M12: Thin Films

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Also:
Vacuum – Ov
Coatings – Qo
Plasmas - LcG

Introduction

Examples of properties of Thin Films:

Due to: **Low Thickness**	**High Surface to Volume Ratio**	**Microstructural Control**
optical interference effects	gas adsorption	high hardness
electron tunnelling	diffusion	optical absorption
high resistivity	catalytic activity	corrosion protection
planar magnetization		

A few examples of applications:

Categorize by **Film Type**:	Or by **Function:**
Metallic Films electrical contacts, ferromagnetic alloys for data storage, mirrors **Ionic Films** antireflection coatings, integrated optics, transparent conductors **Covalent Films** semiconductors, diamond, hard coatings (SiC, TiC, BN) **Polymer Films** protective coatings	**Decorative** Cr on plastic for car trim **Packaging** Al coated plastics **Corrosion Protection** Ni-Cr-Al-Y coatings on turbine blades **Mechanical** dry film lubricants **Biomedical** pyrolytic carbon on implants **Optical** **Thermal Barriers** **Electrical** **Catalysts** **Magnetic** **Photovoltaic Devices**

Major role in high technology industry:

- microelectronics
- communications
- optical electronics
- protective coatings
- energy generation
- energy conservation

Largest markets:

- semiconductor devices
- recording media
- plastic and paper packaging
- architectural glass coating
- optical coatings

Continued pressure for advances:

- size reduction
- uniformity
- control / reproducibility
- complexity
- purity
- manufacturing speed and automation
- etc. etc.

1. Deposition Techniques

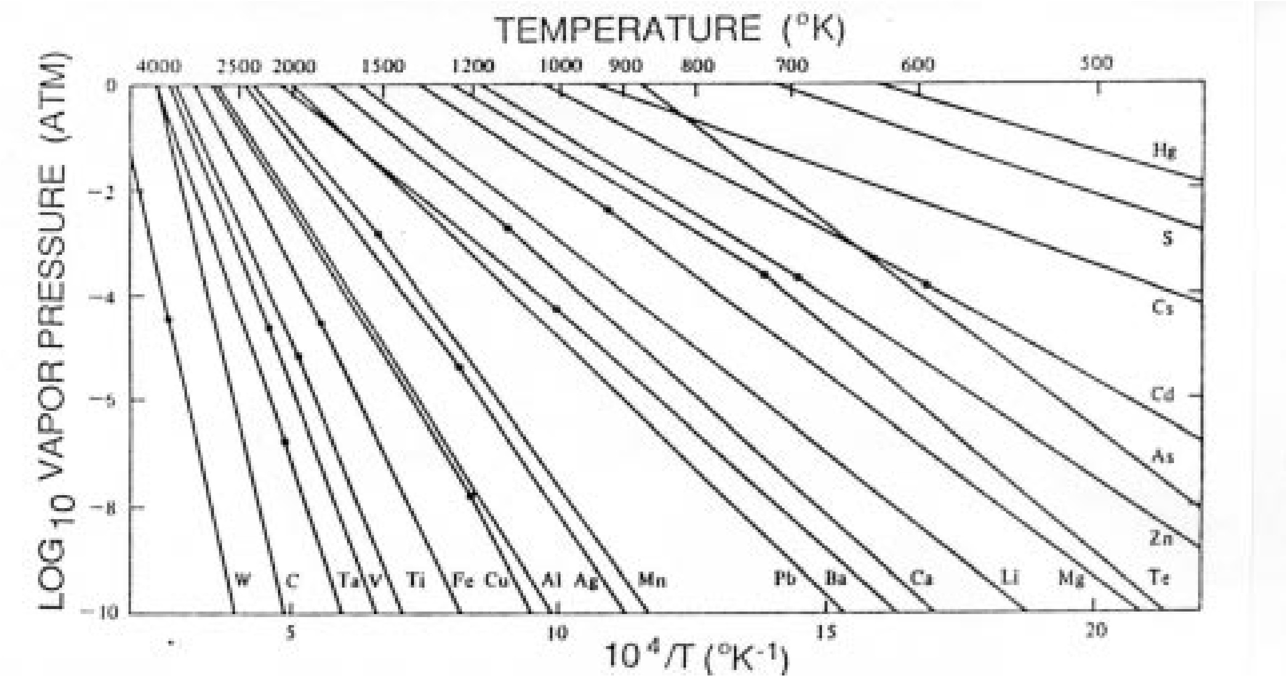
1.1 Physical Vapour Deposition

Generation of vapour source → transport to substrates → nucleation and growth

1.1.1 Evaporation

Supply heat for solid – vapour transition

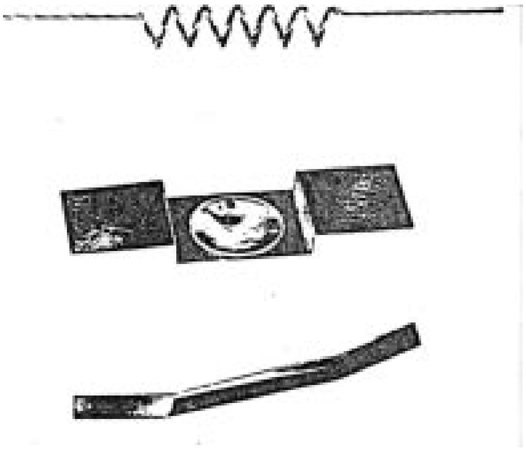
$$P_V \propto \exp \frac{-\Delta H}{RT}$$

