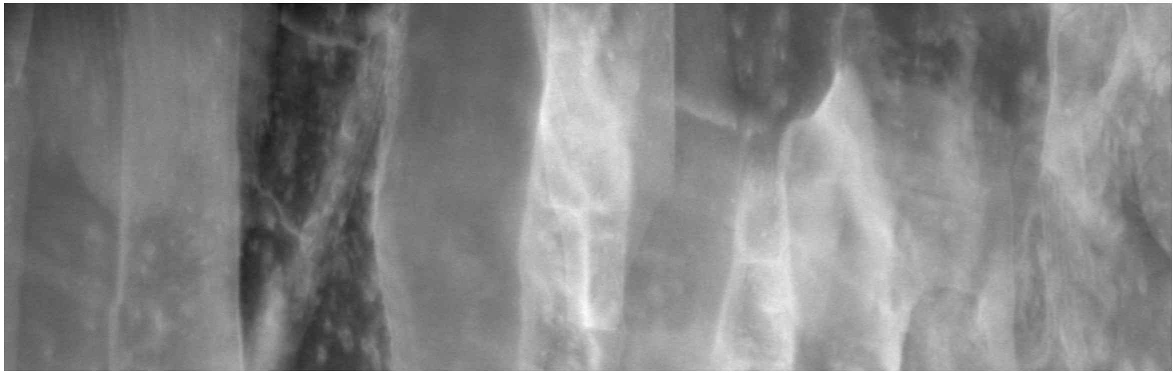
SAND2014-4024C

*Exceptional service in the national interest*

Sandia National Laboratories



# Thin Films Deposition Methods

## *Adding Functionality One Atom At A Time*

**R.S. Goeke**

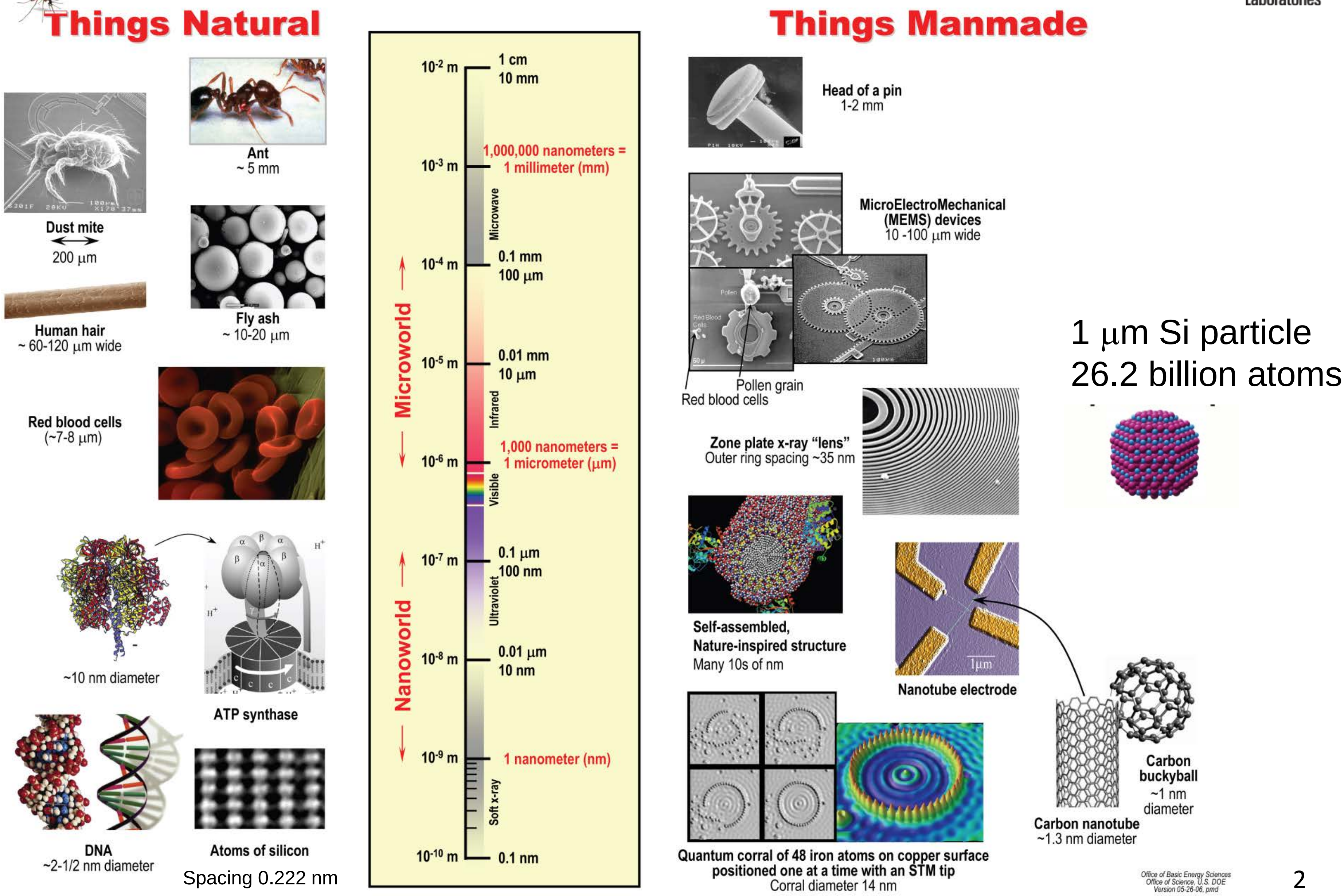
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

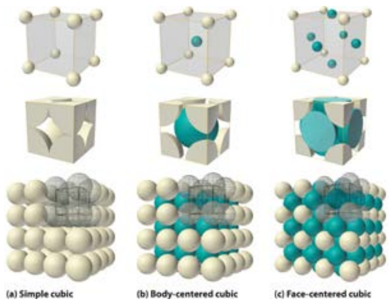
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

# The Scale of Things – Nanometers and More

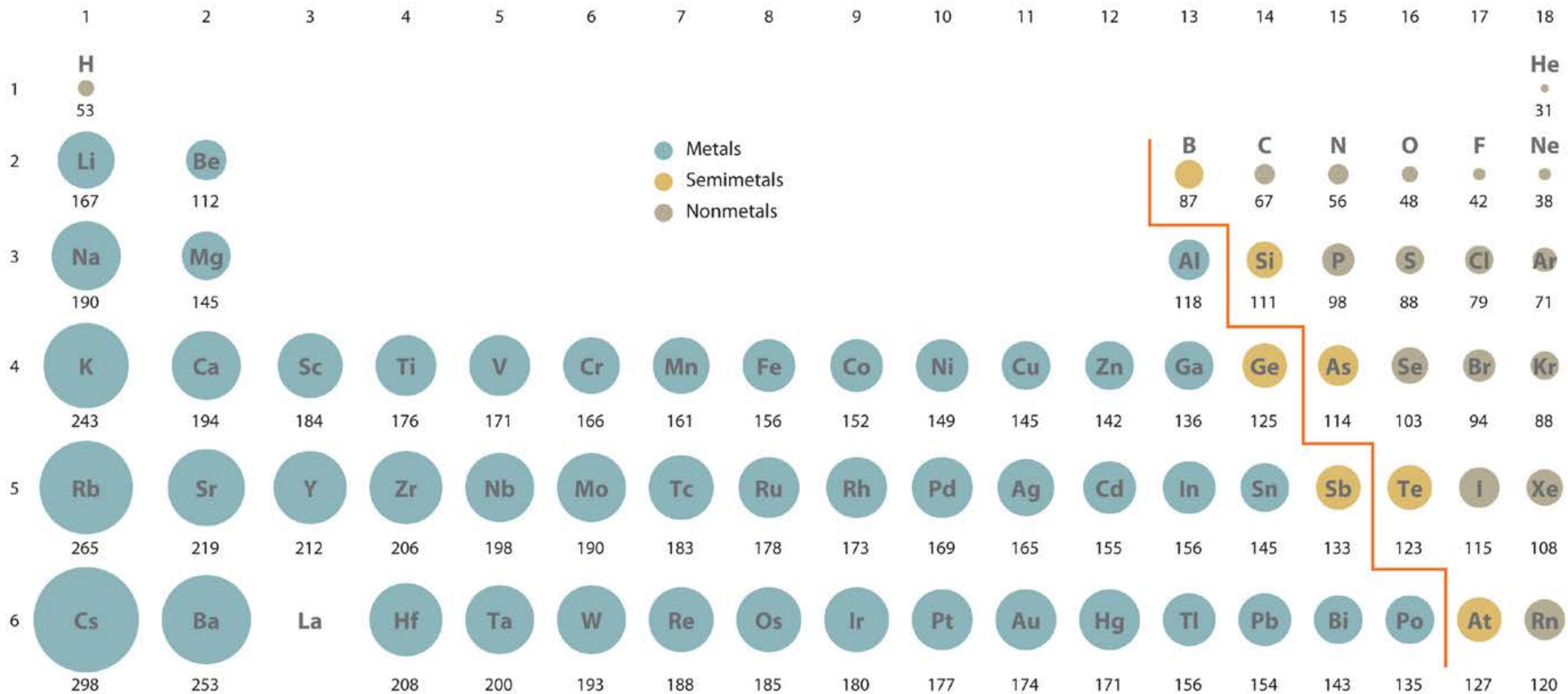
Sandia National Laboratories



# Atomic Sizes

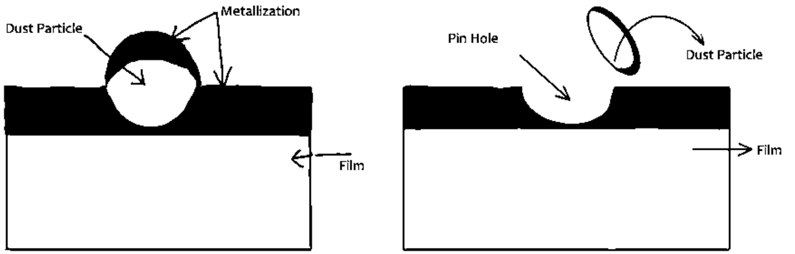



Sizes are radii in picometers



# Cleanliness Matters

Dust particles are huge at the "nanoscale" (film defects, pin holes,…)
Deposition systems are located in cleanrooms
Operators required to wear bunny suits





