Deposited thin films

- need to be able to add materials “on top” of silicon
  - both conductors and insulators
- deposition methods
  - physical vapor deposition (PVD)
    - thermal evaporation
    - sputtering
  - chemical vapor deposition (CVD)
- general requirements
  - good electrical characteristics
  - free from pin-holes, cracks
  - low stress
  - good adhesion
  - chemical compatibility
    - with both layer “below” and “above”
    - at room temperature and under deposition conditions

Kinetic theory of gases

- for a gas at STP:
  - N ~ 2.7 x 10^{19} molecules/cm^3
  - N $\propto$ pressure
    - one atmosphere = 1.0132 x 10^5 pascal = 1.01 bar
      = 760 Torr (mm Hg)
      - 1 Pascal = 1/132 Torr ~ 10^{-5} atms
- fraction of molecules traveling distance d without colliding is

$$\frac{n_{\text{no collisions}}}{n_{\text{gas}}} = e^{-\frac{d}{\lambda}}$$

  - λ is the mean free path

$$\lambda = \frac{k \cdot \overbrace{T}^{\text{temperature}}}{\underbrace{P}_{\text{pressure}} \cdot \underbrace{\pi \cdot \sigma^2}_{\text{"area" of molecule}} \cdot \sqrt{2}}$$

    - at room temp
      λ ~ 0.7 cm / P (in pascals)
      ~ 5.3 x 10^{-3} cm / P (in Torr)
    - at room temp and one atmosphere
      λ ~ 0.07 µm

Velocity distribution

- for ideal gas, velocity distribution is Maxwellian
  - we'll use $$\bar{c} = \sqrt{\frac{kT}{2\pi m}}$$
  - ~ 900 miles/hour at rm temp
- rate of surface bombardment (flux)

$$j_{gas}\left(\#/unit\ \ area \cdot time\right) = n_{gas}^{unit\ \ volume} \cdot velocity = \underbrace{\left(\frac{P}{kT}\right)}_{\substack{ideal\ \ gas\ \ law \\ P\ \cdot \underbrace{V}_{unit\ vol} = n \cdot k \cdot T}} \cdot \bar{c} = \frac{P}{\sqrt{2\pi\ m\ kT}}$$

  - j = 3.4 x 10^{22} (# / cm^2 • sec) • P / √MT
    - P in Torr, M is gram-molecular mass
- monolayer formation time τ
  - # molecules per unit area / bombard rate

$$\tau \approx \frac{10^{15}\ cm^{-2}}{j} \approx \frac{2.6 \times 10^{-6}}{P\ (in\ \ Torr)}\ \mathrm{sec}$$

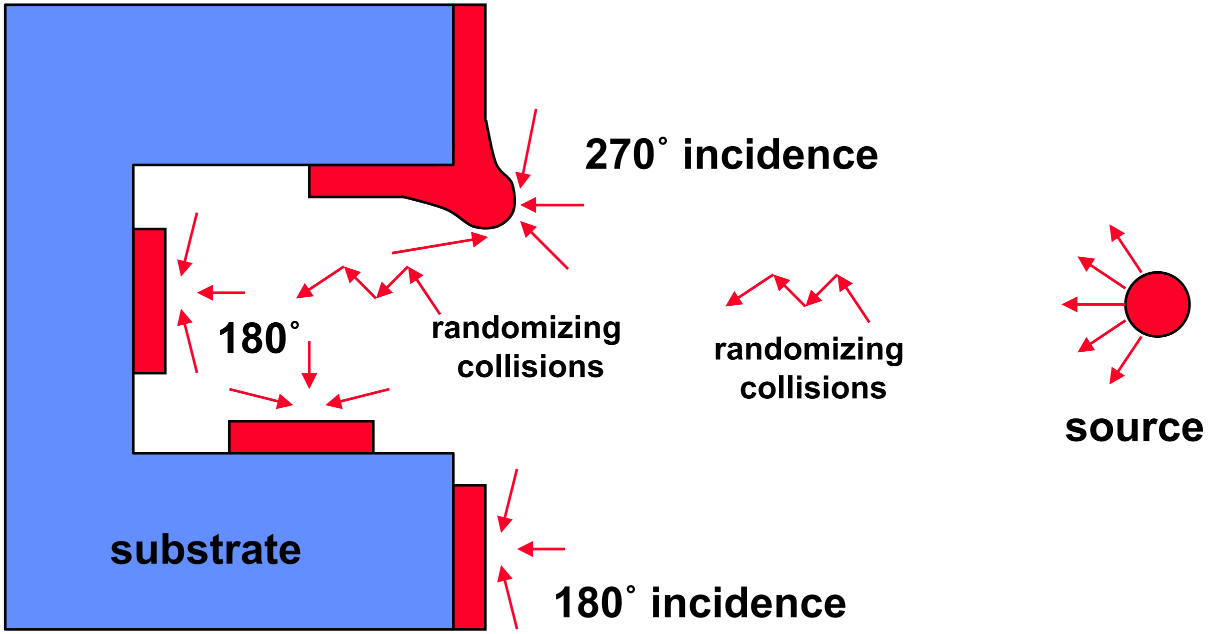
Impact of pressure on deposition conditions