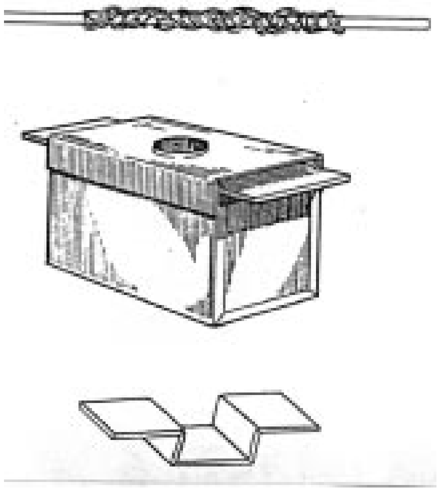


Need: continuous monitoring, or
very accurate temperature control

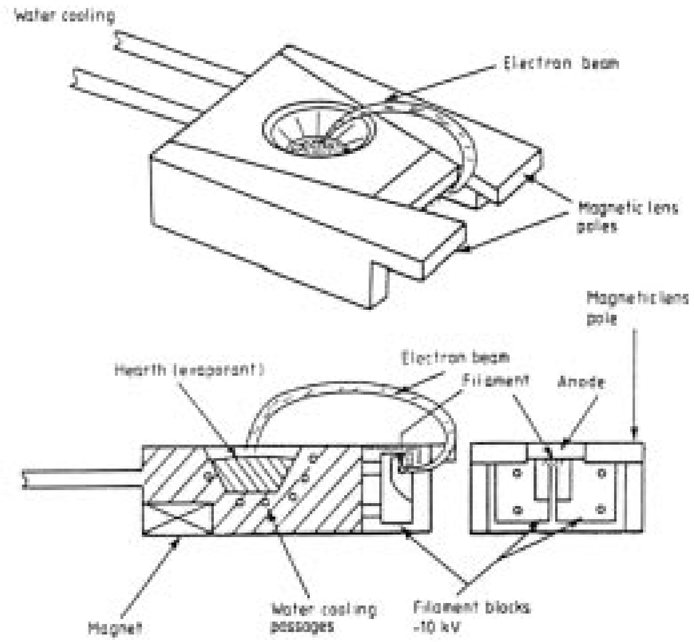
Energy of evaporated atoms typically ~ 0.1 - 0.3 eV

Resistance Evaporation



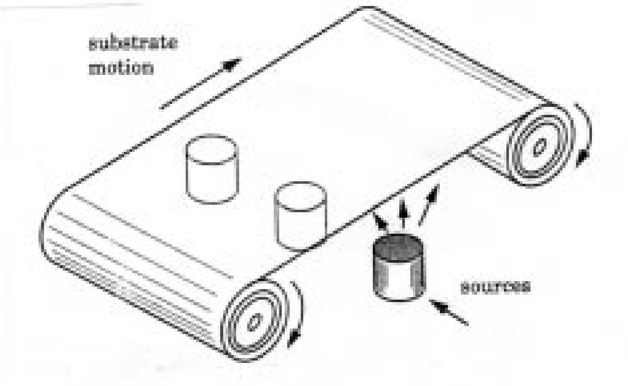


Electron–beam Evaporation



heat charge directly in hearth ⇒ high purity, and for reactive materials

Web Coating



Continuous coating, e.g.
videotape
metal on Mylar for capacitors
Al or SiO_2 moisture barriers on plastic
multilayer coatings for windows

Alloys

- co-evaporation from 2, or more sources
- flash evaporation
- "special alloys," compensated for low P_v component

Compounds

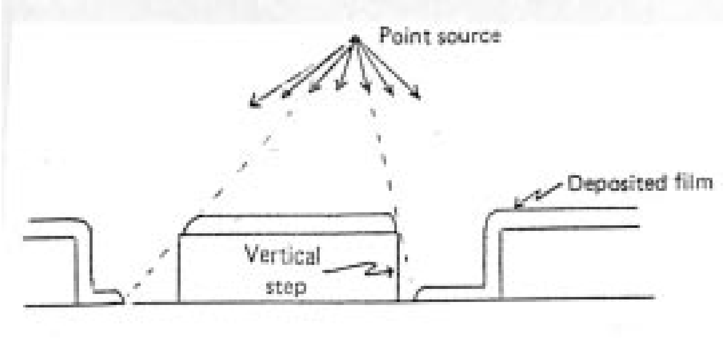
- evaporate directly
  (depends on whether they dissociate)
- reactive evaporation (e.g. add N_2 or O_2 for compound formation)

Heterostructures

- multiple sources

Uniformity

Assume flux from a point source, or cosine emitter:



Activated Reactive Evaporation (ARE): reactive evaporation + source of ionization

Ion Assisted Deposition, Ion Plating: plasma + electrical bias at substrates, or separate ion gun

Molecular Beam Epitaxy (MBE)

Neutral thermal energy beams (molecular or atomic) impinge on a substrate in ultra-high vacuum

- *molecular beam*: m.f.p. > chamber dimension
- *epitaxy*: film derives its crystalline orientation from the substrate

Mean Free Path:

(a) electron in gas, with n molecules per m^3

consider molecule as stationary

cross section $= \frac{\pi d^2}{4}$

$$\Rightarrow \lambda_e = \frac{4}{\pi d^2 n}$$

(c) another **molecule**

consider both particles as moving; $\Rightarrow \sqrt{2}c$

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

(b) ion

cross section $= \pi d^2$

$$\Rightarrow \lambda_i = \frac{1}{\pi d^2 n}$$

e.g. air at room temp.:

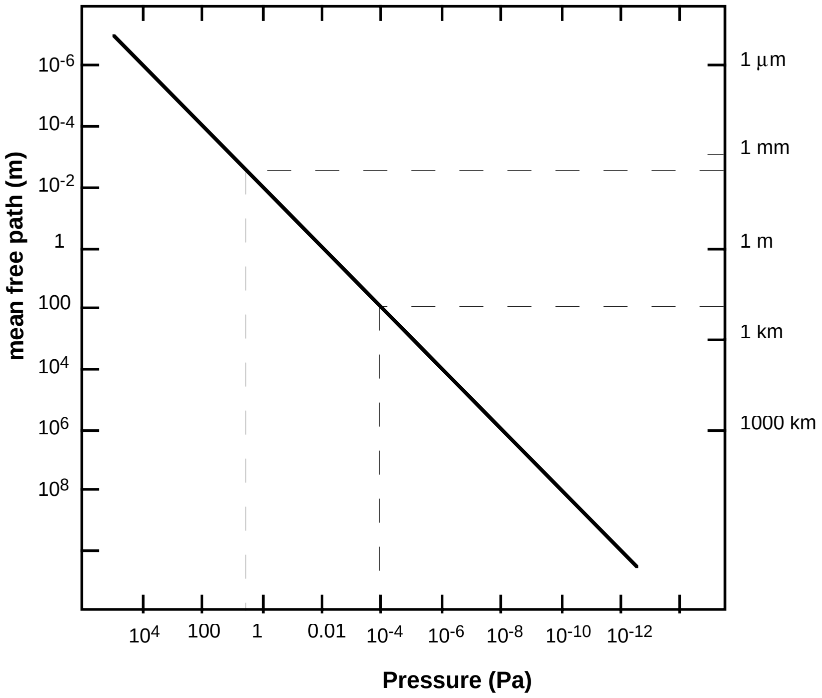
Ideal Gas Law $P\,N_A = n\,R\,T$

⇨ $n \approx 3.10^{25}\ m^{-3}$

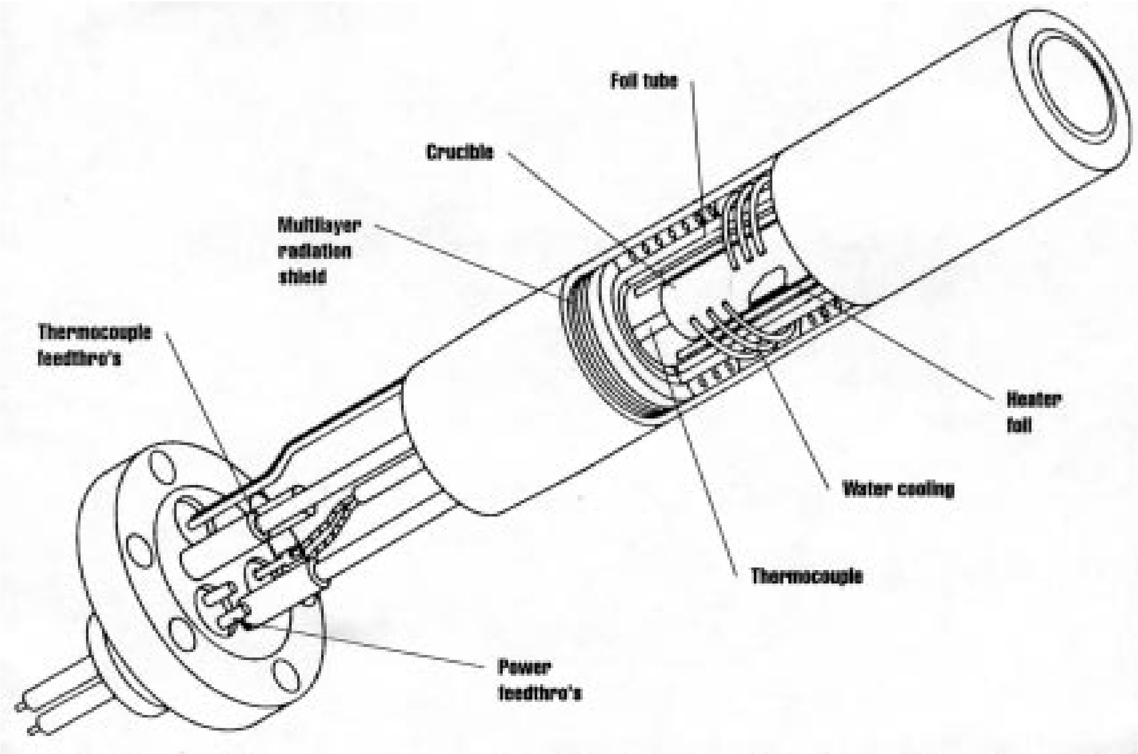
$d \sim 0.5$ nm

⇨ $\lambda \sim 50$ nm

at 2.5 Pa → m.f.p. ~ 2.5 mm



Knudsen Cell, or **Effusion Cell**:



Cracker cell - 2 zones; low T (*sublimation*) + high T (e.g. 800 - 1000°C) (*cracking*)

- Deposition onto single crystal substrates at raised temperature (e.g. 0.6 m.pt.)

  ⇒ surface diffusion

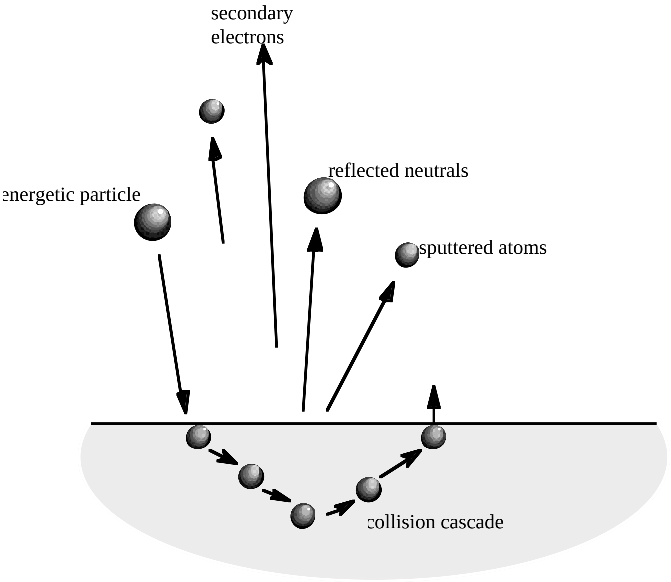
- Ultra-high vacuum

  ⇒ very high purity ⇒ *in situ* analysis and real time growth monitoring

- Low growth rates; e.g. 1 monolayer s^{-1}
- Use substrate rotation for producing uniform films
- Use shutters to interrupt deposition instantaneously (e.g. for heterostructures)

- complex
- slow
- expensive ⇒ limited production applications
- not continuous
- long down times

1.1.2. Sputtering



- sputtered flux mainly atoms with energies of a few eV – a few 10s eV (random direction)

  ⇒ etching ⇒ deposition (from any target material)