# Vacuum

- Surfaces are constantly being bombarded by our atmosphere
- Surfaces are covered by absorbed molecules of water, oxygen, hydrocarbons,…
- Thin film deposition is performed at very low pressures “high vacuum”

Vacuum
(logarithmic scale)

| mmHg (torr) | atm | |
|---|---|---|
| 760 | 1 | sea level |
| 76 | 0.1 | |
| 7.6 | 0.01 | |
| 0.76 | 0.001 | |
| $7.6E^{-2}$ | 0.0001 | |
| $7.6E^{-3}$ | 0.00001 | |
| $7.6E^{-4}$ | 0.000001 | |
| $7.6E^{-5}$ | 0.0000001 | |
| $7.6E^{-6}$ | 0.00000001 | |
| $7.6E^{-7}$ | 0.000000001 | |
| $7.6E^{-8}$ | 0.0000000001 | |

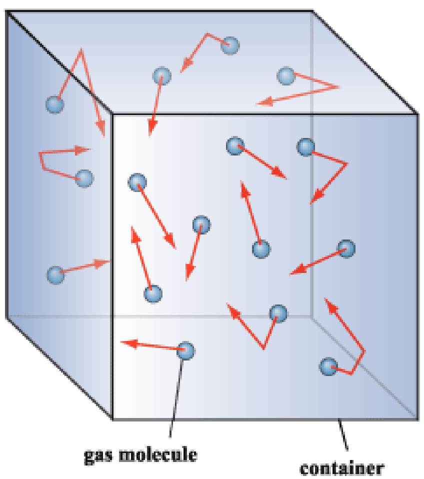
Albuquerque 630 torr

Top of atmosphere (100 km)

Rough Vacuum

High Vacuum

UHV



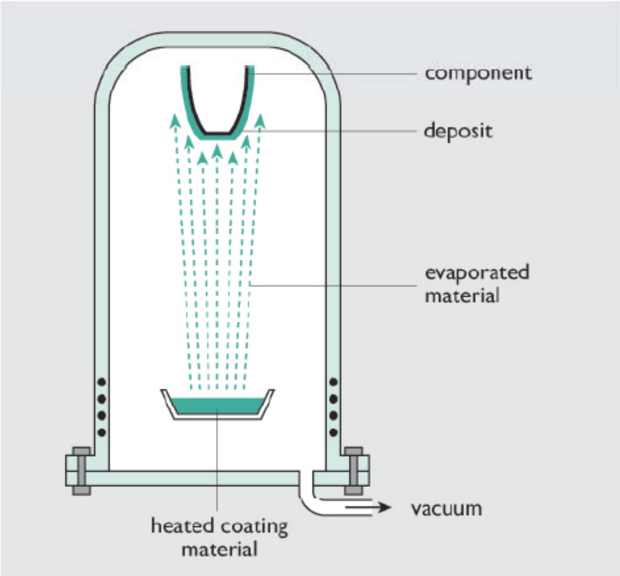

1 monolayer exposure known as 1 Langmuir (1 ML/sec ~ $1E^{-6}$ torr)

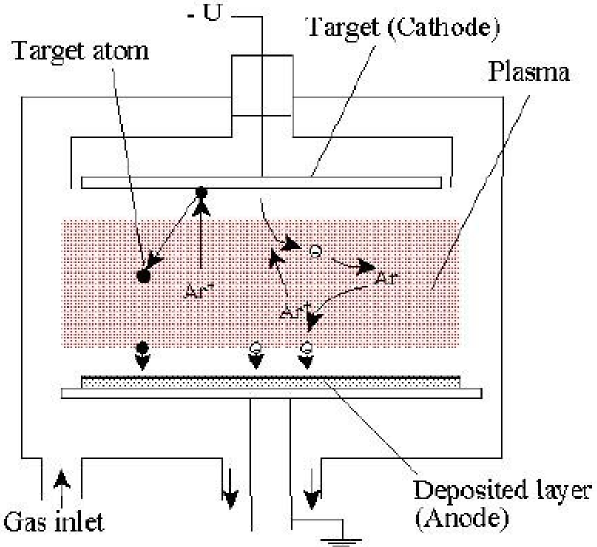
# Thin Film Deposition Methods - PVD

Physical Vapor Deposition (PVD): Material is removed from a target and deposited on to a substrate

Several different methods: Sputtering, Evaporation, Laser Ablation, etc.

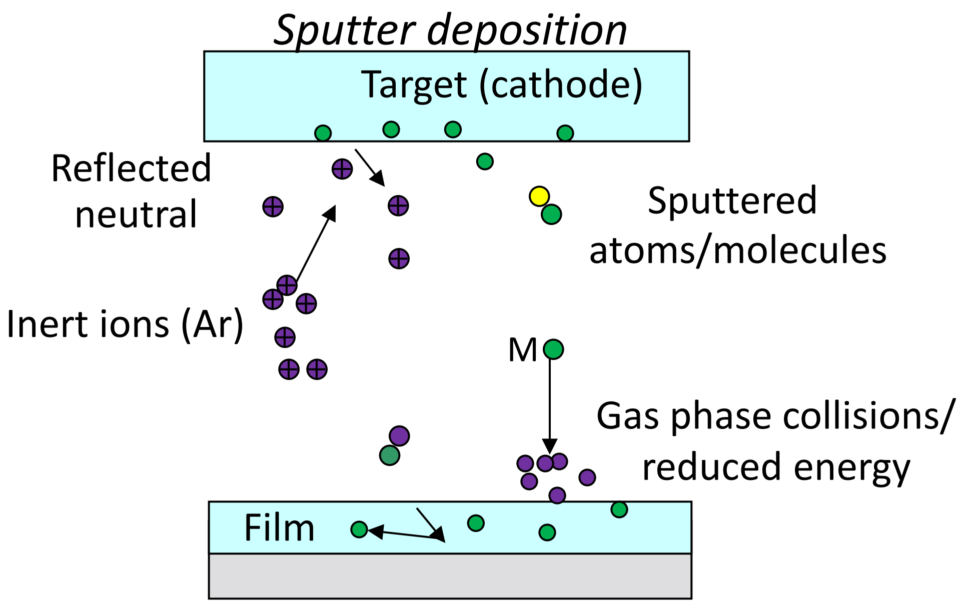
a. Sputtering – Use of Plasma and Ion Acceleration to remove material ("sputter") from target then deposit on substrate.
b. Evaporation – Condensation of metal vapor in high vacuum on a substrate
c. Can also do reactive deposition



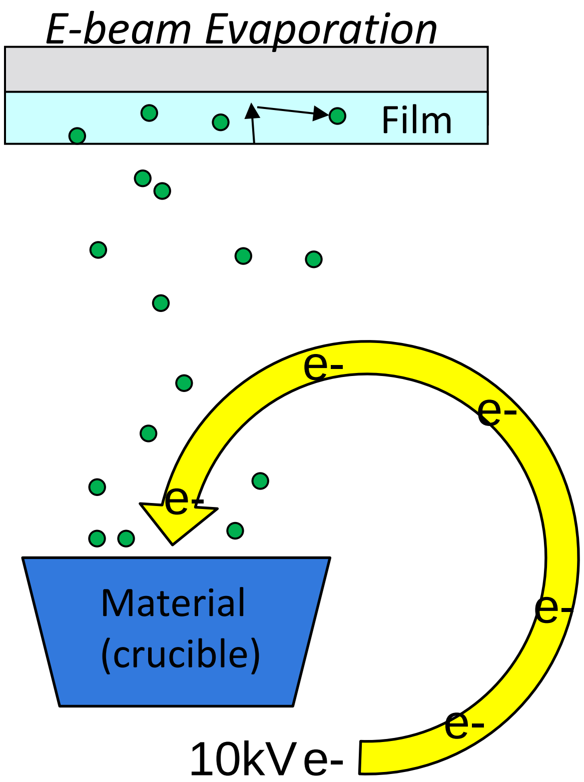




http://burkett.eng.ua.edu/ECE438538/Lectures/Ch12.pdf

# Physical Vapor Deposition (PVD)




- Target material removed by kinetic energy of inert ions
- Requires plasma ignition for ionization of sputter gas (Ar)
- Good control over film properties (pressure, power, biasing, temperature)




- Target material vaporized by thermal energy from electron beam
- Terrific rate control with feedback from QCM
- Can deposit at extremely slow rates (ppm level composition control)

# Thin Film Deposition Techniques

Evaporation requires a suitable vapor pressure for this technique to work.

