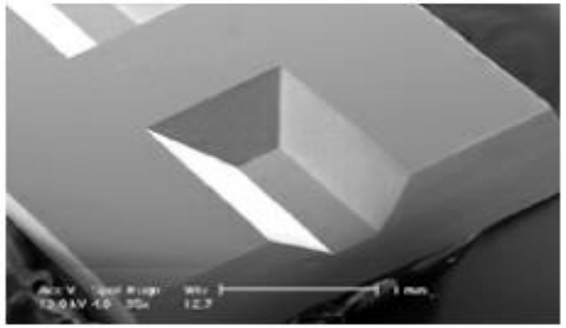


Anisotropic wet etching on (110) silicon

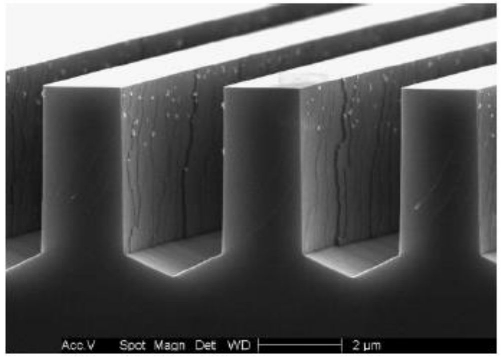


Anisotropic

- Etch rate depends on crystalline orientation
- Typical solution is KOH > 20% at elevated temperature (80-90 C)
- Relative etch rates: (110) > (100) > (111)
- Etch ratio of (100): (111) crystallographic planes is ~400:1
- Also common is 40% tetramethylammonium hydroxide (TMAH) and ethylenediamine pyrocathecol (EDP)
- Can create an etch stop by doping with boron



Anisotropic etch in Si(100) with KOH

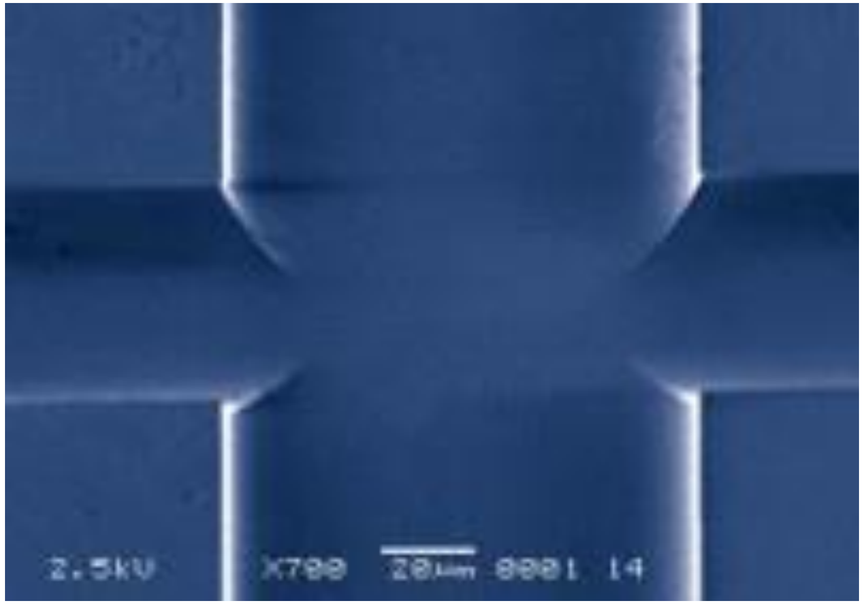


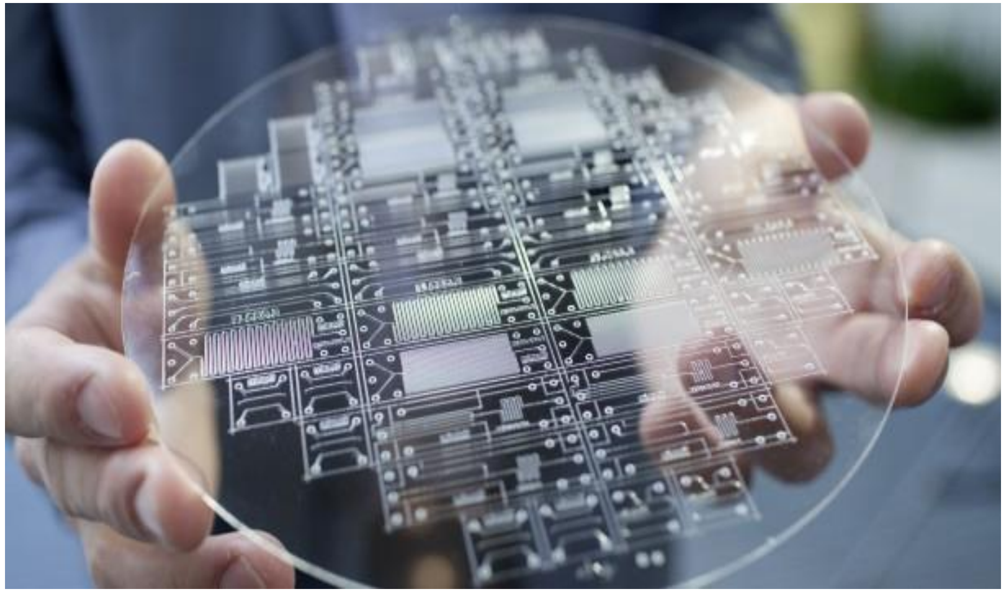
Anisotropic etch in Si(110) with KOH

“How to Make It and How to Use It”, The University of Kansas, Lawrence, KS August 2019

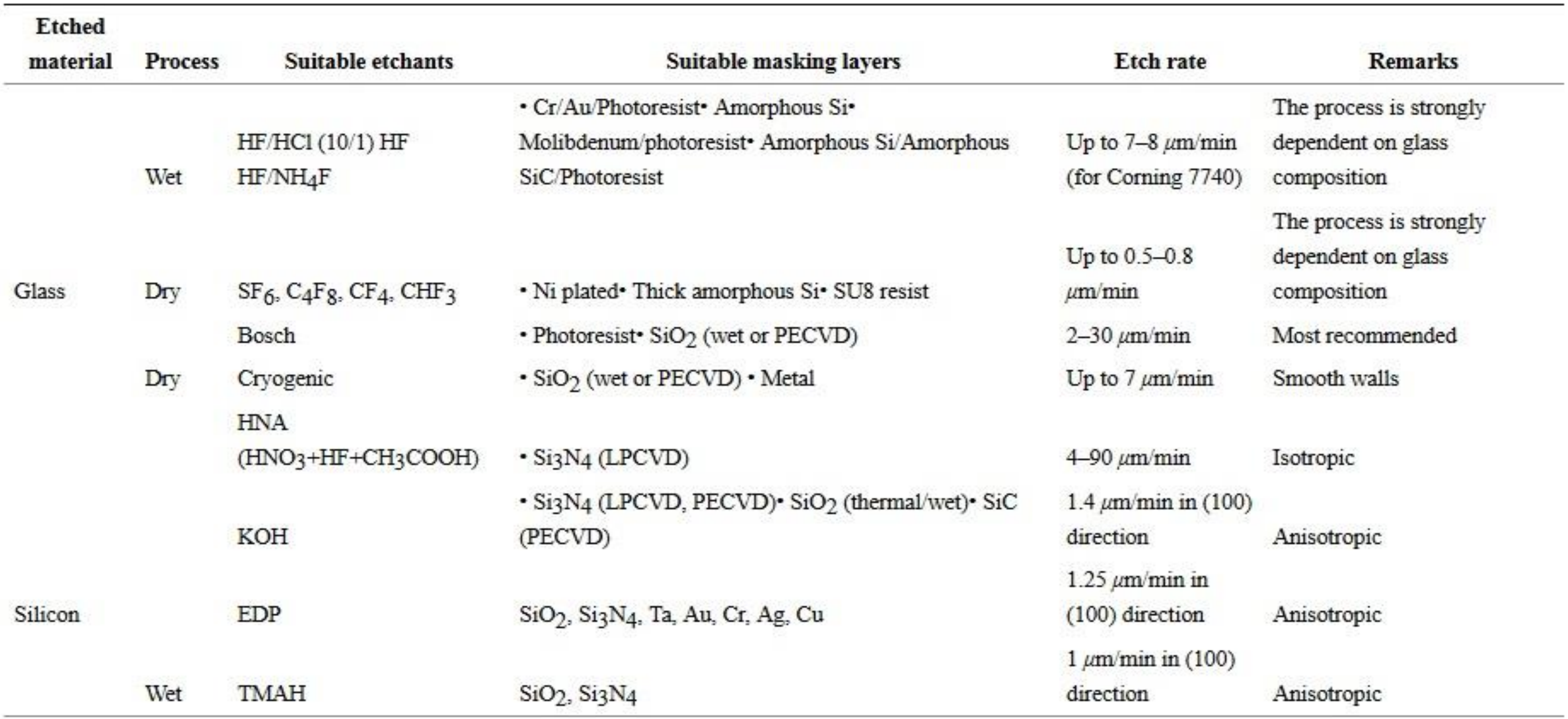
Wet Etching in Microfluidics - Glass

- Purely isotropic etch profiles
- Etched with solutions of hydrofluoric acid (HF) (up to 8 µm/min)
- Glass is a mixture of oxides (CaO, MgO, Al_2O_3) whose composition affects etching behavior
- HCl or H_3PO_4 can be added to remove insoluble products and improve etch quality (rate, morphology)
- Choice of masking layer is important to avoid pinholes and delamination. Options include:
  - Photoresist
  - Amorphous Si
  - Cr/Au
  - Cr/photoresist