Elastic Binary Collisions

M_1 moving, M_2 stationary:

angle between initial trajectory and line joining centres at contact

$$\frac{E_2}{E_1} = \frac{4M_1M_2}{(M_1+M_2)^2}\cos^2\theta$$

energy transfer coefficient

⇨ similar masses → efficient energy transfer

- **Sputter Yield, S** (number of ejected particles per incident particle)

For incident energy, $E_i < 1$ keV:

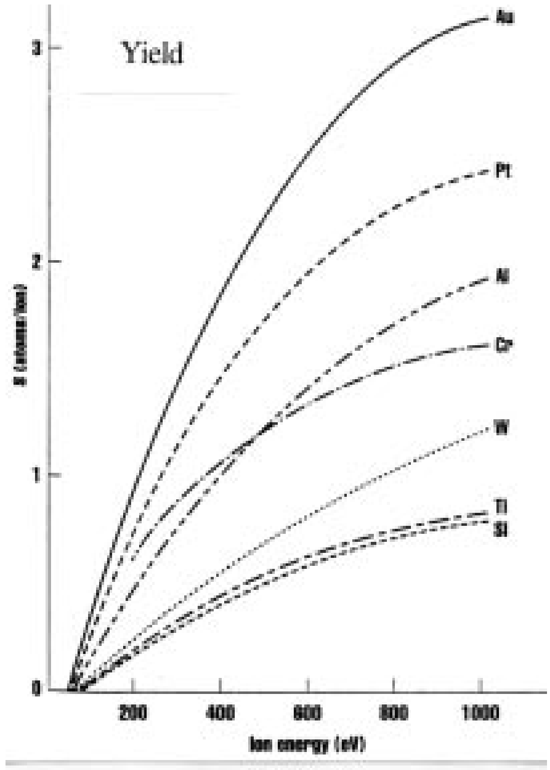
$$S \propto \frac{kE_tE_i}{U}$$

Typically, use Ar at 100 – 500 eV:

- $S \approx 1$ for most metals
- $S \propto \frac{M_t}{T_{m.pt.}}$.

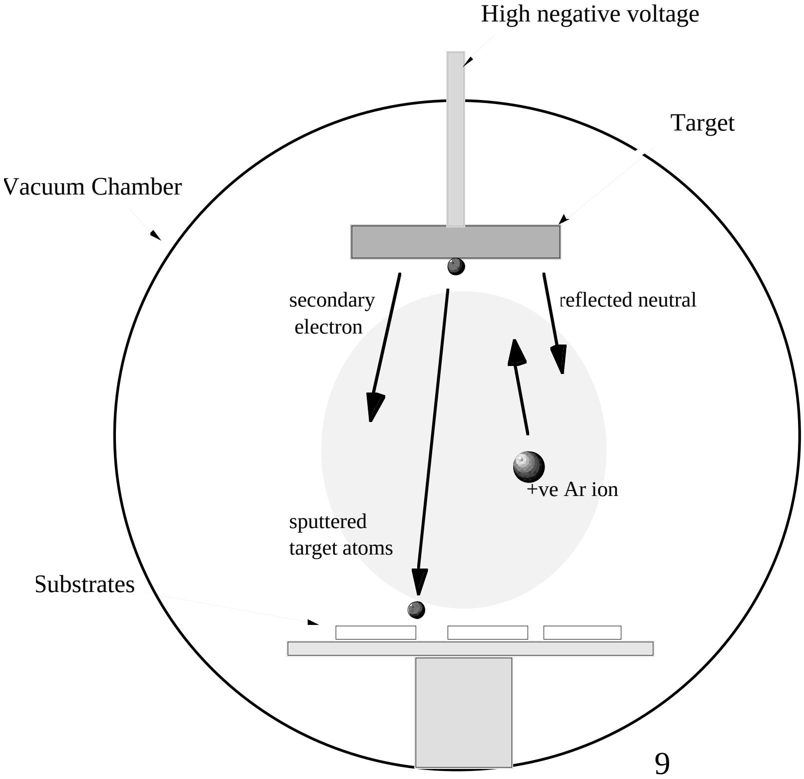
Element	Sputtering Yield (atoms/ion) (for Ar at 500 eV)	Ar Threshold Energy (eV)
Al	1.05	13
Au	2.40	20
C	0.12	-
Ni	1.45	21
Si	0.50	-
Ta	0.57	26

Element	**He** **(500 eV)**	**Ne** **(500 eV)**	**Ar** **(500 eV)**	**Ar** **(1 keV)**	**Kr** **(500 eV)**	**Xe** **(500 eV)**
Al	0.16	0.73	1.05	1.0	0.96	0.82
Au	0.07	1.08	2.40	3.6	3.06	3.01



- levels off at high E_i due to implantation

DC Glow Discharge Sputter Deposition



Cathode / Crookes Dark Space:

- most voltage drop
- secondary electrons accelerated away from cathode
- positive gas ions accelerated to cathode

Negative Glow:

- accelerated electrons have enough energy to impact-ionize neutral gas atoms

DC Sputtering

- Need relatively high pressure ⇒ sputtered flux has to pass through gas ⇒ low efficiency
- Need a conducting target

RF Sputtering

- Develop negative potential on target since electrons are more mobile than ions
- Electron oscillations ⇒ ionization ⇒ maintain discharge at lower pressures
- Rf voltage couples through any impedance ⇒ insulating targets possible