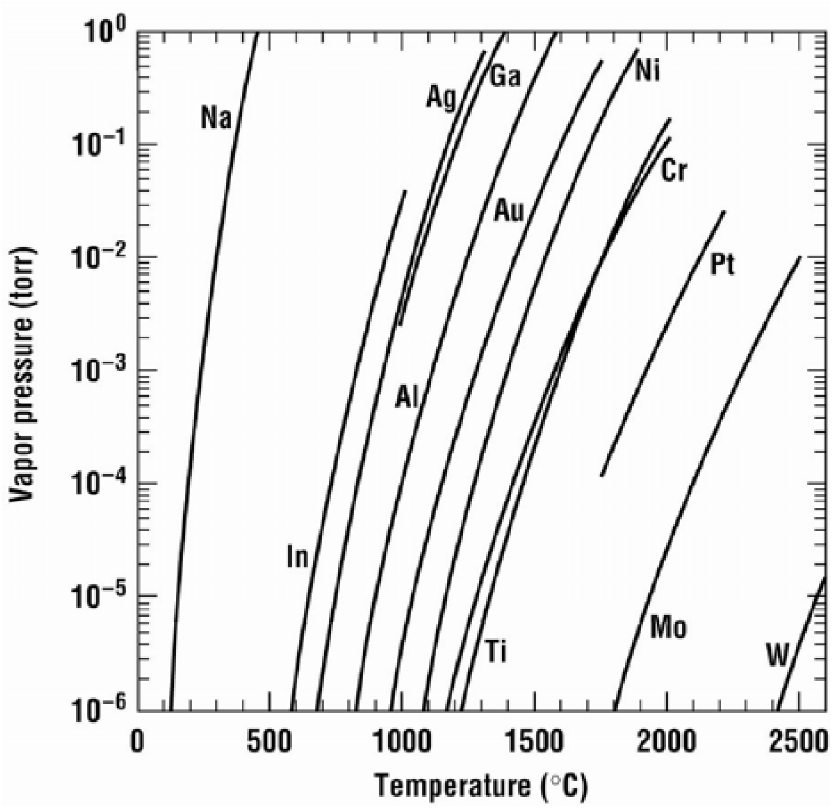



**Figure 12.2** Vapor pressure curves for some commonly evaporated materials *(data adapted from Alcock et al.)*.

http://burkett.eng.ua.edu/ECE438538/Lectures/Ch12.pdf

# Thin Film E-beam Evaporation

## Equipment

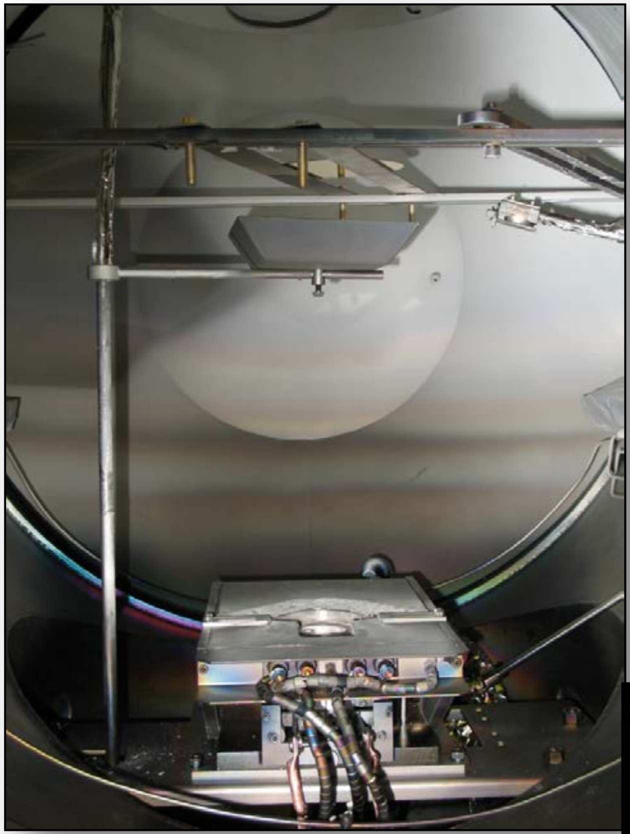
- High Vacuum e-beam system

## Capabilities

- A variety of elements and compounds
- Thickness control from 0.1Å to > 10 µm
- Multilayer depositions (4 materials per vacuum cycle).
- Substrate heating to 500°C
- Glow discharge cleaning
- Reactive deposition for oxides, nitrides and hydrides.
- Up to 500 mm substrates

## Advantages

- Excellent line of sight deposition compared to other vapor deposition techniques makes it ideal for shadow masking patterns



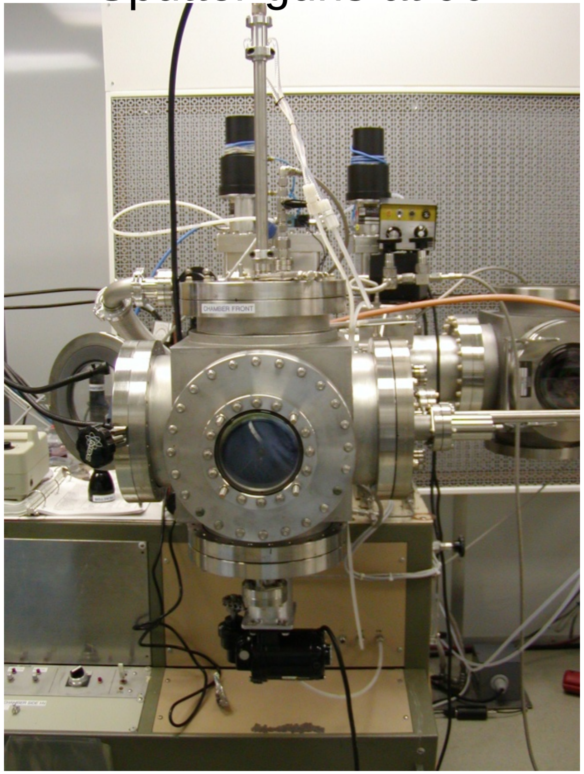
*Four pocket rotary turret 10kV electron beam gun, and molten material during deposition*

# Sputter Deposition

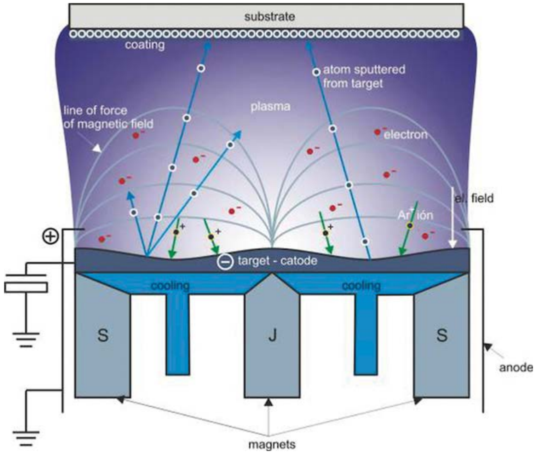
DC Magnetron Sputtering for metals

RF Magnetron for insulating materials

Sputter guns at 90°



Two 2” sputter targets

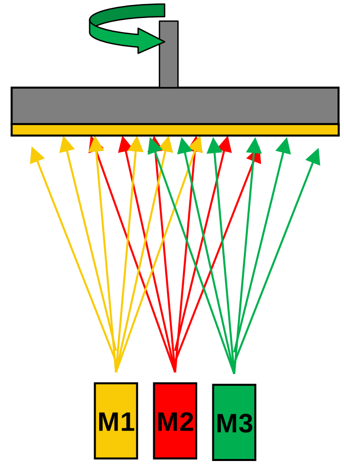


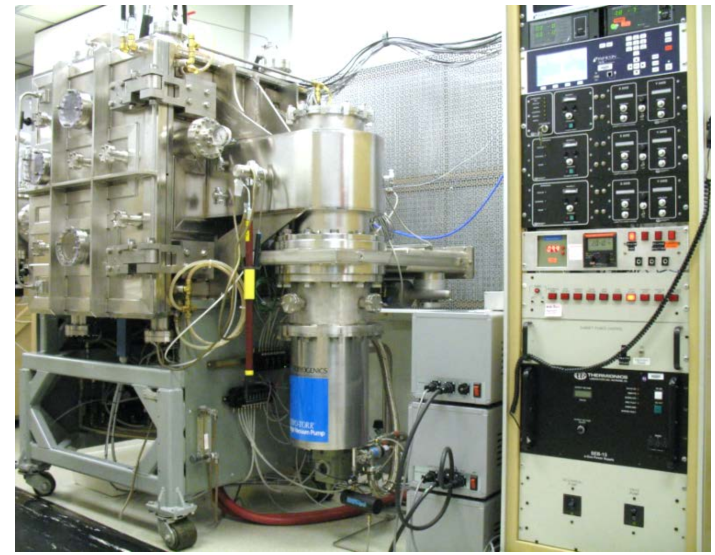

Glow discharge during dep.

# Thin Film Co-Deposition

## Evaporation:

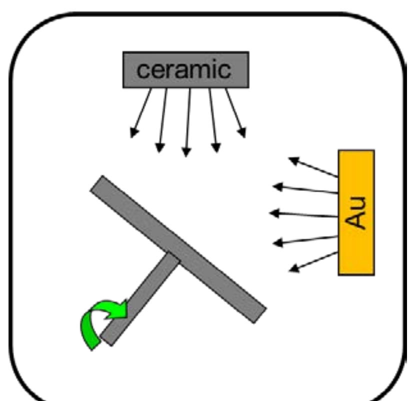
- Triad e-beam evaporation of ternary alloy thin films
- Shutter in front of substrate for consistent composition, graded or layered films
- Independent QCM control of material deposition rate
- Compositional control to < 0.1%

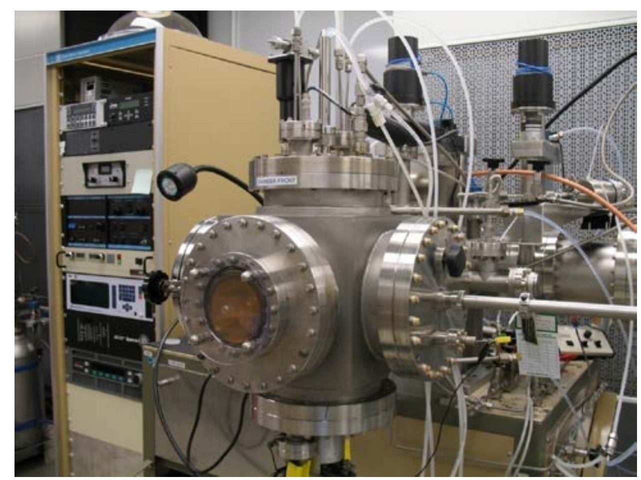


## Sputtering:

- Co-deposition of elements, alloys and compounds
- Composition control to ~1-2%, limited by minimum power required for plasma ignition
- Composite targets expensive and limits experimental compositional range