Glass and Si WET Etchants for Microfluidics

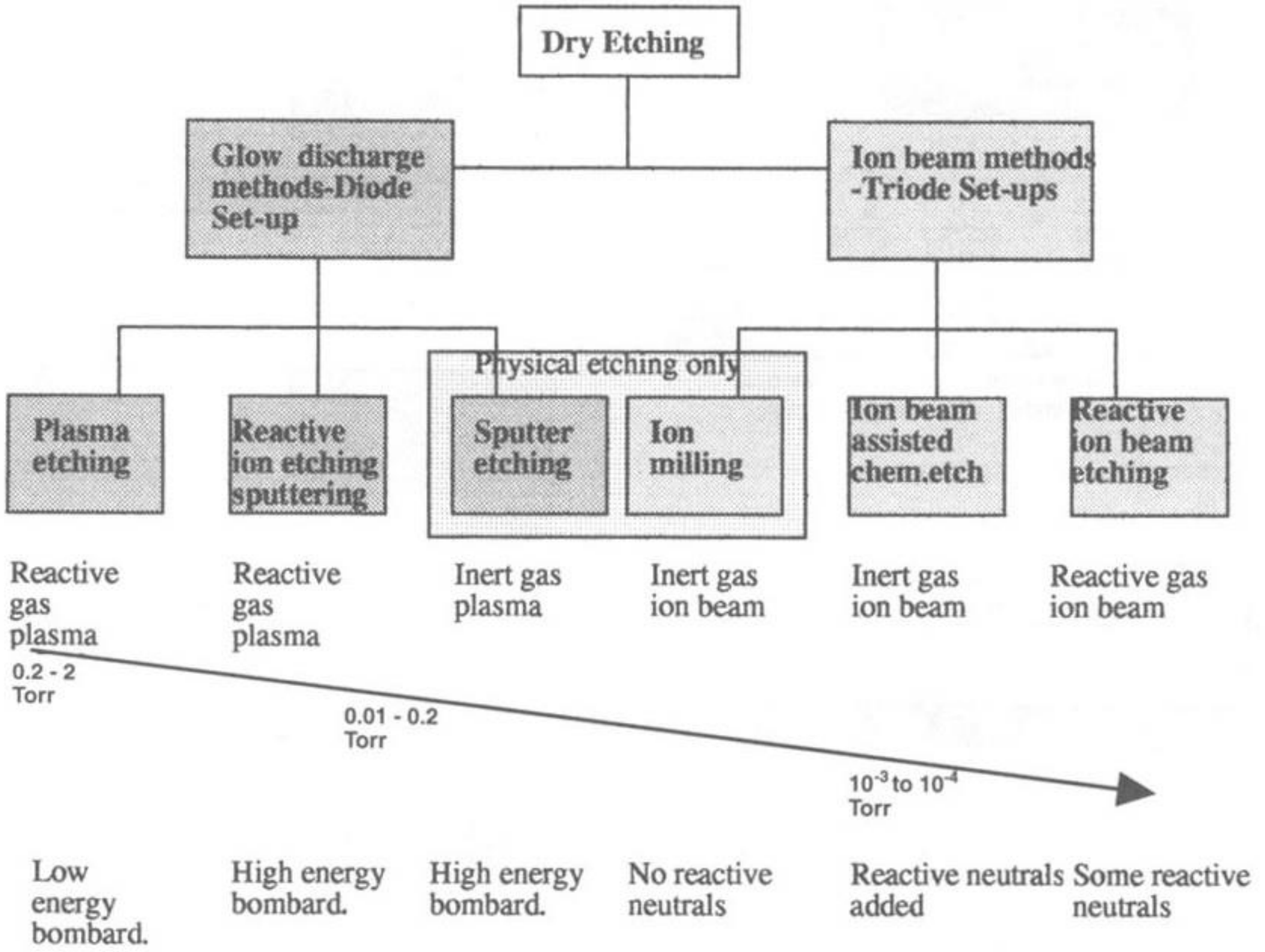


Etched material	Process	Suitable etchants	Suitable masking layers	Etch rate	Remarks
Glass	Wet	HF/HCl (10/1) HF HF/NH_4F	• Cr/Au/Photoresist• Amorphous Si• Molibdenum/photoresist• Amorphous Si/Amorphous SiC/Photoresist	Up to 7–8 μm/min (for Corning 7740)	The process is strongly dependent on glass composition
	Dry	SF_6, C_4F_8, CF_4, CHF_3	• Ni plated• Thick amorphous Si• SU8 resist	Up to 0.5–0.8 μm/min	The process is strongly dependent on glass composition
Silicon	Dry	Bosch	• Photoresist• SiO_2 (wet or PECVD)	2–30 μm/min	Most recommended
		Cryogenic	• SiO_2 (wet or PECVD) • Metal	Up to 7 μm/min	Smooth walls
	Wet	HNA (HNO_3+HF+CH_3COOH)	• Si_3N_4 (LPCVD)	4–90 μm/min	Isotropic
		KOH	• Si_3N_4 (LPCVD, PECVD)• SiO_2 (thermal/wet)• SiC (PECVD)	1.4 μm/min in (100) direction	Anisotropic
		EDP	SiO_2, Si_3N_4, Ta, Au, Cr, Ag, Cu	1.25 μm/min in (100) direction	Anisotropic
		TMAH	SiO_2, Si_3N_4	1 μm/min in (100) direction	Anisotropic

Iliescu, Ciprian et al. “A Practical Guide for the Fabrication of Microfluidic Devices Using Glass and Silicon.” *Biomicrofluidics* 6.1 (2012): 016505–016505–16. *PMC*. Web. 26 July 2016.

Dry Etching Process

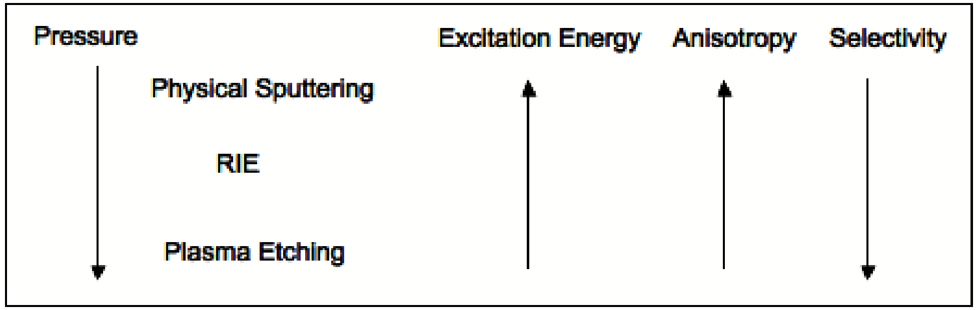
- In dry etching, the etch reactants come from a gas or vapor-phase source and are typically ionized
  - atoms or ions from the gas are the reactive species that etch the exposed film
- Solid surface is etched in gas/vapor phase by physical methods (sputtering, ion beam milling) or chemical reaction (using reactive gases or plasma) or with combination of both chemical and physical bombardment (reactive ion etching)



Types of Dry Etching

Type of Etching	Excitation Energy	Pressure
Plasma Etching *- isotropic, chemical, selective*	10’s to 100’s of Watts	Medium (>100 torr)
Reactive Ion Etching *- directional, physical & chemical, fairly selective*	100’s of Watts	Low (10-100 mtorr)
Sputter Etching *- directional, physical, low selectivity*	100’s to 1000’s of Watts	Low (~10 mtorr)

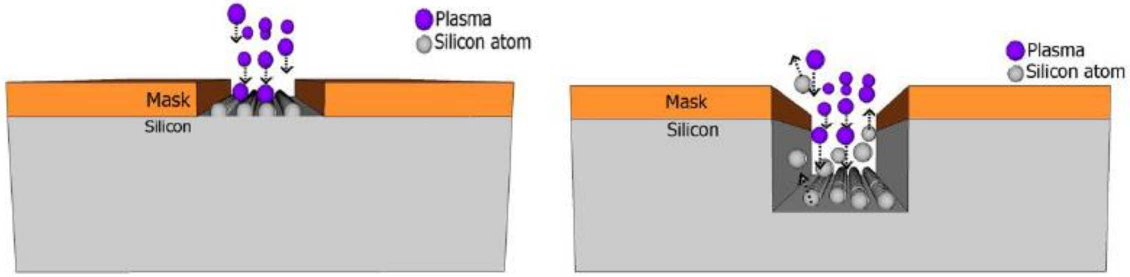
Dry etching spectrum



Dry Etching

Physical dry etching

- Etching occurs as a result of a physical effect, namely momentum transfer between energetic Ar+ ions and the substrate surface
- No chemical reaction involved
- Example : Sputtering and ion beam milling
- Plasma source can be dc or RF discharge