Magnetron Sputtering

electric + magnetic field → cycloidal motion

Trap electrons near target surface

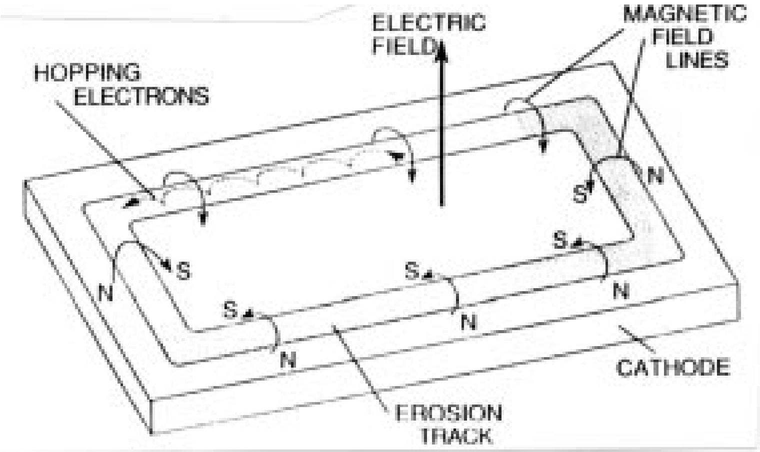
⇒ increase path length,

prolong residence time

- enhance collision probability
- increase pressure range
- increase deposition rate
  (more sputtering, less scattering)

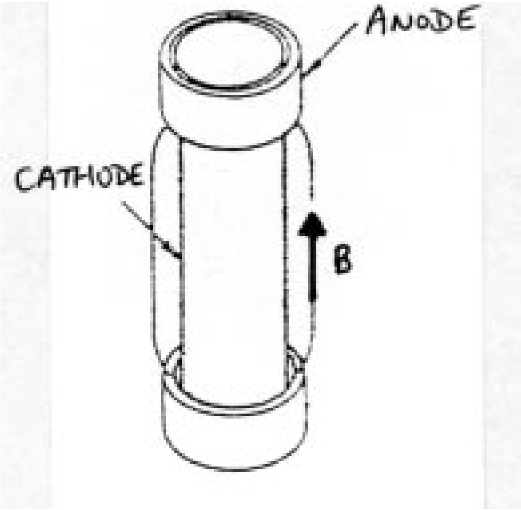
2 track erosion ⇒ poor material utilisation

Planar Magnetron

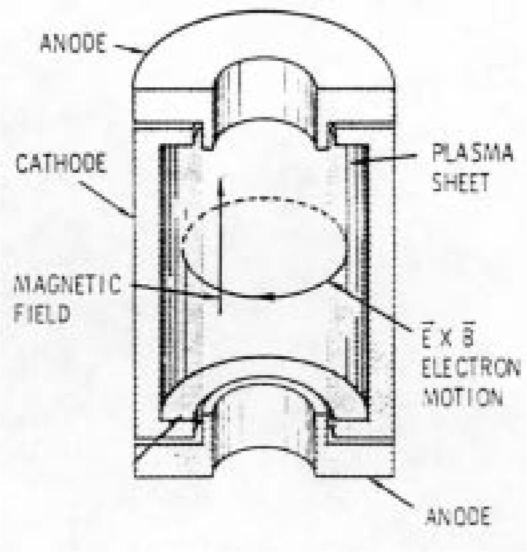


Cylindrical Post-Cathode

Hollow Cylindrical Cathode



→ coating inside hollow shapes



→ coat all faces of complex objects

Alloys

- 2, or more targets
- composite target
- alloy target

Compounds

- compound target
- reactive sputtering

Examples of Reactive Sputter Deposition:

Film type	Target, e.g.	Reactive gas	Product
oxides	Al, In, Sn, Si, Ta	O_2	Al_2O_3, In_2O_3, SnO_2, SiO_2, Ta_2O_5
nitrides	Ta, Ti, Al, Si	N_2, NH_3	TaN, TiN, AlN, Si_3N_4
carbides	Ti, W, Si	CH_4, C_2H_2	TiC, WC, SiC
sulphides	Cd, Cu, Zn	H_2S	CdS, CuS, ZnS

✓metal targets

✓higher rates

✓control of stoichiometry

✗several gases / gas flow control

Heterostructures

- multiple targets

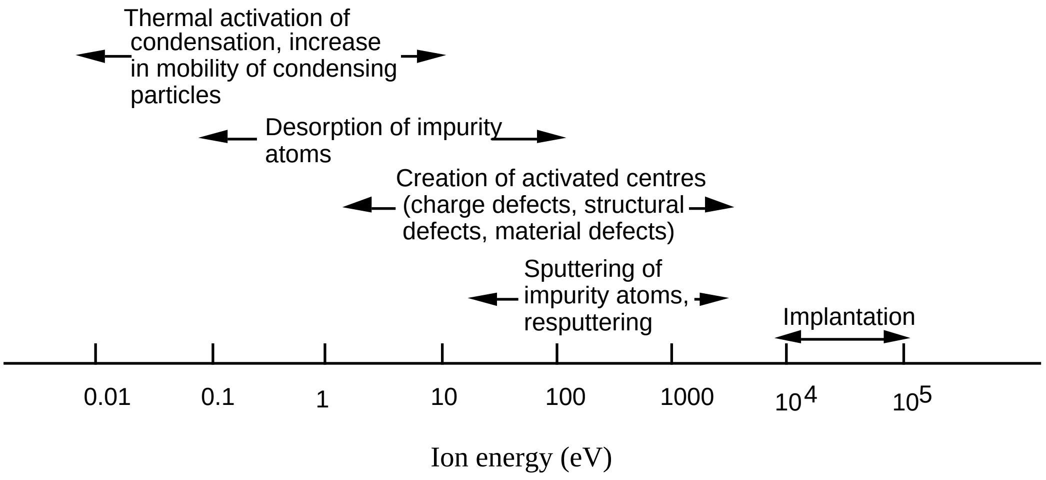
Uniformity

- dependent upon geometry
- presence of sputtering gas ⇒ scattering ⇒ throwing power *if* feature size > m.f.p.