# PVD Microstructure

## Film morphology

Zone model (Zones 1, 2, 3, T) indicates the films final characteristics based on the substrate temperature and ion energy; T-region is characterized by very small grains

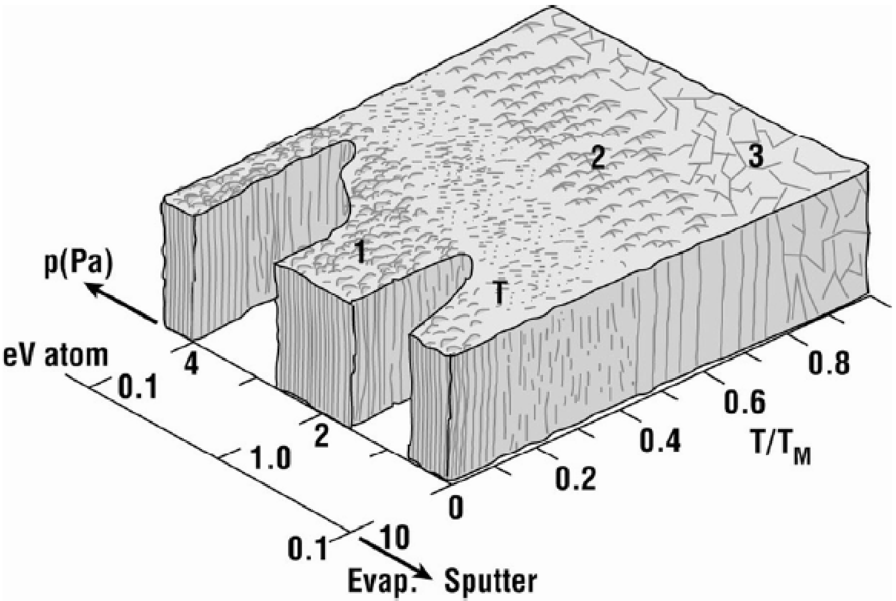


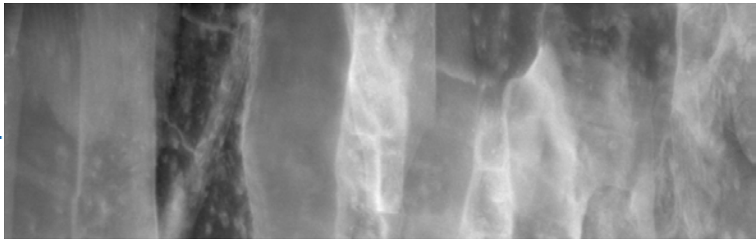

**Figure 12.21** The three-zone model of film deposition as proposed by Movchan and Demchishin *(after Thornton, reprinted by permission, AIP)*.

Zone1-low T, low ion energy yields amorphous, porous materials; Raise T or lower P moves to T-zone

Zone2-Increase T and/or increase ion energy will increase grain size - tall columnar grains

Zone3-Increase T, film has large 3-D grains – surface may be rough and hazy

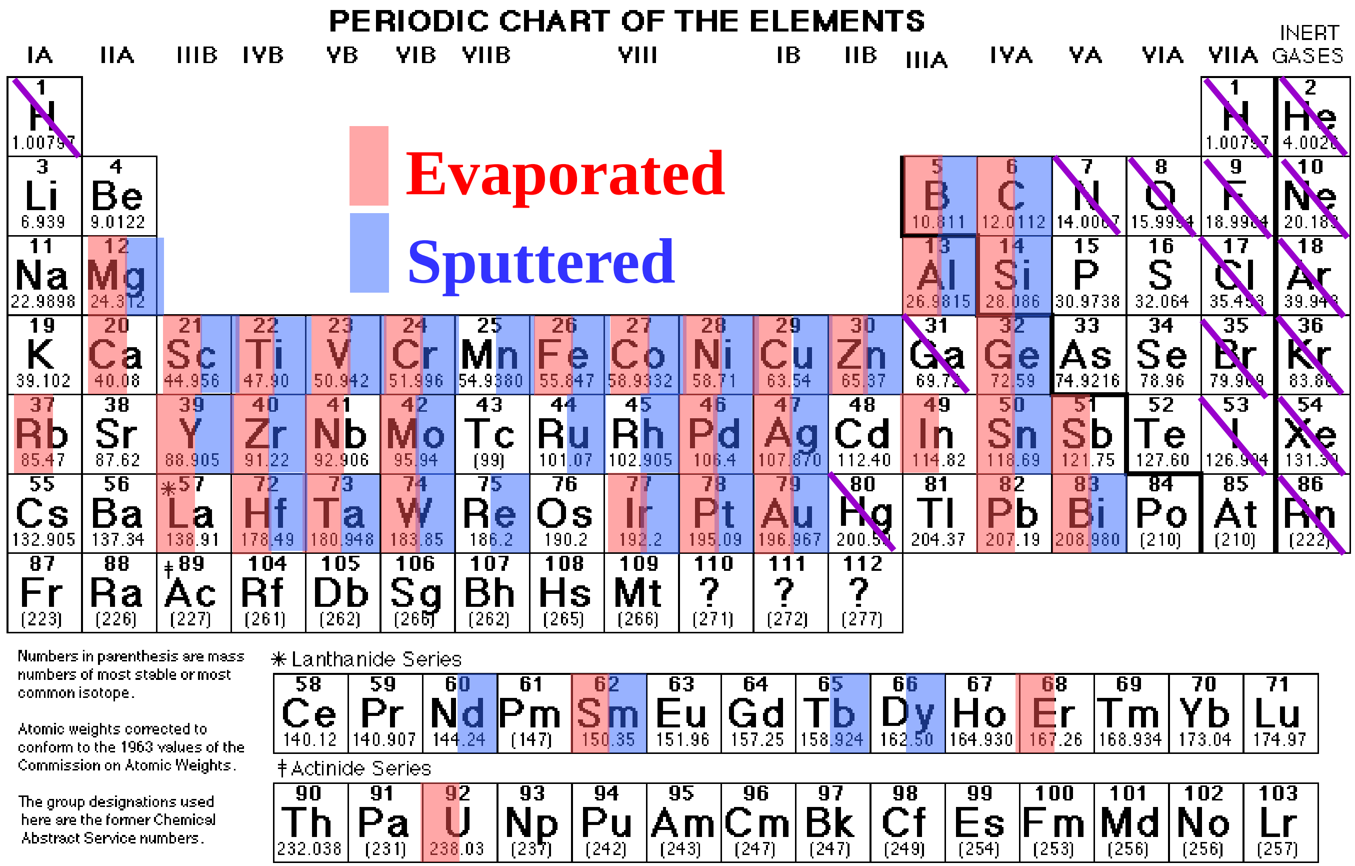
X-sect TEM Evaporated Au Thin Film



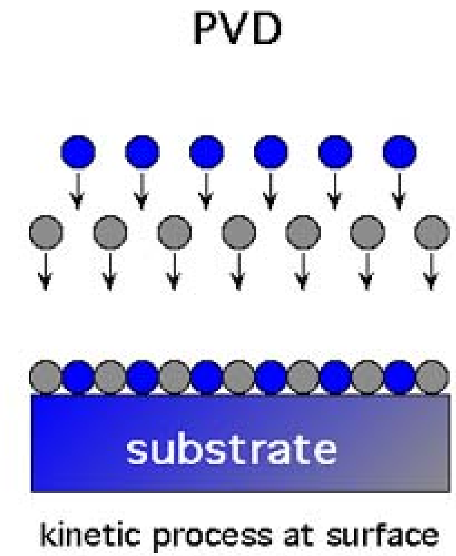
# Thin Film Research & Development

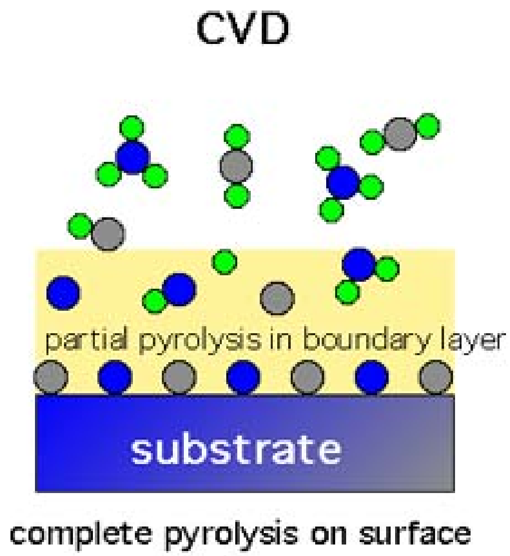
Sandia National Laboratories

**We have deposited: (1) elements, (2) oxides, nitrides, sulfides, or hydrides of selected elements using reactive deposition, and many (3) intermetallic compounds.**