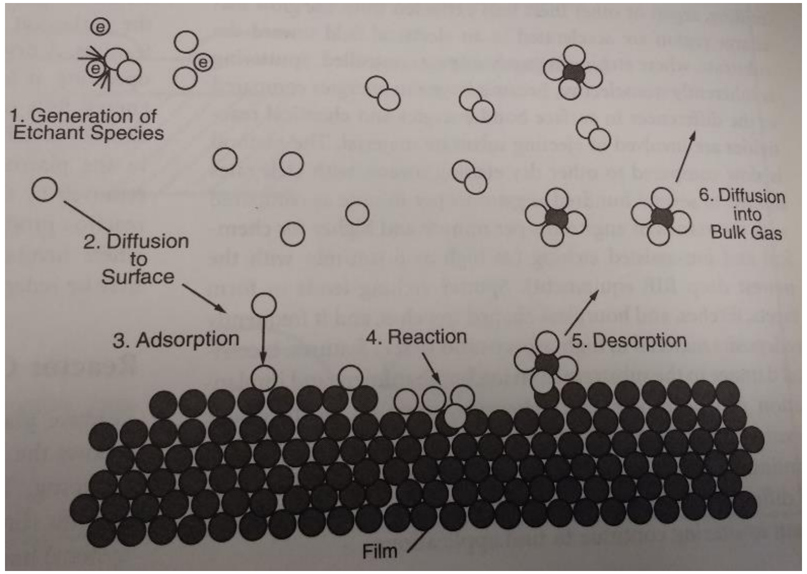


Plasma etching

- Only role of plasma is to supply gaseous, reactive etchant species
- Neutral chemical species responsible for most of reactive etching (not ions)
- Ions rarely act as reactant species
- Volatile products removed by vacuum system
- Non-reactive species may decrease reaction rate by blocking surface sites

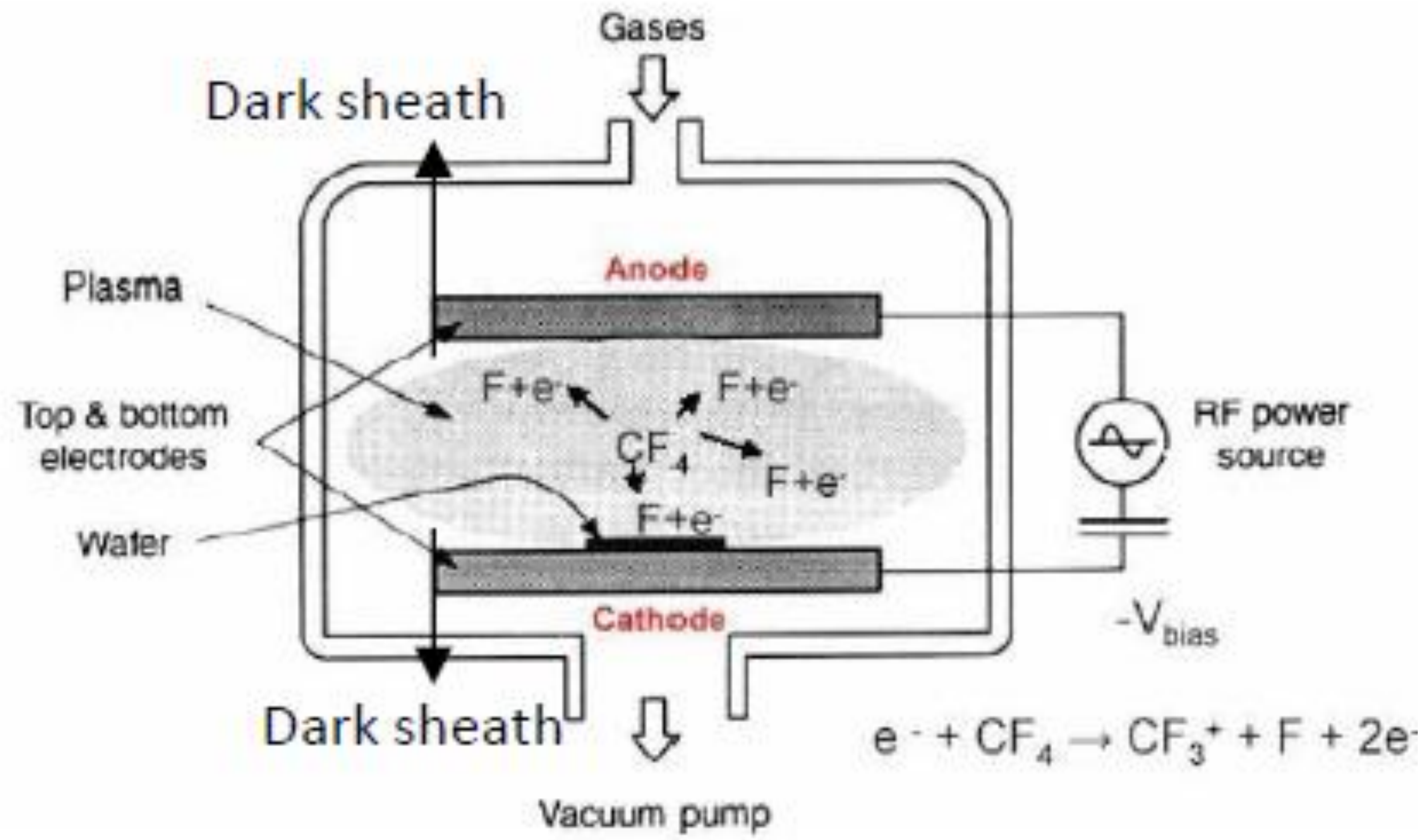
Reactive Ion etching

- Combines physical etching with chemical reactions
- Plasma etching with ion bombardment
- Ion-surface interactions promote dry etching by disrupting unreactive substrate and causes damage (dangling bonds, dislocations) resulting in substrate that is more reactive to etchant
- Dry etchants for Si – CF_4, SF_6 & BCl_2+Cl_2 with etch rate of ~50nm/min.



Reactive Ion Etching (Dry Etching)

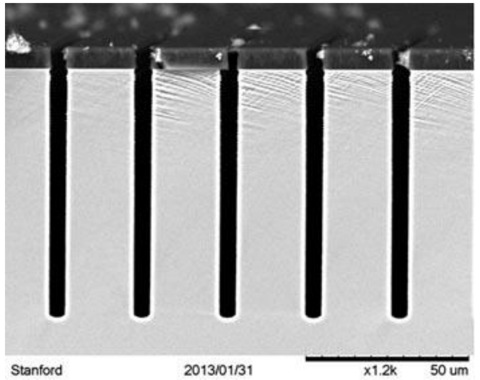
1. Wafer is grounded
2. Another electrode is connected to the RF power source
3. Oscillating (RF) electric field applied to ionize gas (~13 MHz)
4. Gas enters top of chamber and exits bottom of chamber using pump
5. Type of gas and pressure depend on etch material and structure demands (SF_6 used for Si)
6. Gas ions (+) form in the chamber, e- bombard the wafer, create (-) surface
7. Voltage difference causes gas ions to sputter material from wafer



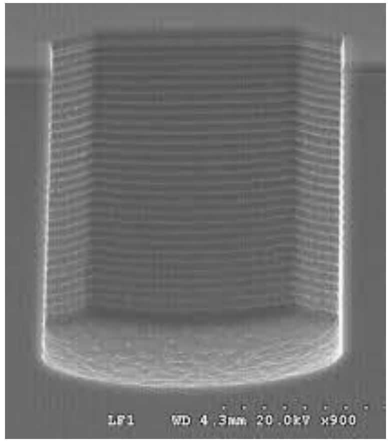
$e^- + CF_4 \rightarrow CF_3^+ + F + 2e^-$

Dry etching - Deep Reactive Ion Etching (DRIE)

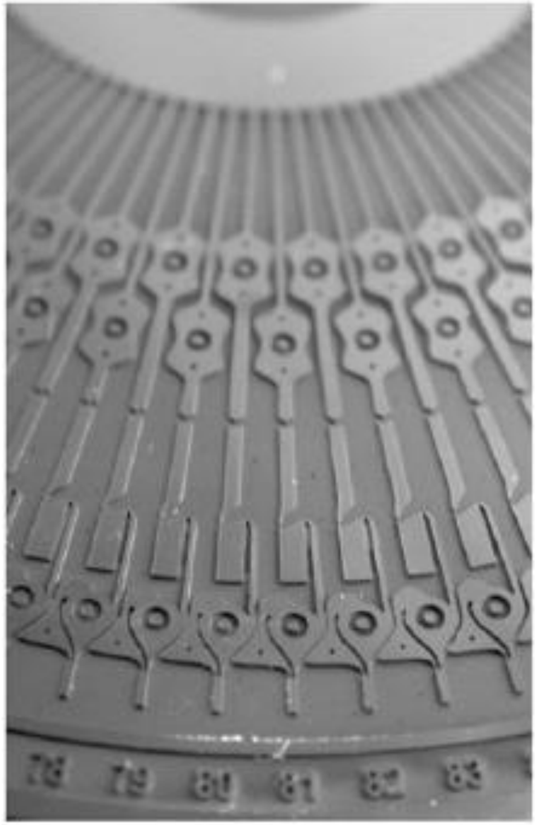
- Dry etching technique used for creating high aspect ratio structures in Si, SiO_2, quartz, and some metals
- High density plasma enables etch rates much higher than standard RIE
- High aspect ratio features are achieved using the Bosch process (cryogenic DRIE also capable of high aspect ratios)
- Preferred method of etching Si compared to wet etching