Sputtered atoms and reflected neutrals:

relatively high K.E. ⇒ energetic bombardment of growing film

- resputtering
- forward sputtering
- compaction
- energy input to surface species → enhanced mobility
- incorporation / implantation
- formation of defects / nucleation sites



Bias Sputtering: electrical bias at substrates ⇒ bombardment by plasma ions + any ionised depositing species

Ion Sputtering: sputter from target using an independent ion gun ⇒ independent control of flux, angle of incidence and pressure

Sputter Deposition - Summary

✓ Range of materials

✓ Rate control

Energy input

Flux scattering

✓ Range of geometry

✓ Easily automated / scaled up

1.1.3 Laser Ablation / Pulsed Laser Deposition (PLD)

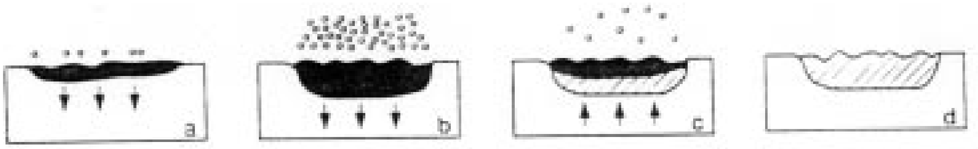
intense energy pulse in shallow depth:

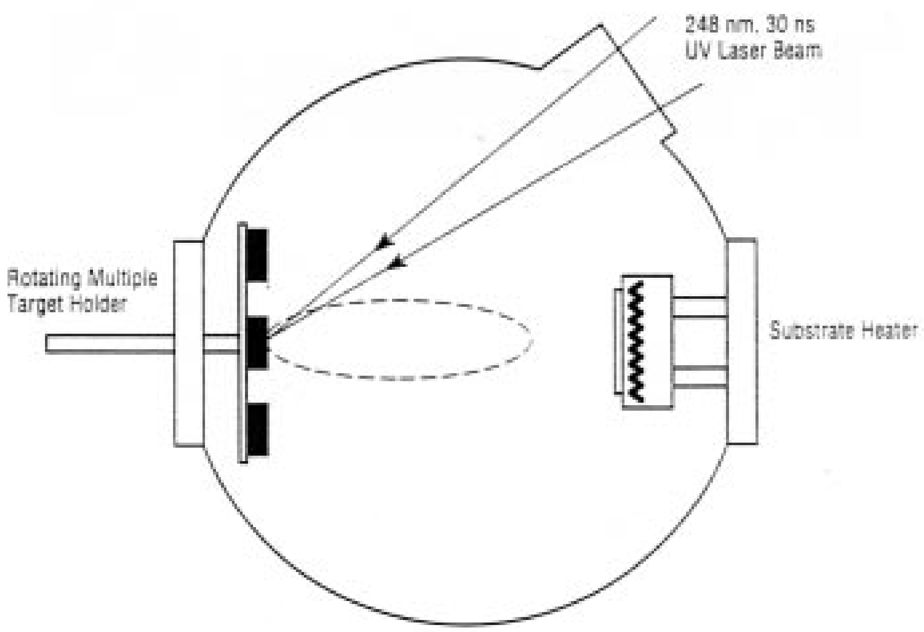
“explosive evaporation”

small clusters of atoms ejected; some droplets

energy ~ 10s eV

pulsed laser, e.g. λ = 200 - 300 nm; 6 - 12 ns





Alloys / Compounds

- alloy / compound target → stoichiometric films e.g. complex compounds
- composite target
- several targets

Heterostructures

- several targets

Uniformity

- *can* be line of sight … or not!

PLD – Summary

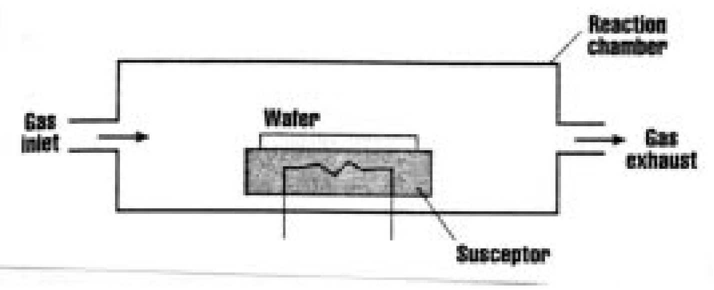
✓ no contamination sources
✓ high rate
✓ range of materials

✓ complex compounds
✓ any environment
✓ active laser plume

✗ expensive
✗ safety issues
✗ difficult to scale up

1.2 Chemical Vapour Deposition

Deposition of solid films from chemical precursors in the vapour phase

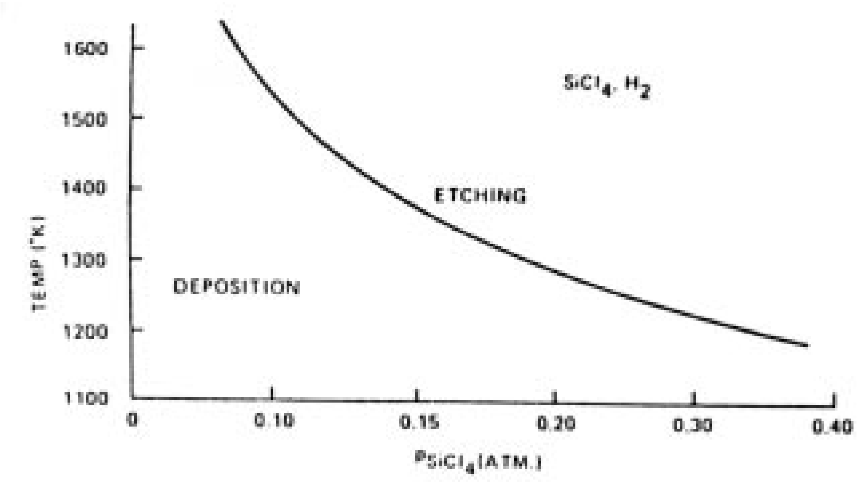


e.g. Decomposition, or Pyrolysis

$SiH_4\,(g) \rightarrow Si\,(s) + 2H_2\,(g)$ (650°C)

e.g. Reduction

(a) $SiCl_4\,(g) + 2\,H_2\,(g) \rightarrow Si\,(s) + 4HCl\,(g)$ (1200°C) → epitaxial Si on Si wafers



reversible reaction ⇒
substrate vapour cleaning
followed by deposition

(b) WF_6 (g) + $3H_2$ → W (s) + 6HF (g) (300°C) → metallization

or WF_6 reacts directly with exposed Si → W (+ SiF_4 (g))
⇨ *selective deposition* (SiO_2 surfaces uncoated)

e.g. Oxidation

e.g. $SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$

dependent upon T and P

$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$

other oxidants; CO_2, N_2O, NO, NO_2, O_3

homogeneous reactions and transfer of reactants to the substrates
(gas phase phenomena)