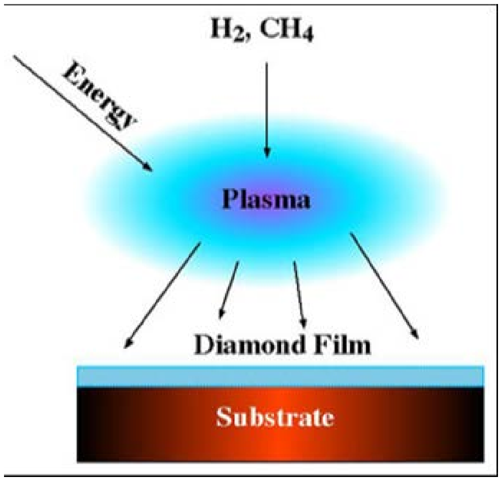


# CVD




PECVD

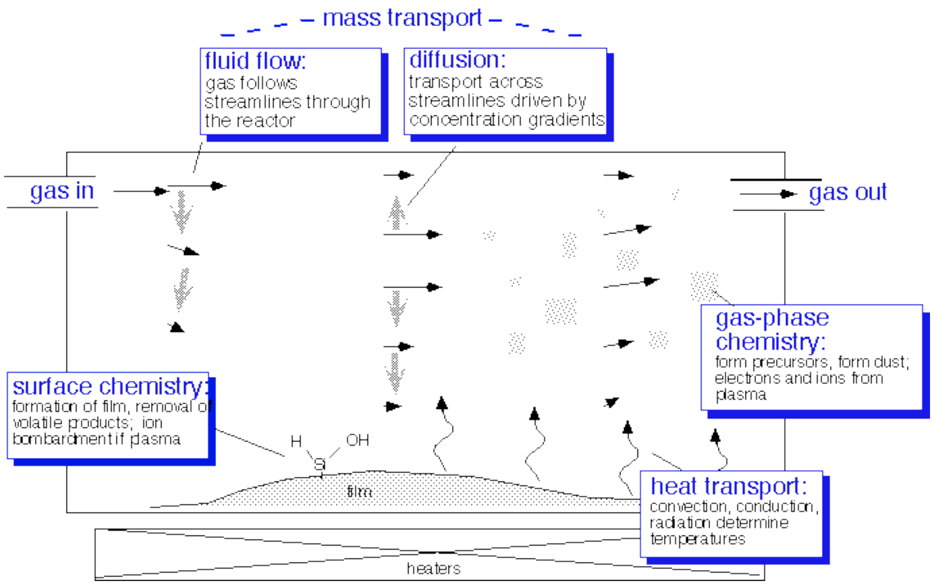



- Complex combination of chemical reactions and gas kinetics
- Uses hazardous precursors
- Gas-phase and surface reactions both must be controlled
- Typically operated at high temperatures T>300°C

# Thin Film Deposition Techniques

Chemical Vapor Deposition (CVD): "Material synthesis method in which the constituents of the vapor phase react to form a solid film at some surface."
Semiconductors, Oxides, Nitrides, Organics, Metals

1. Solid formed depends on chemical reaction (pyrolysis, reduction, oxidation, hydrolysis, nitridation, carbidization, combinations)
2. Transport processes are critical: diffusion of reactants to surface, surface event, removal of products

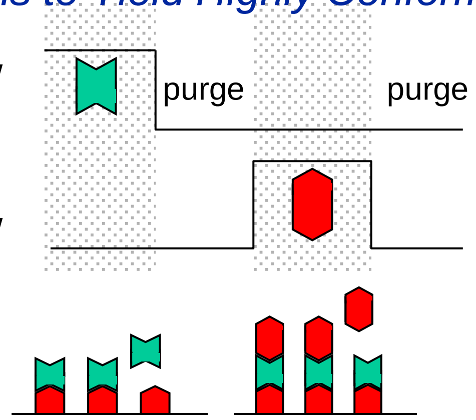



http://www.enigmatic-consulting.com/semiconductor_processing/CVD_Fundamentals/introduction/intro_images/chamber_closeup_1.GIF

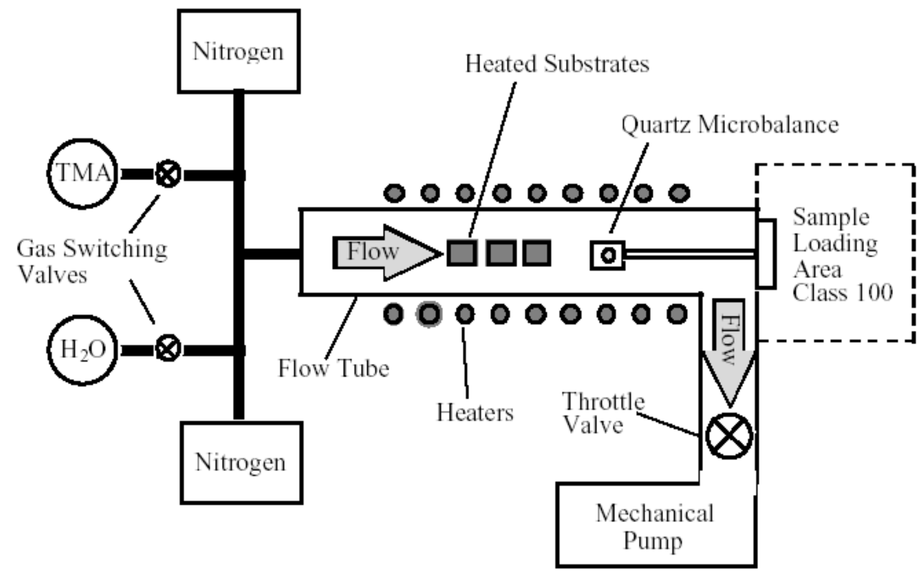
J. Vossen & W. Kern, eds., Thin Film Processes, Academic Press, 1978

# ALD – a special type of CVD

*Atomic Layer Deposition (ALD) - Uses Sequential Reagent Exposures and Surface Limited Reactions to Yield Highly Conformal Coatings with Exquisite Control of Film Thickness*




| "A" | "B" | film |
|---|---|---|
| $Al(CH3)_3$ - TMA | $H_2O$ | $Al_2O_3$ |
| $WF_6$ | $Si_2H_6$ | W |
| $(MeCp)Pt(Me)_3$ | $O_2$ | Pt |




$Al_2O_3$ CVD - reaction:

$$2Al(CH_3)_3(g) + 3H_2O(g) \rightarrow Al_2O_3(s) + 6CH_4(g)$$

ALD $Al_2O_3$ half-reactions: (150°C ~ 1.0 Å/cycle)

$$Al(CH_3)_3(g) + Al\text{-}OH^* \rightarrow Al\text{-}OAl(CH_3)_2^* + CH_4(g)$$

$$2H_2O(g) + \text{-}Al(CH_3)_2^* \rightarrow \text{-}Al(OH)_2^* + 2CH_4(g)$$

W CVD - reaction:

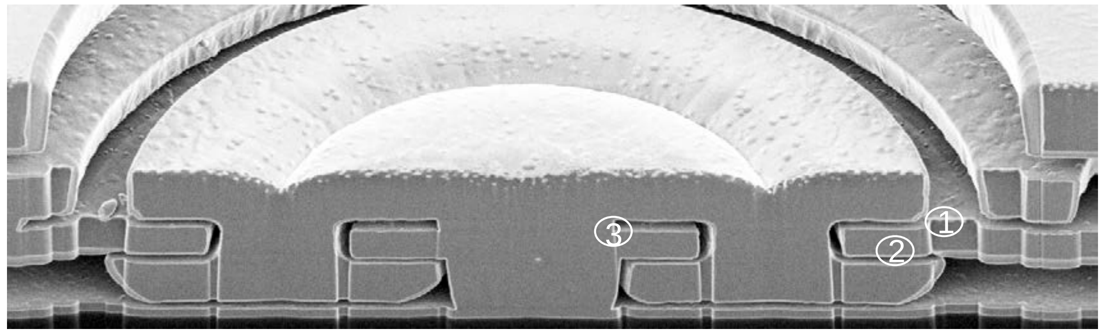
$$WF_6(g) + Si_2H_6(g) \rightarrow W(s)\ 2SiHF_3(g) + 2H_2(g)$$

W-ALD - half-reactions: (150°C ~ 2.5 Å/cycle)

$$W\text{-}SiH_yF_z^* + WF_6(g) \rightarrow W\text{-}WF_x^* + SiH_aF_b\,(g)$$

$$W\text{-}WF_x^* + Si_2H_6(g) \rightarrow W\text{-}SiH_yF_z^* + 2H_2(g) + SiH_aF_b(g)$$