High aspect ratio features in Si

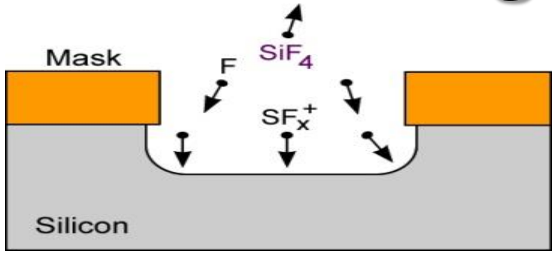


Characteristic scallops from Bosch process



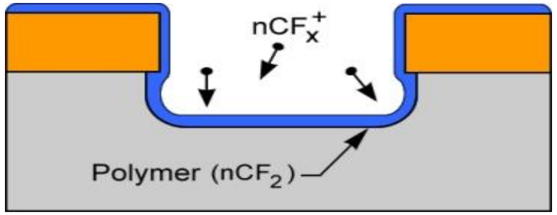
Microfluidic mold etched in Si by DRIE

Bosch Process



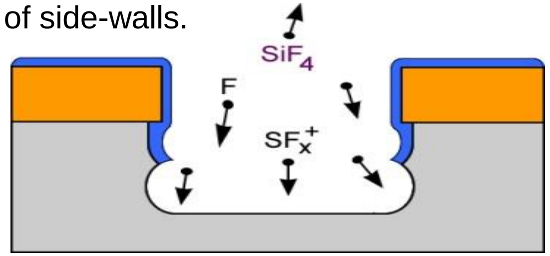
Step 1: Etch

- Etching occurs when fluorine radials react with the Si surface to form the volatile reaction product SiF_4 and is pumped away.
- A negative voltage bias on the wafer is used to control the flux of positive ions from the plasma to the wafer surface.
- Etching is enhanced when SF_x^+ ions bombard the Si surface, making it more reactive.



Step 2: Deposit Polymer

- A fluorocarbon (nCF_2) passivation layer is deposited to prevent etching of side-walls.



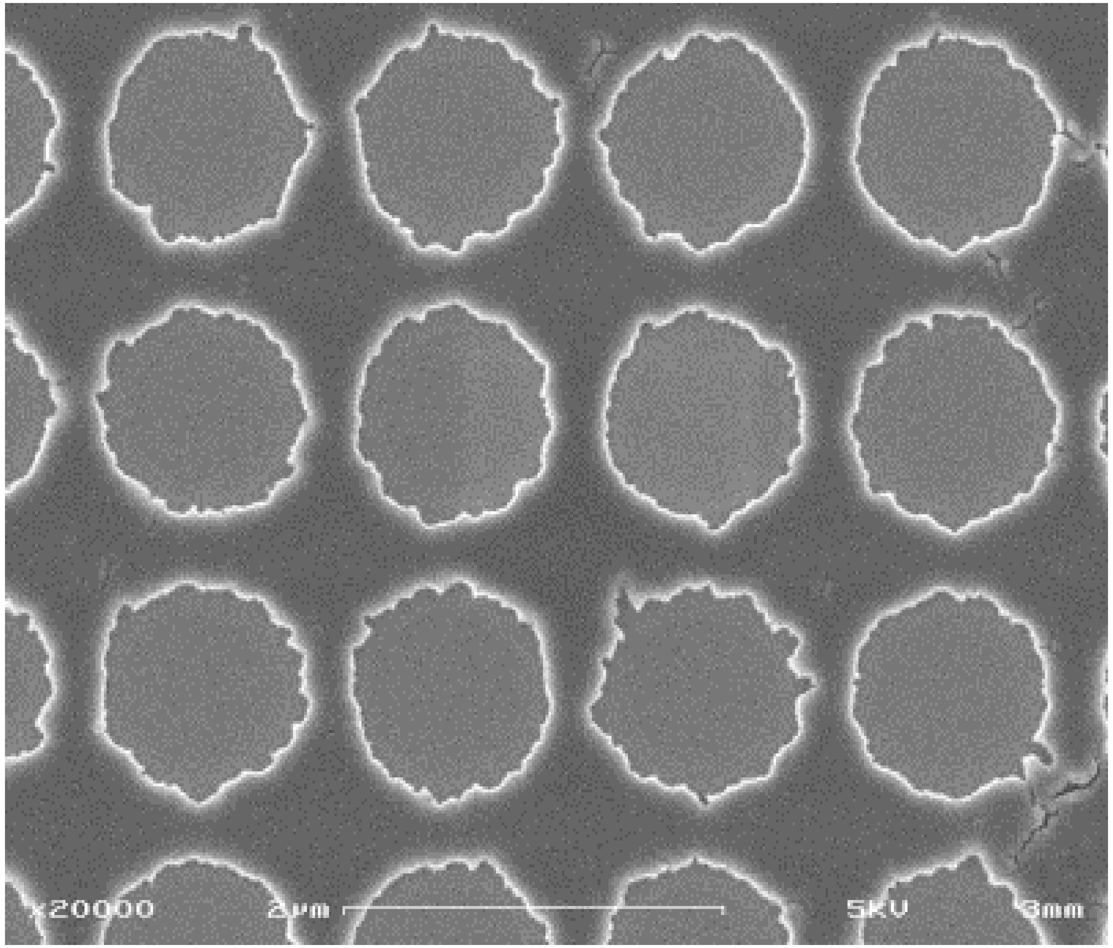
Step 3: Repeat Etch

- By quickly cycling between passivation and etching steps, very high aspect ratio features (etch depth/feature width) can be created.
- An inherent characteristic of the Bosch process due to alternating passivation/etch steps is side-wall scalloping.

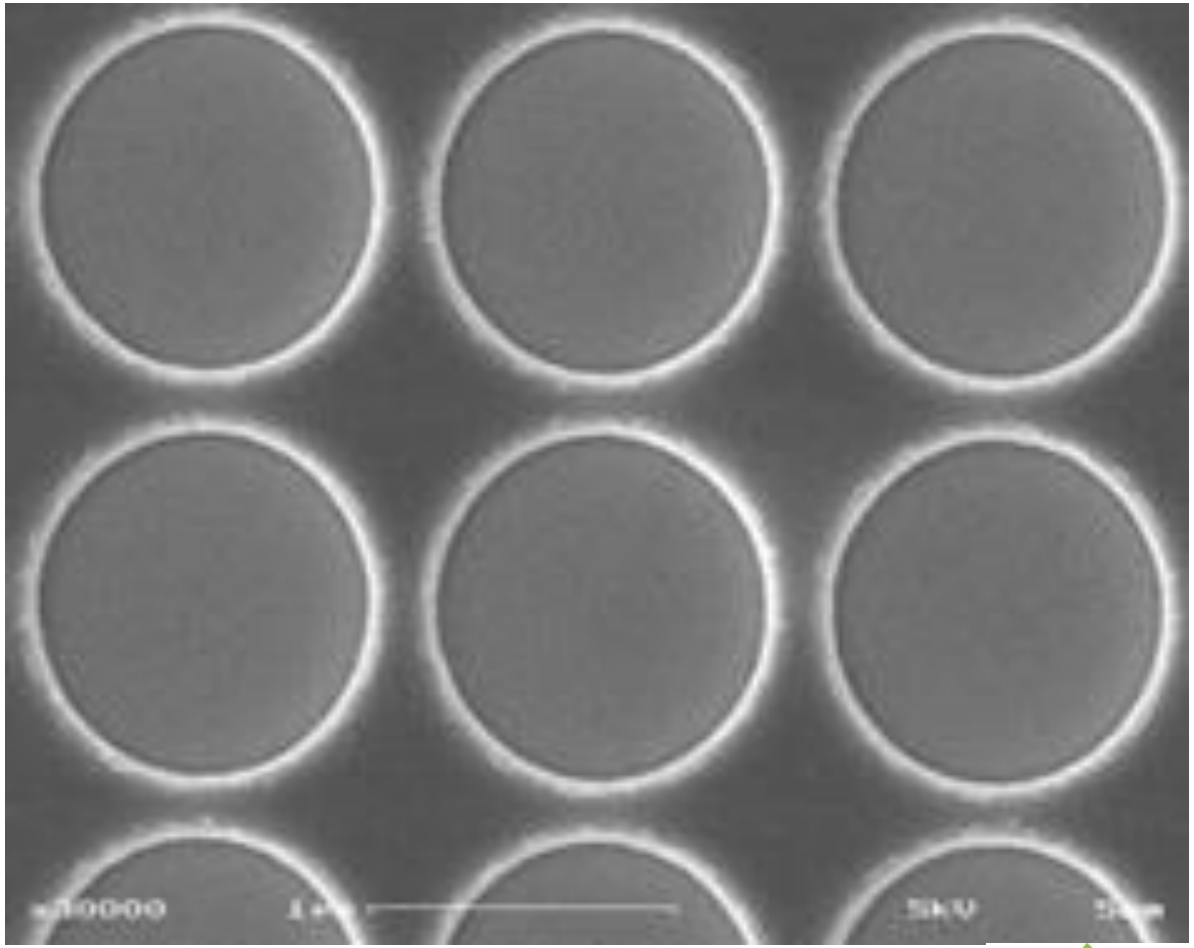
Wet vs. Dry Etching

Wet Etching	Dry Etching
High selectivity (up to 100:1)	Relatively low selectivity (1:1 but much higher with metals)
High etch rate (many microns/minute)	Relatively slow etch rates (< 1um/min but can be much higher)
Low cost	Expensive
Batch system with high throughput	High aspect ratio features due to high anisotropy (> 20:1)
Limited resolution (inadequate for <1 um)	Capable of defining submicron features
Generally isotropic (anisotropic possible for single crystalline materials)	Vertical profiles can be produced in crystalline, polycrystalline, and amorphous materials
Generates a lot of waste	Clean process
Hard to control (not reproducible)	Potential heat/radiation damage