↓

adsorption of reactants; heterogeneous chemical reactions; surface migration; lattice incorporation
(surface phenomena)

↓

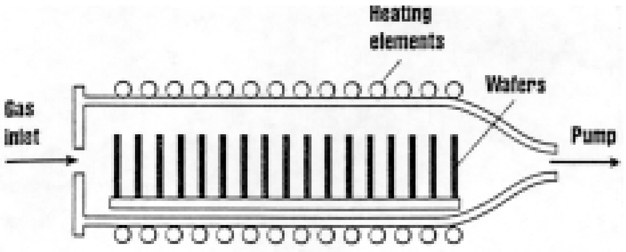
desorption of reaction by-products and transport away from substrates
(gas phase)

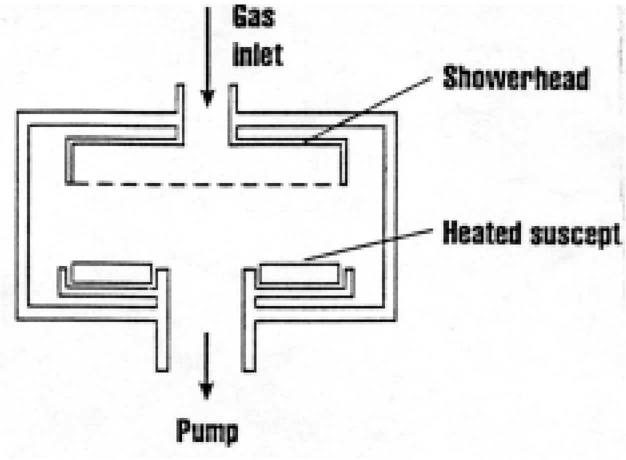
Some more examples:

Reaction	Sources	T_d (°C)	Deposit
Pyrolysis	$SiH_4 + GeH_4$	800 - 850	$Si_{1-x}Ge_x$
Reduction	$GeCl_4$, H_2	600 - 900	Ge (epi.)
	$MoCl_5$, H_2	900 - 1300	Mo
Oxidation	$Zn(C_2H_5)_2$, O_2	250 - 500	ZnO
	$Al(CH_3)_3$, O_2	275 - 475	Al_2O_3
Hydrolysis	$AlCl_3$, CO_2, H_2	850 - 1100	Al_2O_3
	$SnCl_4$, H_2O	450	SnO_2
	$PbCl_2$, $TiCl_4$, H_2O, O_2	500	$PbTiO_3$

Reaction	**Sources**	**T_d (°C)**	**Deposit**
Nitridation	$SiCl_2H_2$, NH_3	750 - 900	Si_3N_4
	$TiCl_4$, N_2, H_2	1100	TiN
Disproportionation	GaCl		Ga
Compound formation / Synthesis	$SiCl_4$, CH_4	1400	SiC
	Zn, H_2S, H_2	825	ZnS
Chemical Transport relatively non-volatile solid source + transport agent → volatile species	Ga, Al, AsH_3, HCl, H_2 In, PH_3, HCl, H_2	670 – 770 700 / 630	$Al_xGa_{1-x}As$ InP