# ALD conformally coats very high aspect ratio structures

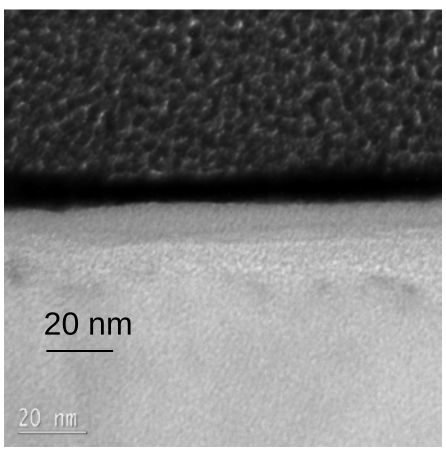


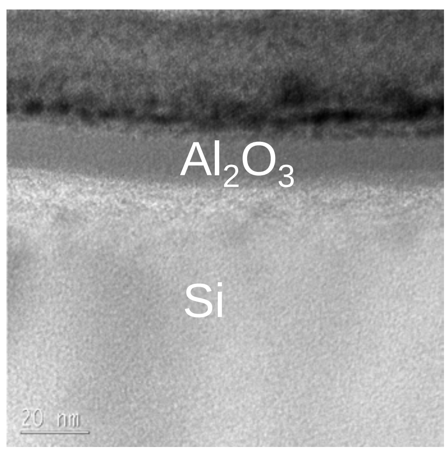

Microengine hub cross section

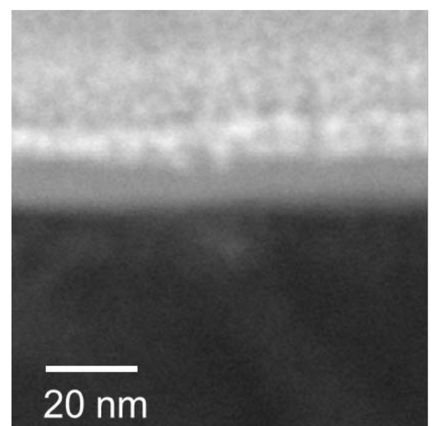
1. Gear top

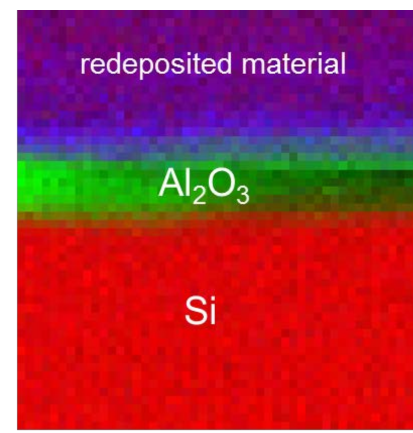
2. Gear bottom

3. Hub interior



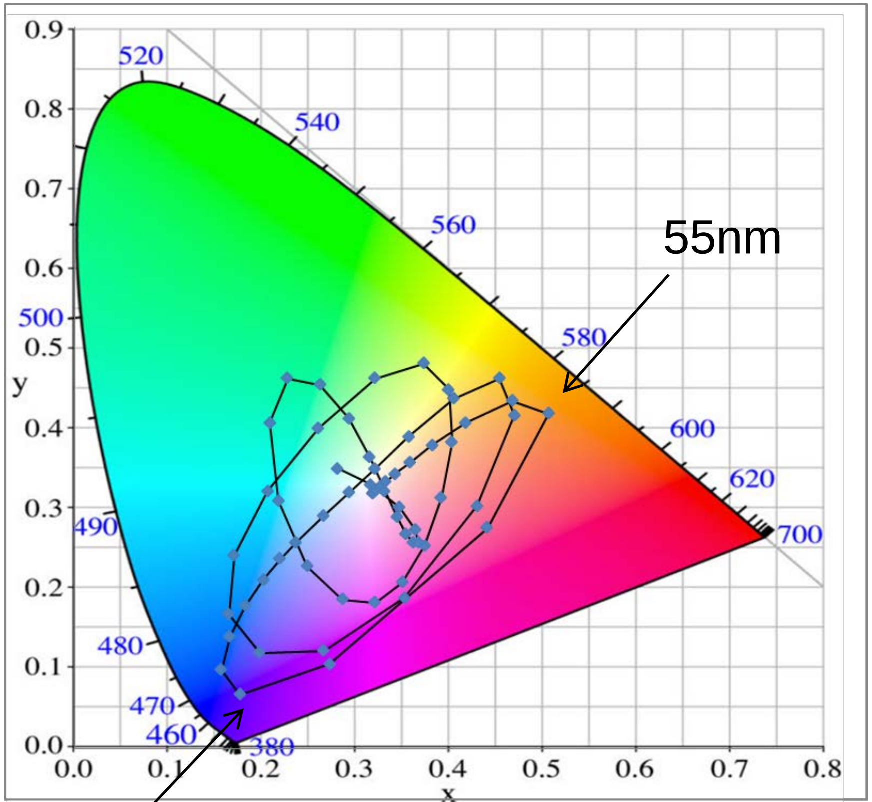



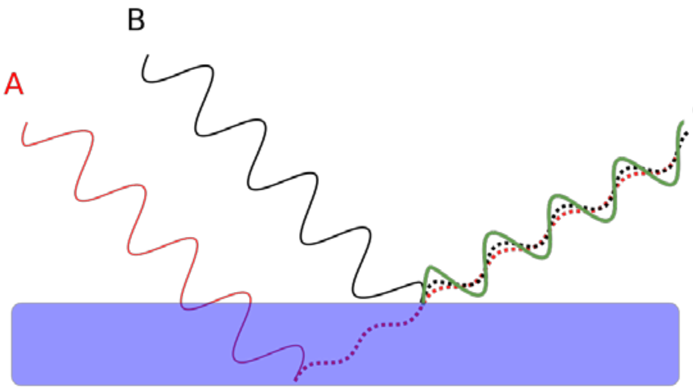



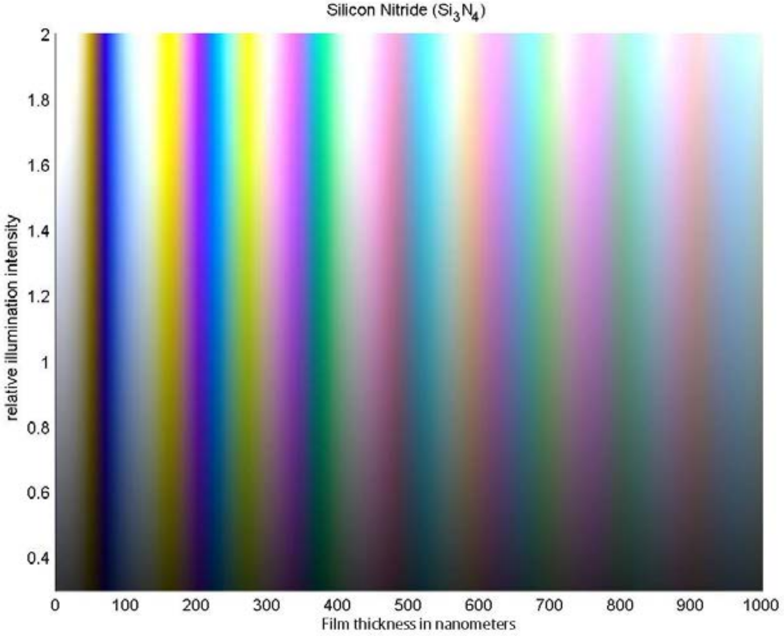
# Optical Films

White Light, $Si_3N_4$ on Si




5 to 500nm of $Si_3N_4$



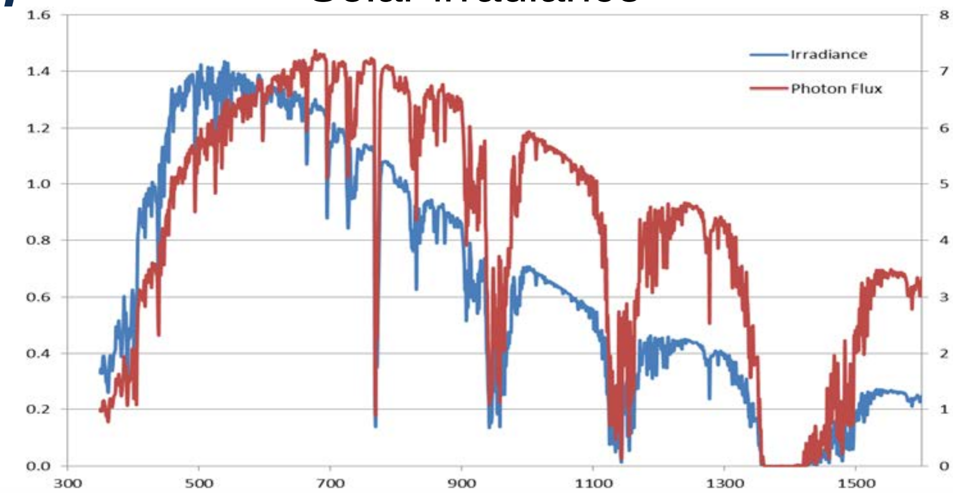


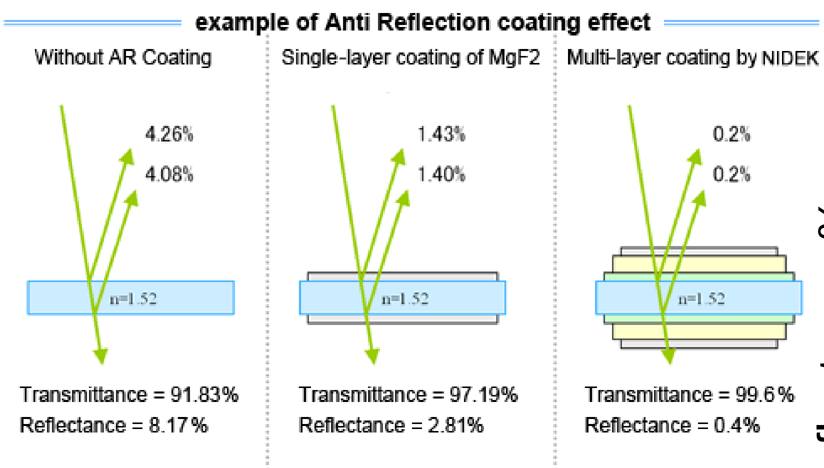

http://www.cleanroom.byu.edu/color_chart.parts/sin_chart.jpg

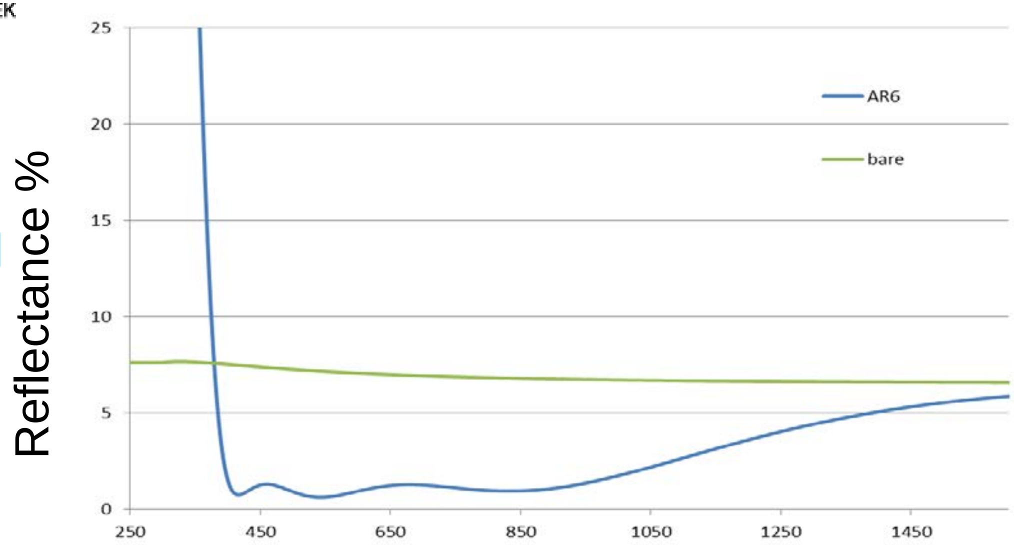
# Optical Thin Films (AR Coating on Glass)

Alternating thin films of transparent materials with high and low refractive index values are used to reduce the light reflection from glass in front on photovoltaics.