Wet vs. Dry Etching - Example



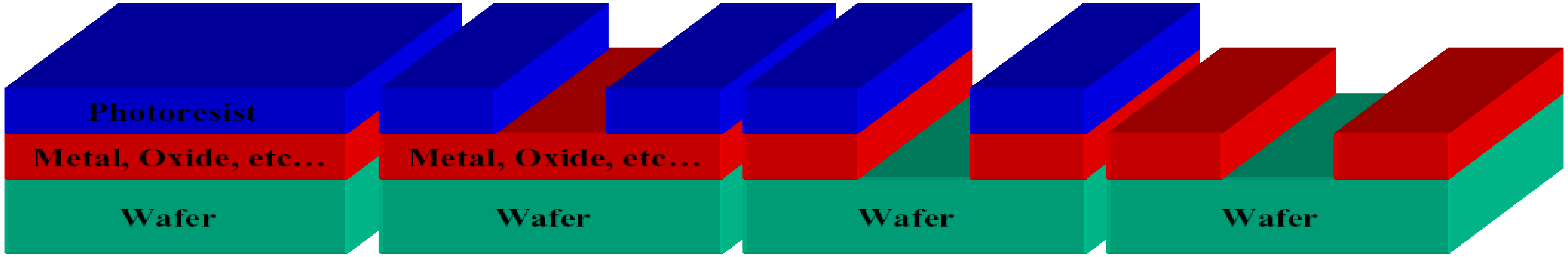
Wet etched Cr



Dry etched (RIE) Cr

Putting Down Thin Films

1. Etching processes:


Spin photoresist (PR)

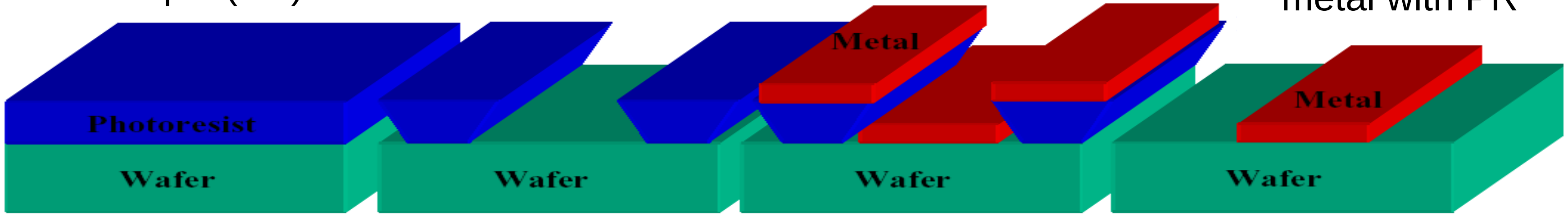
Photolithography

Etch using PR as mask

Remove PR

preparation of optical masks, patterning metals, oxides, etc…, patterning microfluidic channels in glass, silicon

2. Lift off processes


Spin (PR)

Photolithography

Evaporate metal

Lift Off excess metal with PR

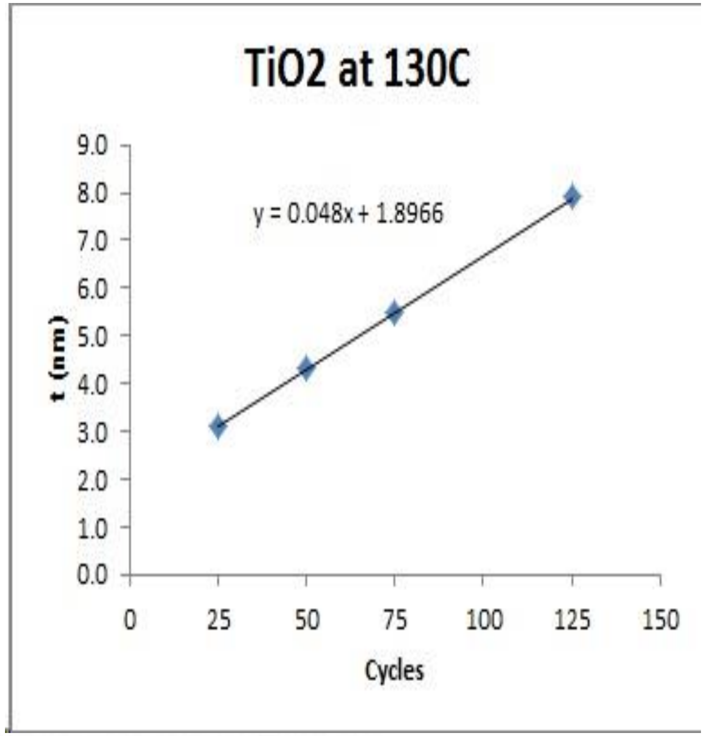
patterning of difficult to etch metals (Pt)

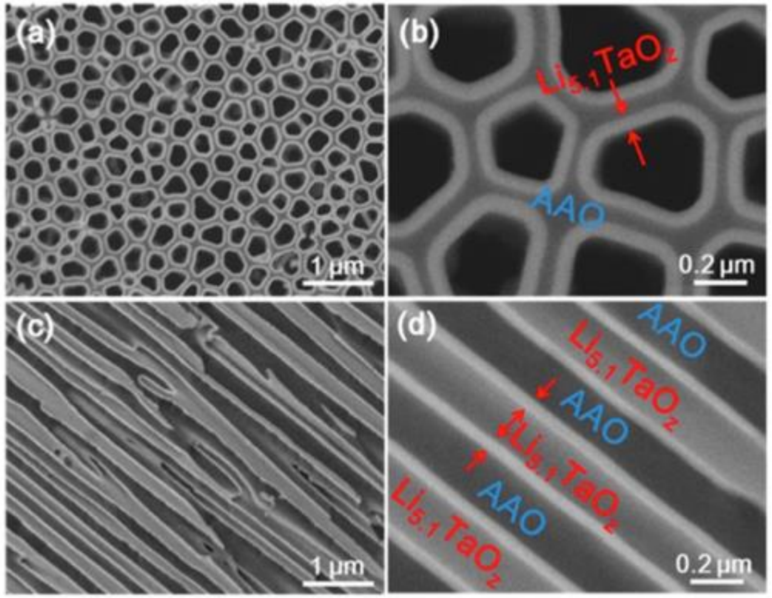
Atomic Layer Deposition (ALD)

Advantages

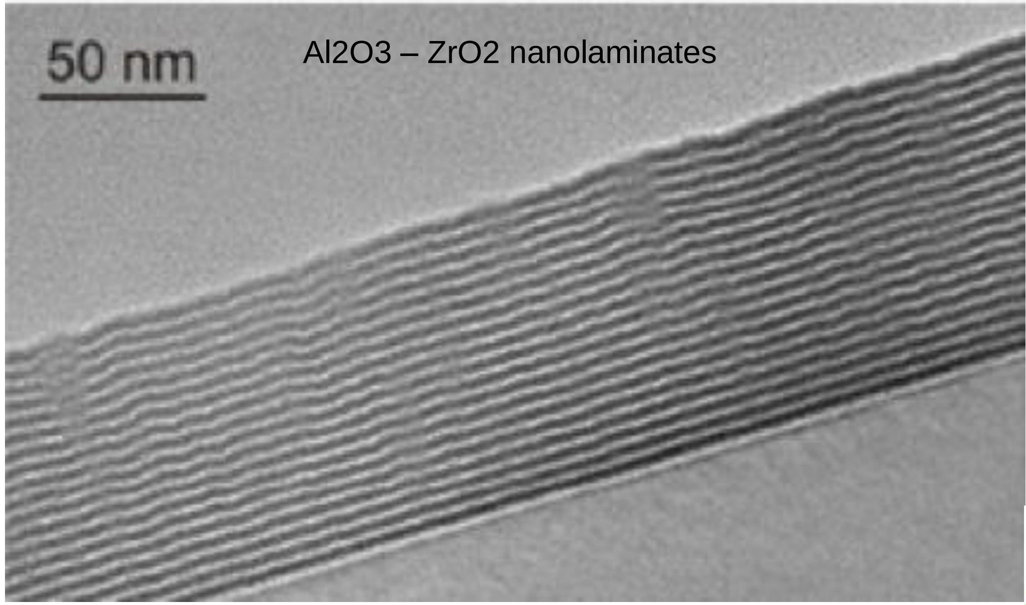
- Precise control of layer thickness
- Films are highly conformal – uniform coating on films, particles, and porous samples
- Stoichiometric control
- Low temperature process (as low as RT)
- Excellent adhesion due to chemical bonds at first layer