Also: combined reactions, e.g. pyrolysis + reduction





- *Don't* have independent control of T_d
- Reaction rate given by slowest step

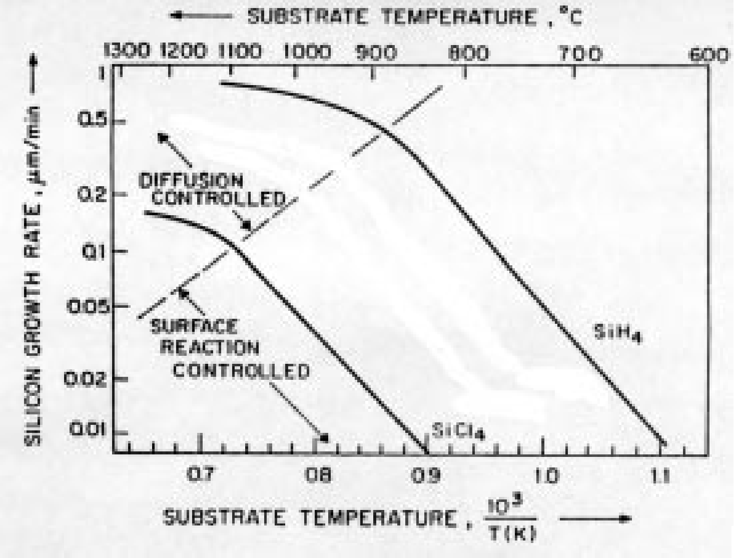
<u>Limiting Step</u>

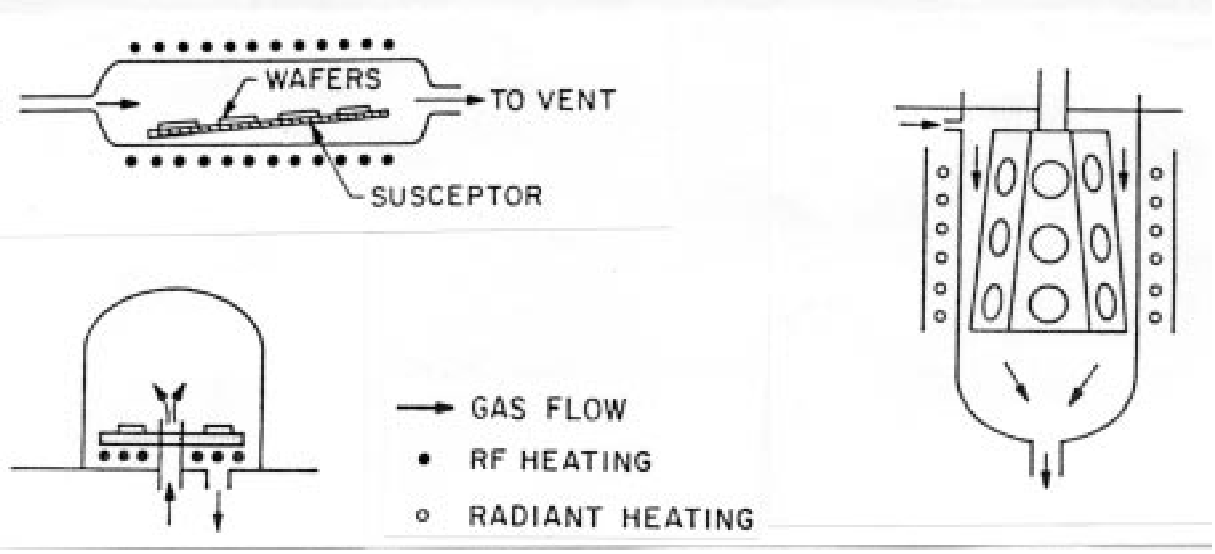
'high' T ➔ mass transport ➔ controlled by supply of reactants
"Reactant Supply Control" *not* sensitive to T_d
need uniform gas supply

'low' T ➔ surface processes ➔ kinetic limited regime
"Reaction Rate Control" *not* sensitive to gas supply

need uniform T_d

⇒ high uniformity
⇒ good step coverage ***conformal* coating**





- **Photo-CVD / Laser Assisted CVD**

  Radiation (e.g. laser spot) locally induces a photochemical reaction
  ⇒ "write" selected area deposition

e.g. $Cd(CH_3)_3$, $Te(CH_3)_3$ → CdTe

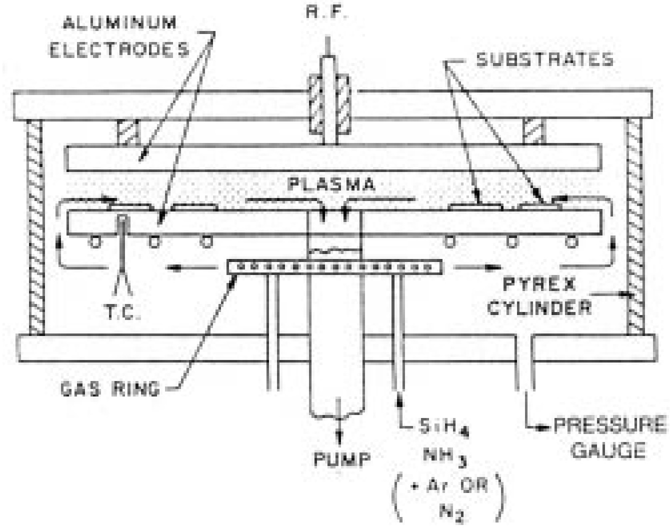
- **Plasma Enhanced CVD (PECVD)**

  Gases dissociated / ionized by discharge (e.g. rf; µ-wave) ⇒ enhance growth rate, allow lower T_d

e.g.

low T (< 350°C) deposition
of **Si_3N_4** passivation layers
$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$

a-Si (~280°C):
$SiH_4 \rightarrow Si + 2H_2$



- **Metalorganic CVD (MOCVD)**

e.g. III - V semiconductors:

R_3M (g) + EH_3 (g) → ME (s) + 3RH (g)

metalorganic precursors, e.g. trimethyl gallium (TMG): $(CH_3)_3Ga$

MOCVD in UHV: Metalorganic MBE (**MOMBE**), or Chemical Beam Epitaxy (**CBE**), or Organometallic Vapour Phase Epitaxy (**OMVPE**)

Alloys / Compounds

- several reactions

Heterostructures

- change reactant supply

Uniformity

- conformal coating by reaction rate control

CVD - Summary

✓ wide variety of materials

✓ can be high purity

✓ *in situ* substrate cleaning /etching

✓ relatively cheap

✓ selective area deposition

✗ complex

✗ T_d cannot be independently controlled

✗ pumping and safety issues

✓ high uniformity over complex shapes and large areas (conformal)

✓ good control of stoichiometry: reproducible, easy to add doping

✓ batch, or semi-continuous coating and scale up

✗ don’t know the relation between processing conditions & structure as well as for PVD

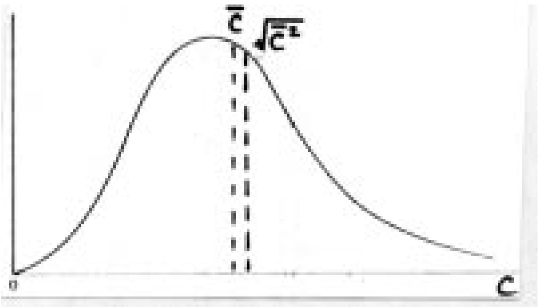
✗ difficult to predict growth mechanism & optimum deposition parameters

1.3 Deposition Systems

Films grown from vapour fluxes ⇒ dependent upon environment

Kinetic Theory

Maxwell-Boltzmann distribution:



$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3RT}{M}}$$

Ideal Gas Law: $PN_A = nRT$

Molecular arrival rate: $\dfrac{n\bar{c}}{4} = \dfrac{PN_A}{\sqrt{2\pi MRT}} \quad m^{-2}s^{-1}$

1 monolayer ~10^{19} atoms m^{-2}

1 atmosphere = 760 mmHg = 760 torr = 101.325 kPa; 1 Pa = 7.5 mtorr; 1 bar = 10^5 Pa

Vacuum Systems

Need to pump:

- process load (e.g. evolved vapour, trapped volume)
- outgassing (desorption of adsorbed and absorbed gases)
- leakage
- backstreaming
- residual gas

Also: vapourisation, diffusion, permeation

Outgassing: High adsorption energy ⇒ very slow desorption

Intermediate

Low adsorption energy ⇒ very rapid desorption