Solar irradiance

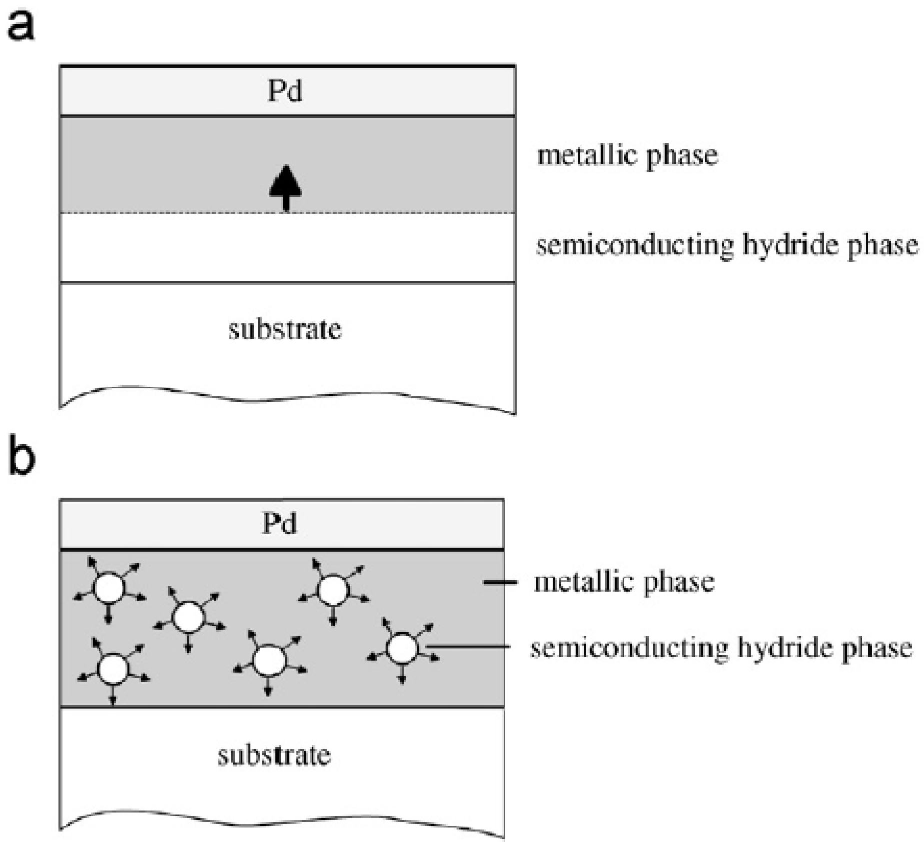


# Switchable Optics

Gasochromic: reversible reflectance change in the presence of $H_2$
$Mg_2NiH_x$ and $MgH_x$ phases are transparent semiconductors




Fabricated by e-beam evaporation.
Codeposition of $Mg_4Ni$ 120nm thick followed by 8 nm of Pd

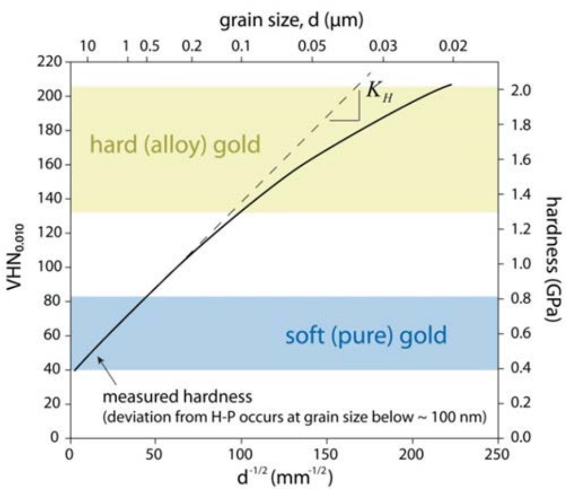


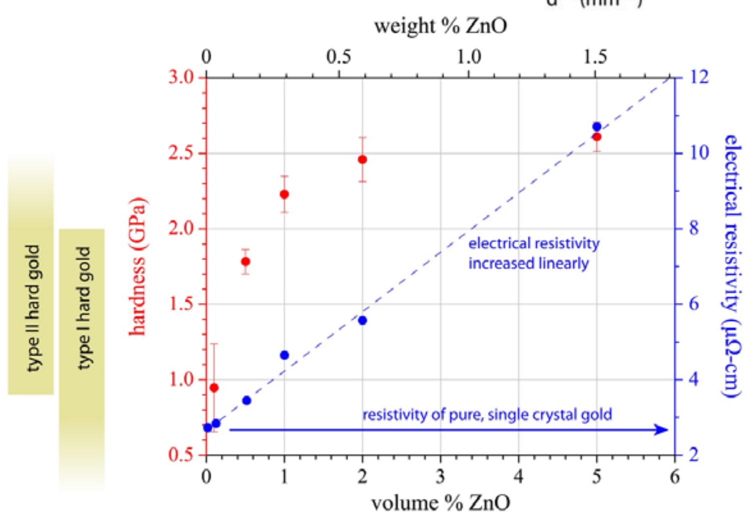
Ell, J., et.al., Solar Energy Mat. & Solar Cells 2007

# Tribology – wear resistant films

Au thin film hardened via Hall-Petch mechanism

***From:*** Lo, Augis, and Pinnel, JAP (1979)



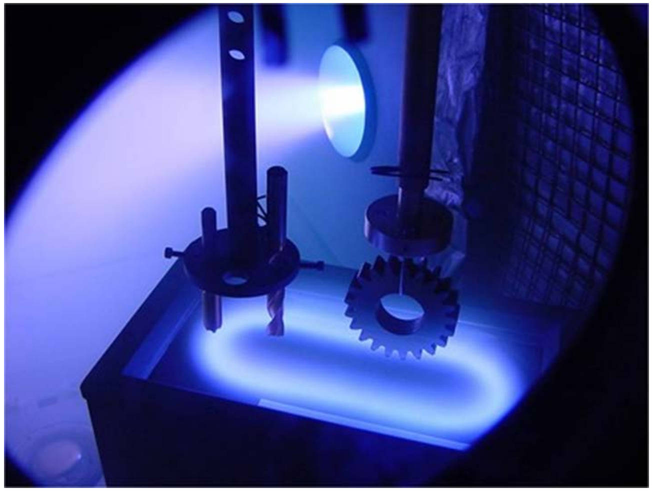




for reference:
0.7 vol % Ni is ~ 0.3 wt % (type I, best ECR performance)
2.2 vol % Ni is ~ 1 wt % (type II, max allowed)

Electrical resistivity measured via van der Pauw method -- square Si wafers pieces coated with composite, no adhesion layers

Dayton Coating Technologies

Tool bits are coated with TiN and other hard materials by sputtering



# Reactive Multilayers

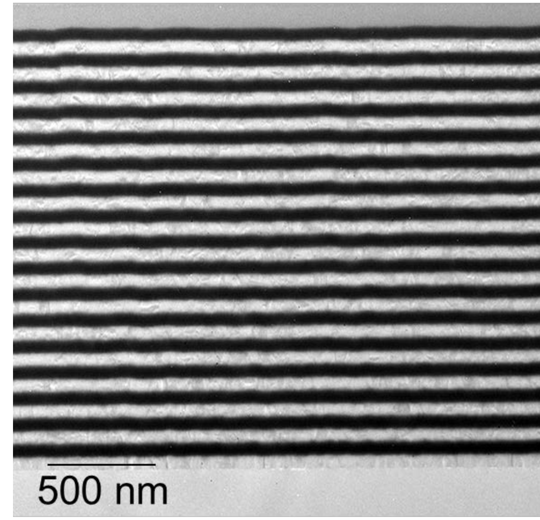
*Platinum/Aluminum*

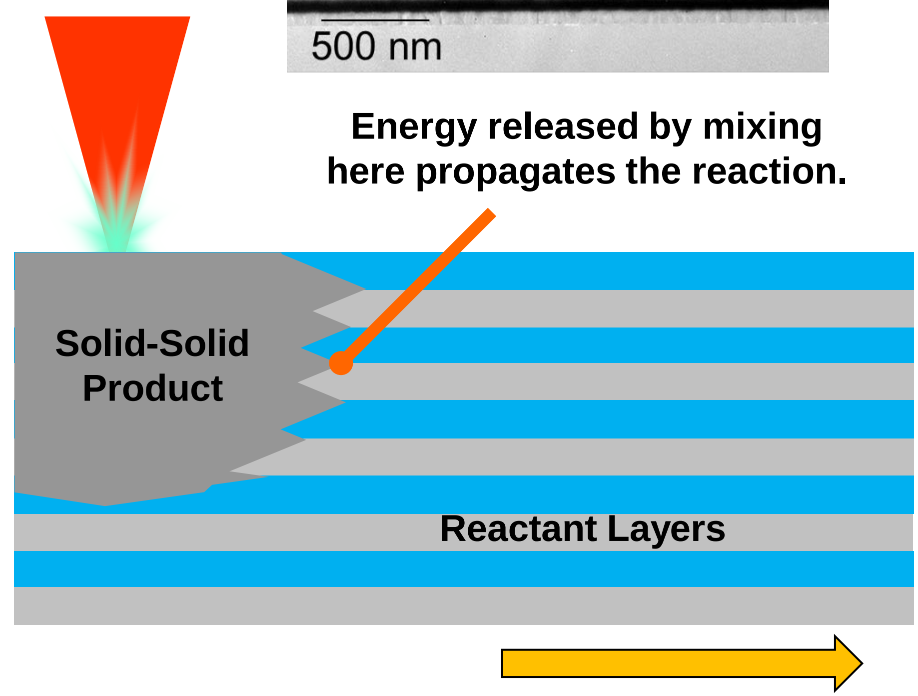
Sandia National Laboratories

Sputtering is used to produce reactive multilayers

Typical design (not requirements):