But, very slow! Many hours for 10's of nms



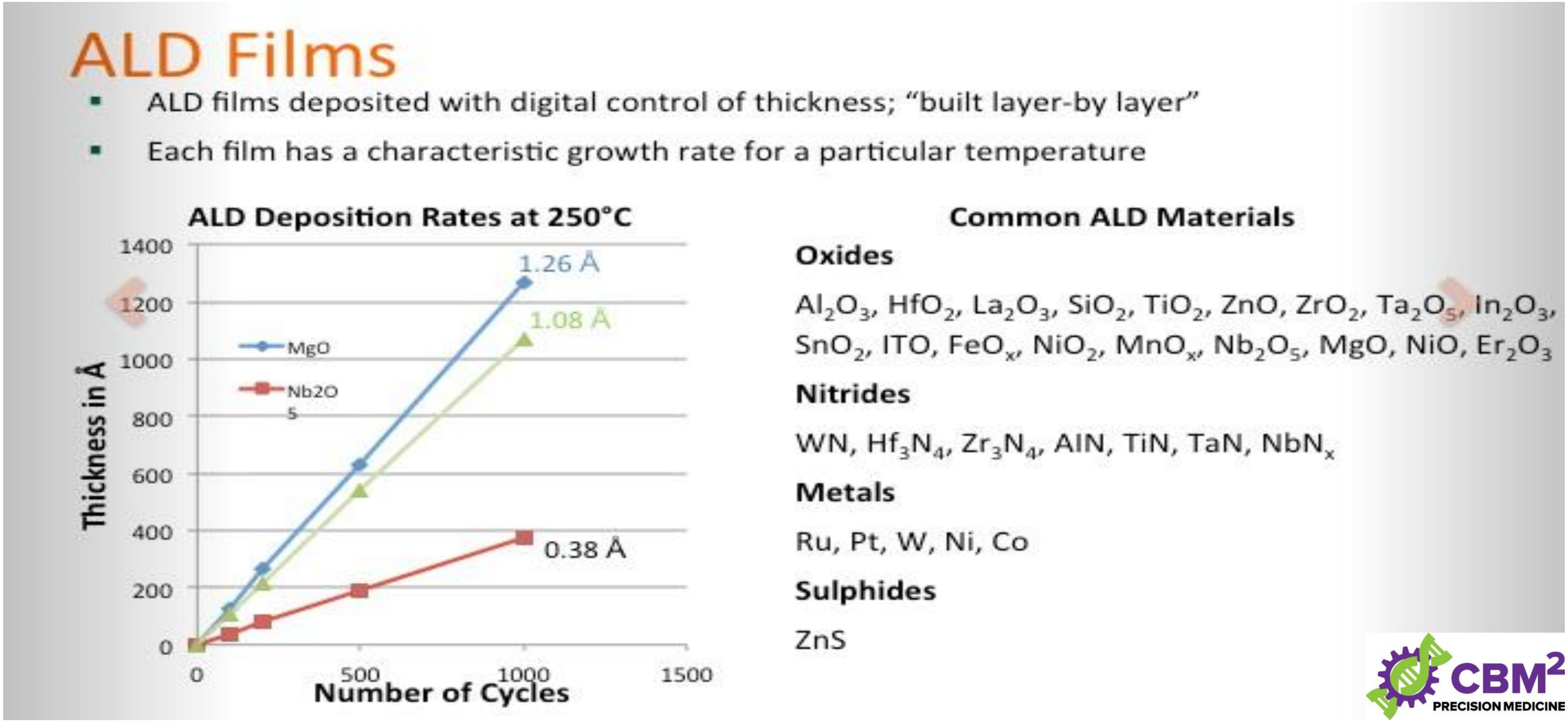


Li_xTiO_y deposited by ALD in 300:1 AAO nanotemplates



Al2O3 – ZrO2 nanolaminates

Atomic Layer Deposition



ALD Films

- ALD films deposited with digital control of thickness; “built layer-by layer”
- Each film has a characteristic growth rate for a particular temperature

ALD Deposition Rates at 250°C

Common ALD Materials

Oxides

Al_2O_3, HfO_2, La_2O_3, SiO_2, TiO_2, ZnO, ZrO_2, Ta_2O_5, In_2O_3, SnO_2, ITO, FeO_x, NiO_2, MnO_x, Nb_2O_5, MgO, NiO, Er_2O_3

Nitrides

WN, Hf_3N_4, Zr_3N_4, AlN, TiN, TaN, NbN_x

Metals

Ru, Pt, W, Ni, Co

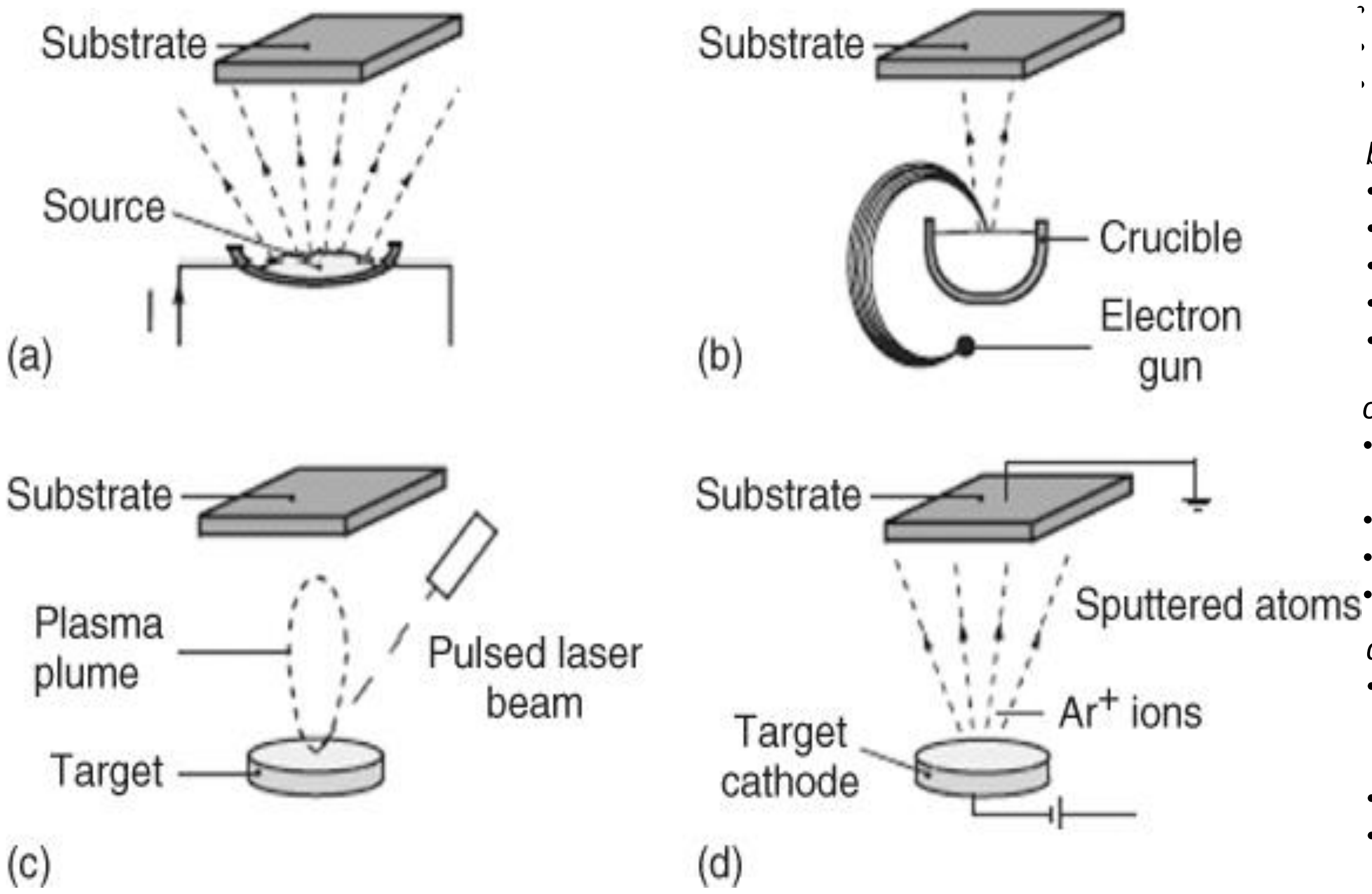
Sulphides

ZnS

“How to Make It and How to Use It”, The University of Kansas, Lawrence, KS August 2019

Physical Vapor Deposition (PVD)

- PVD: Deposition technique in which some form of energy is used to transfer material from a target to the substrate, where it condenses



Thermal evaporation

E-beam evaporation

Pulsed laser deposition

Sputter deposition

a) Thermal evaporation

- Heated filament used to boil off material
- Depositing alloys is difficult
- Poor adhesion
- Poor step coverage
- Not possible for refractory metals (limited choice of materials)

b) Electron beam evaporation

- High intensity electron beam focused on target material causes evaporation
- Deposition rates (10’s nm/min)
- Wider choice of materials
- Higher purity films
- Can cause x-ray and/or ion damage to substrate

c) Pulsed laser deposition

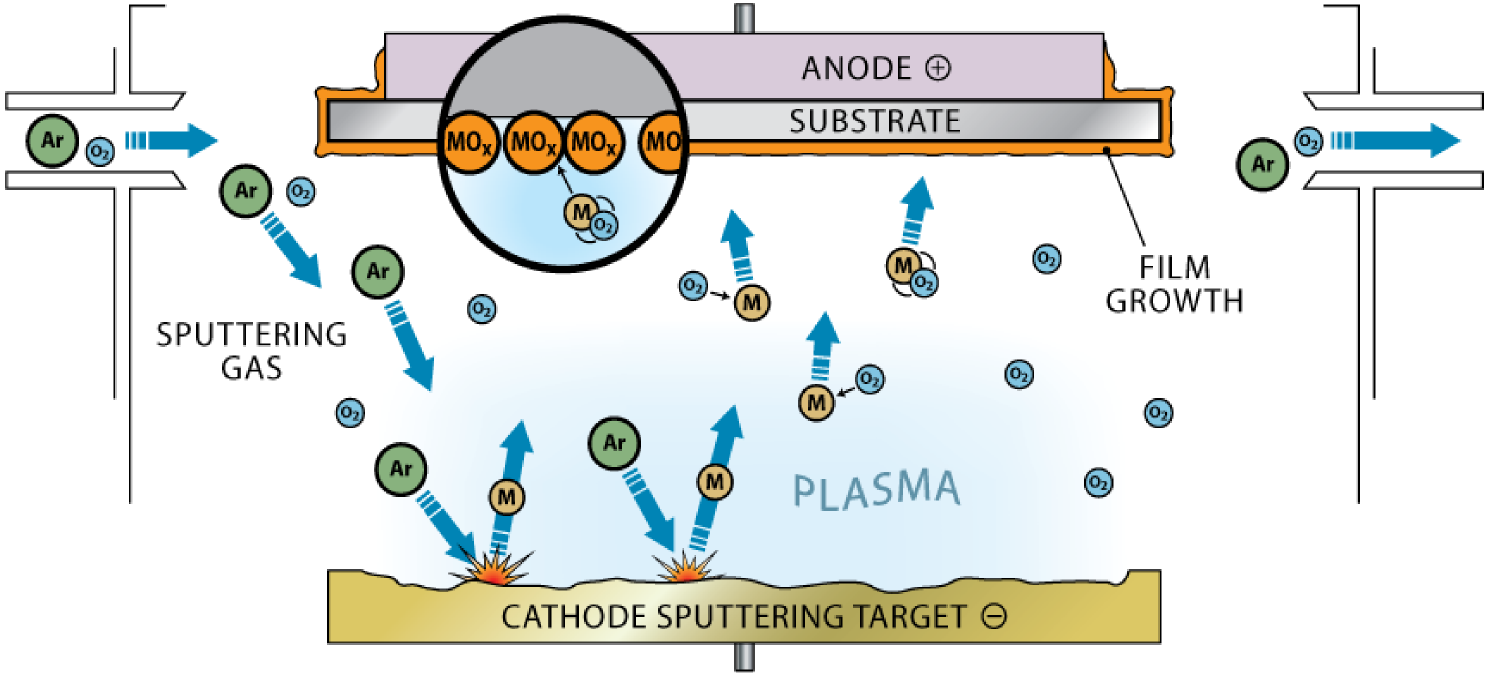
- Like e-beam evaporation, but laser is used instead for removing target material
- Wide choice of target materials
- High purity
- Slow dep. rates

d) Sputter deposition

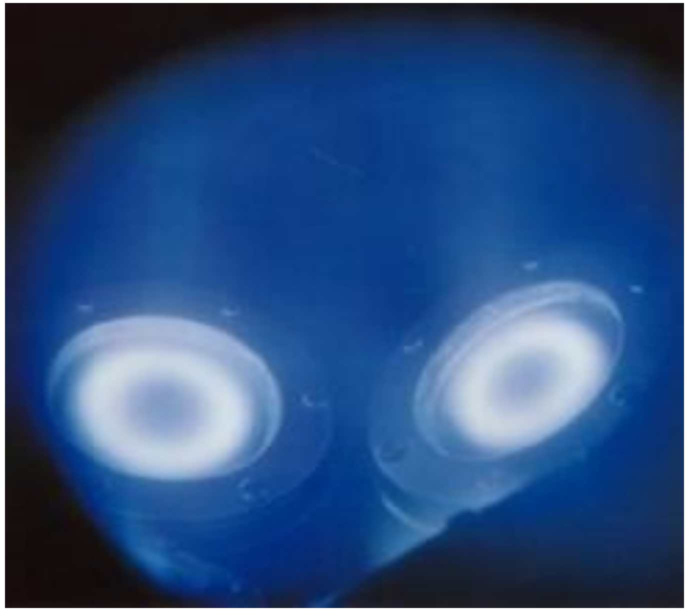
- Plasma creates ions that are accelerated toward target. Momentum transfer from ions to target causes target material to be ejected toward surface (sputtering), where it condenses
- High purity films over large area are possible
- Just about any material can be sputtered – including compounds, but used mainly for metal deposition
- Better step coverage than evaporated films, but not always as smooth
- Deposition rate: 10’s nm/min

“How to Make It and How to Use It”, The University of Kansas, Lawrence, KS August 2019

Sputter Deposition



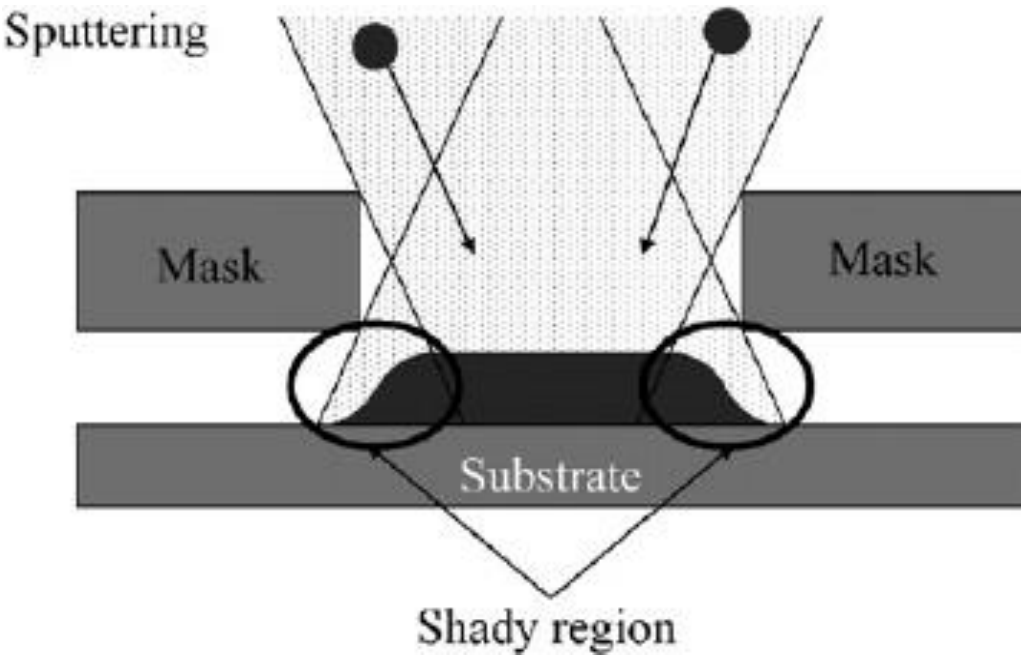
Various sputtering target geometries



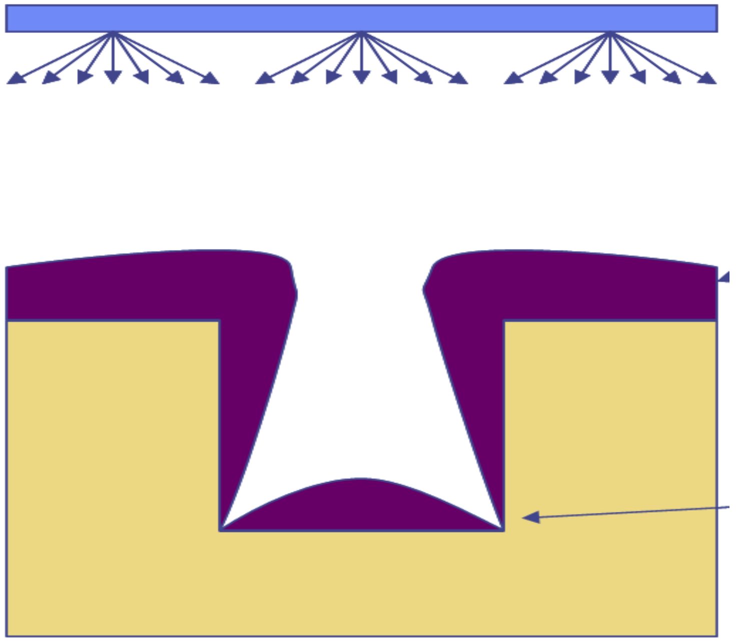
Sputtering targets with plasma ignited

- Voltage is applied across a rarified gas
- Breakdown of the gas forms a plasma
- Positive ions from plasma strike the negative electrode (cathode and target)
- Energy from the ions is transferred to the target atoms
- Some target atoms escape from target surface (they are sputtered)
- The sputtered atoms condense on the substrate
- Deposition of compounds (oxides, nitrides) possible with introduction of reactive gases