- Two reactant species
- Single, out of plane periodicity
- 2-1,000 reactant layers
- Total thickness: 0.25-150 $\mu$m




- Reactant pairs generally have a large heat of reaction, $\Delta H_o$:

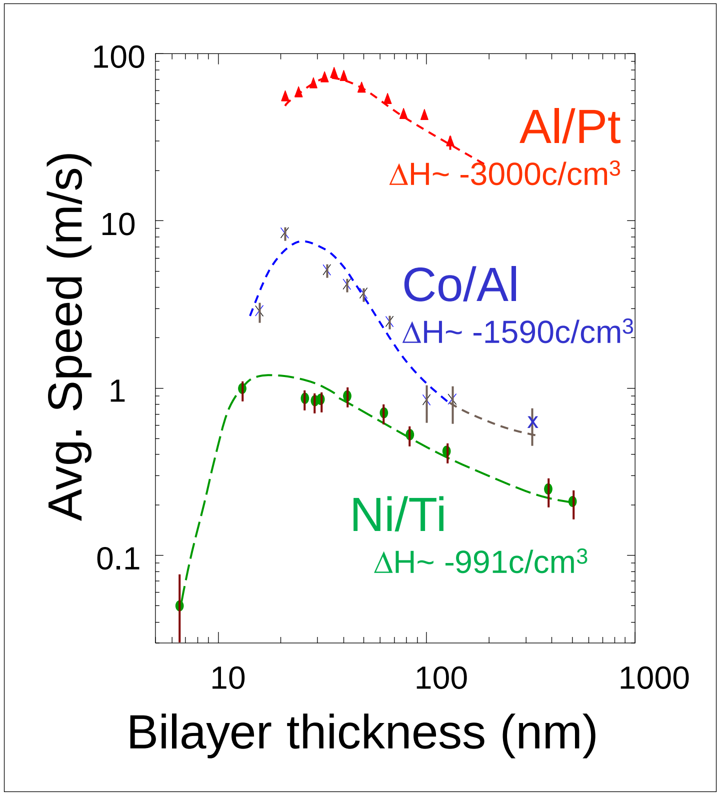
| | | |
|---|---|---|
| Ti/2B | : | - 4.8 kJ/g |
| Al/NiO | : | - 2.2 kJ/g |
| Co/Al | : | - 1.4 kJ/g |
| Al/Pt | : | - 0.9 kJ/g |
| Ni/Ti | : | - 0.6 kJ/g |



From D.P. Adams, R. Reeves, Presentation at ICMCTF 2014

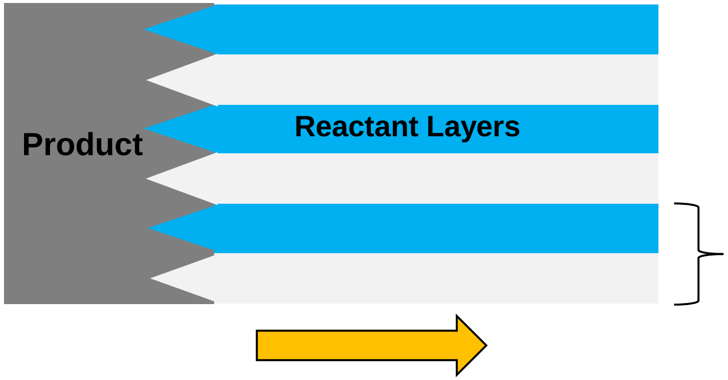
# Propagation speeds vary with bilayer thickness and with material system.

*Reactions in air*

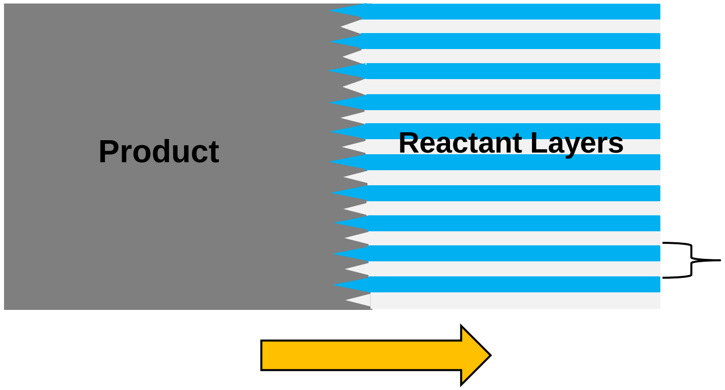



Bilayer thickness affects heat release rate

*Slow release rate*




*Fast release rate*



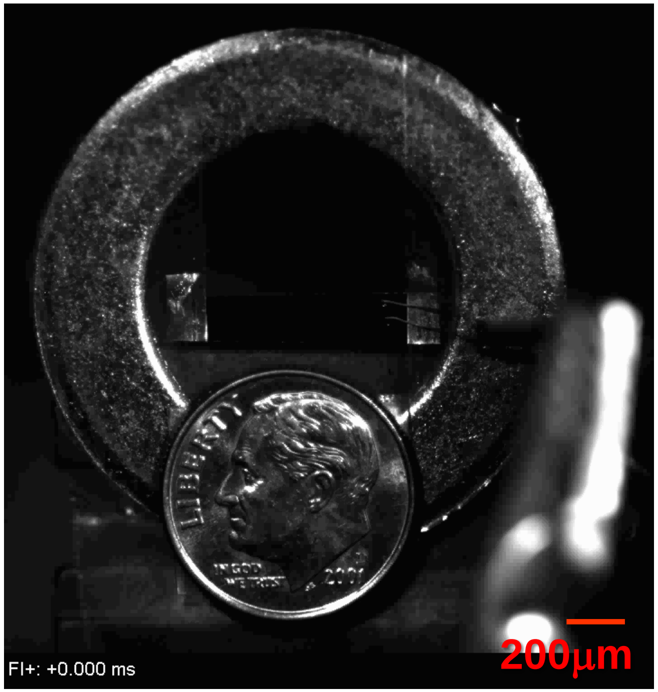



Y. Picard, J. P. McDonald, D.P. Adams, S. Yalisove Appl. Phys. Lett. 93 (2008).

# Reactive Nano-Foils

Sandia National Laboratories

*Ex. Cobalt / Aluminum (7.5 μm)*
*BL = 66 nm*



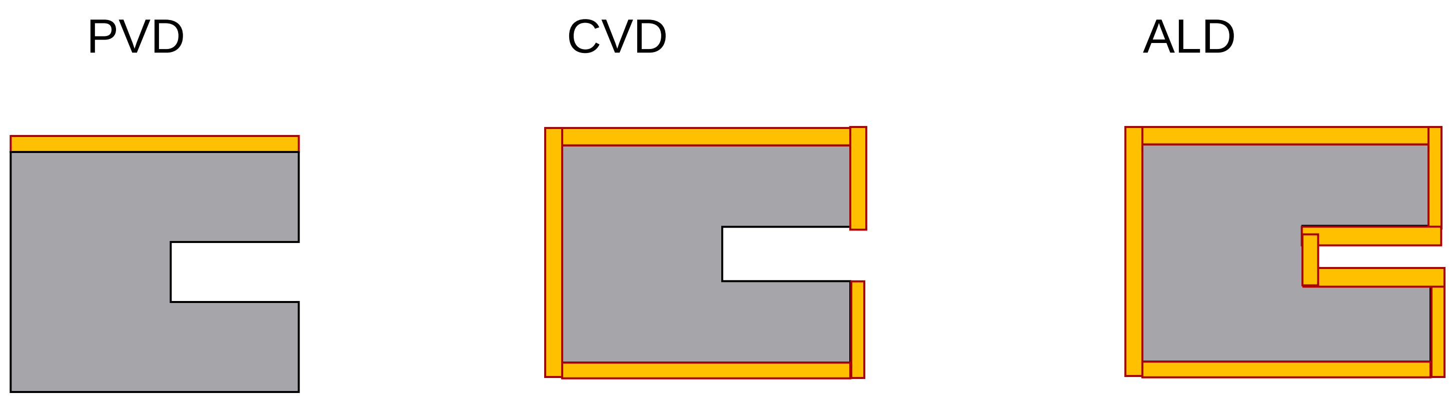

*Heat of reaction used for joining*
*Al/Ni NanoFoil®* Iindium Corp

Now being used to bond sputter targets to water cooled backing plates
Enables bonding temperature sensitive materials and reduces stress from CTE mismatch




www.rntfoil.com

# Summary of Techniques




•PVD (Physical Vapor Deposition) – Material deposited by line of site from a physical source (RT to Moderate Temperature)
•CVD (Chemical Vapor Deposition) – Material deposited by line of site for the gas phase, immediate reaction at the surface (High Temperature)
•ALD (Atomic Layer Deposition) – Material deposited from the gas phase but surface chemistry limited to only one monolayer (Moderate Temperature)