Sputter Deposition – Film profiles



Patterning sputtered films using a shadow mask



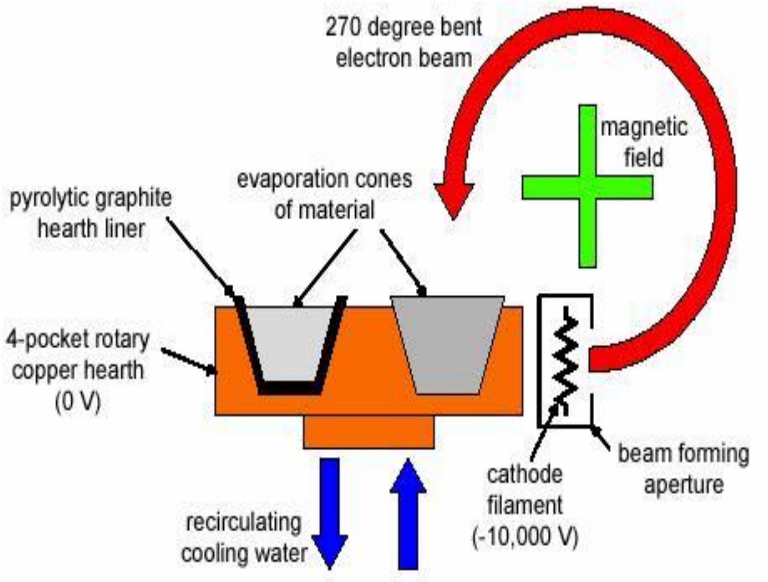
Typical deposition profile of film sputtering into a trench

- Just about any material can be sputtered (including compounds and refractory metals)
- Metal oxides and nitrides can be deposited via reactive sputtering
  - Reactive sputtering: metal sputtering in the presence of a reactive gas
- Better step coverage than evaporated films, but not always as smooth
- Deposition rate: 10’s nm/min
- Not good for shadow masks due to angular distribution of ion trajectory

Electron Beam Evaporation

- Electrons are generated by electron gun (cathode)
- Emitted electrons are accelerated towards crucible (anode) by high voltage potential
- Localized heating of target material (evaporation)
- Deposition with reactive species to create metal oxide/nitrides is possible
- High purity films compared to PVD
- Can be used with shadow masks

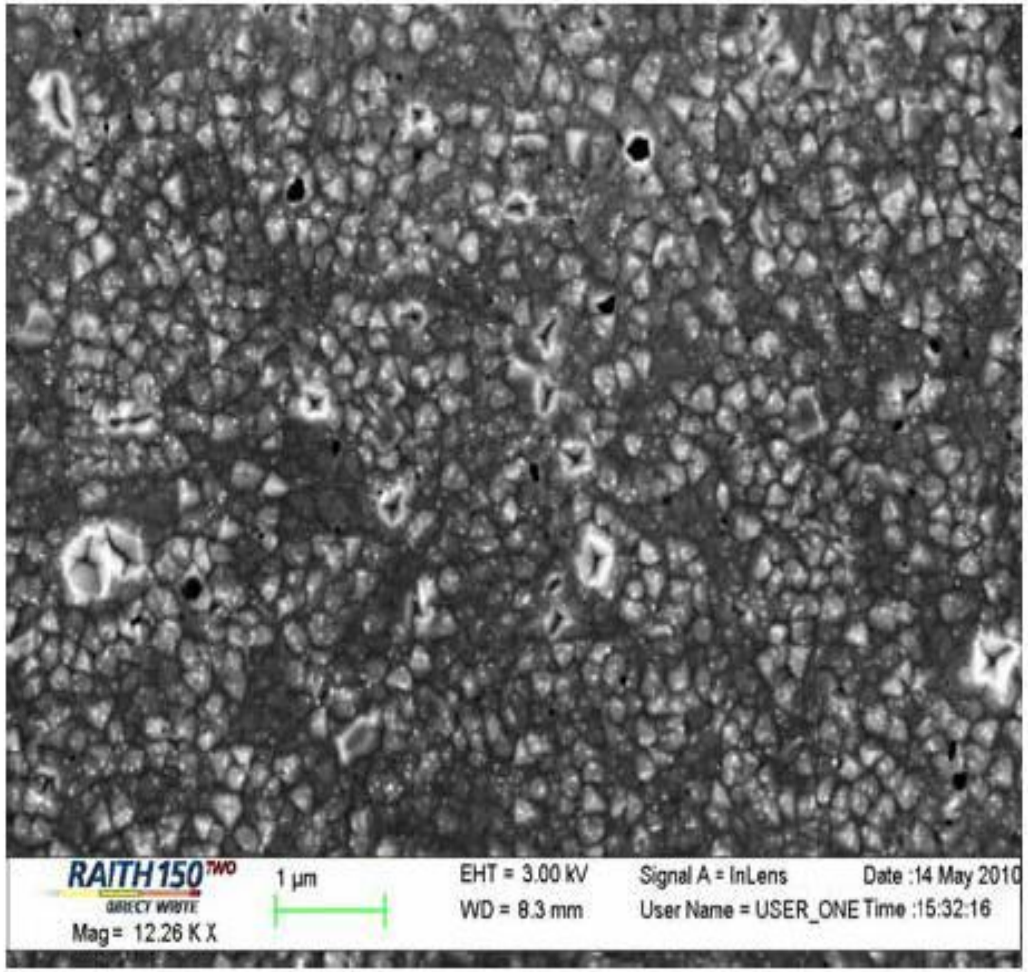
Electron gun for e-beam evaporation system



Schematic of e-beam evaporation system

Electron beam focused on crucible

SEMs of Thermally and E-beam Evaporated Al Films



Mag = 12.26 K X

EHT = 3.00 kV

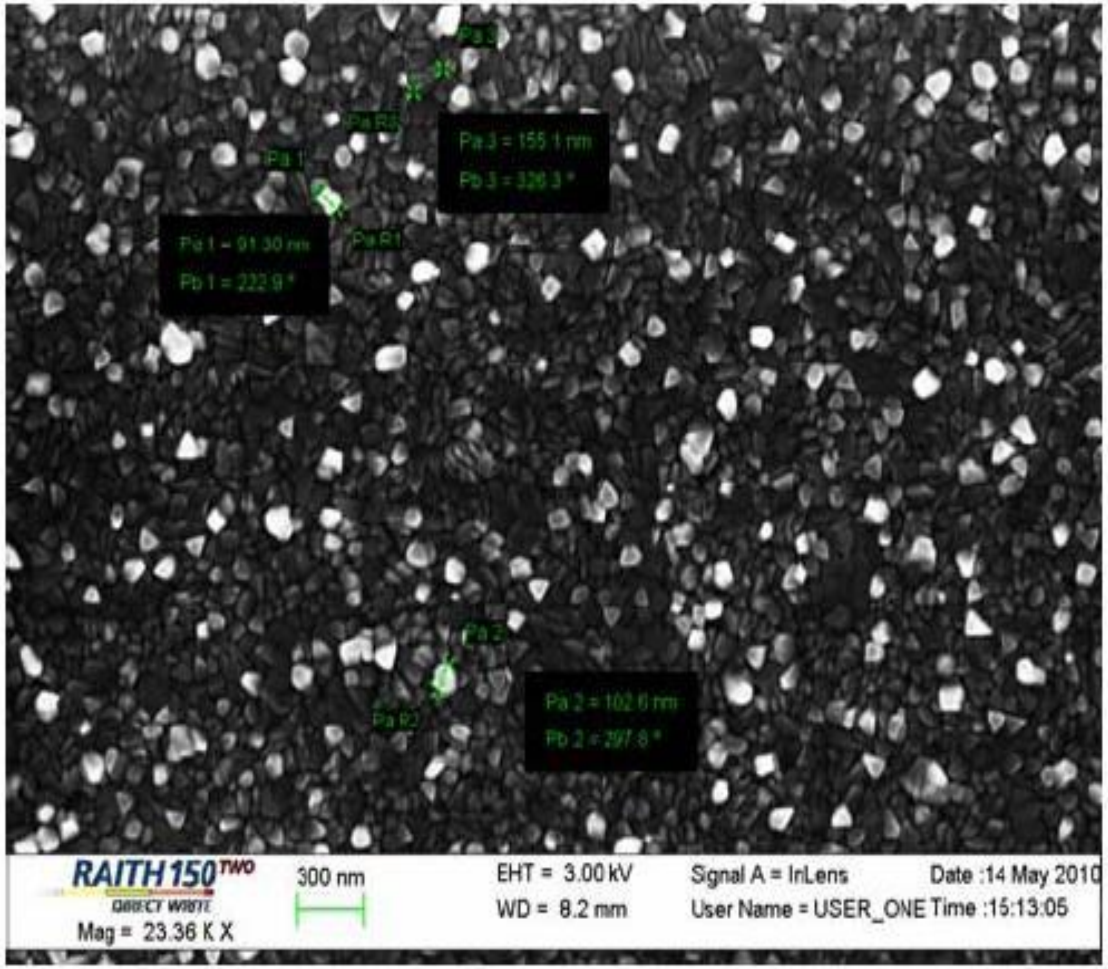
WD = 8.3 mm

Signal A = InLens

User Name = USER_ONE

Date :14 May 2010

Time :15:32:16



Mag = 23.36 K X

EHT = 3.00 kV

WD = 8.2 mm

Signal A = InLens

User Name = USER_ONE

Date :14 May 2010

Time :15:13:05