- pressure influences
  - mean free path: $\lambda \propto 1/P$
  - “contamination rate” : $\tau \propto 1/P$

	pressure (Torr)	number density (#/cm^3)	λ	$n_{d=1m}$	τ
	760	2.7×10^{19}	0.07 µm	~ 0	3.3 nsec
rough vacuum	10^{-3}	3.5×10^{13}	5 cm	2×10^{-7} %	2.5 msec
high vacuum	10^{-6}	3.5×10^{10}	50 m	98 %	2.5 sec
	10^{-9}	3.5×10^{7}	50 km	100 %	42 min
very high vacuum	10^{-12}	3.5×10^{4}	50,000 km		29 days

Impact of pressure on deposition conditions

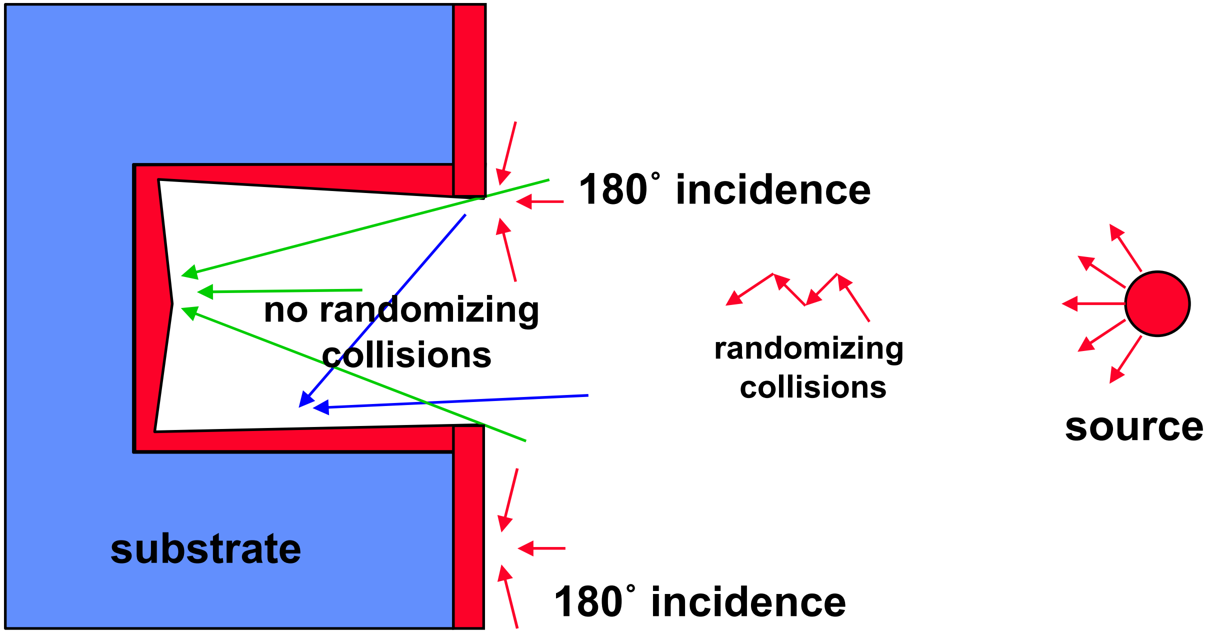
- material arrival angular distribution
  - depends on mean free path compared to both size of system and size of wafer "steps"
- Case I: "atmospheric pressure": 760 Torr ➡ $\lambda = 0.07\ \mu\text{m}$
  - λ << system & steps
  - isotropic arrival on ALL surfaces
    - flat surfaces: 180°
    - inside corners: 90° ➡ thinner
    - outside corners: 270° ➡ thicker



assume material does NOT migrate after arrival!!

“low” pressure: λ << system, λ > step

- Case II: 10^{-1} Torr ➡ λ = 0.5 mm
  - small compared to system, large compared to wafer features
  - isotropic arrival at “flat” surface
- BUT no scattering inside “hole”!!
  - top flat surface: 180˚
  - “inside” surface: depends on location!
  - shadowing by corners of features
- “anisotropic” deposition

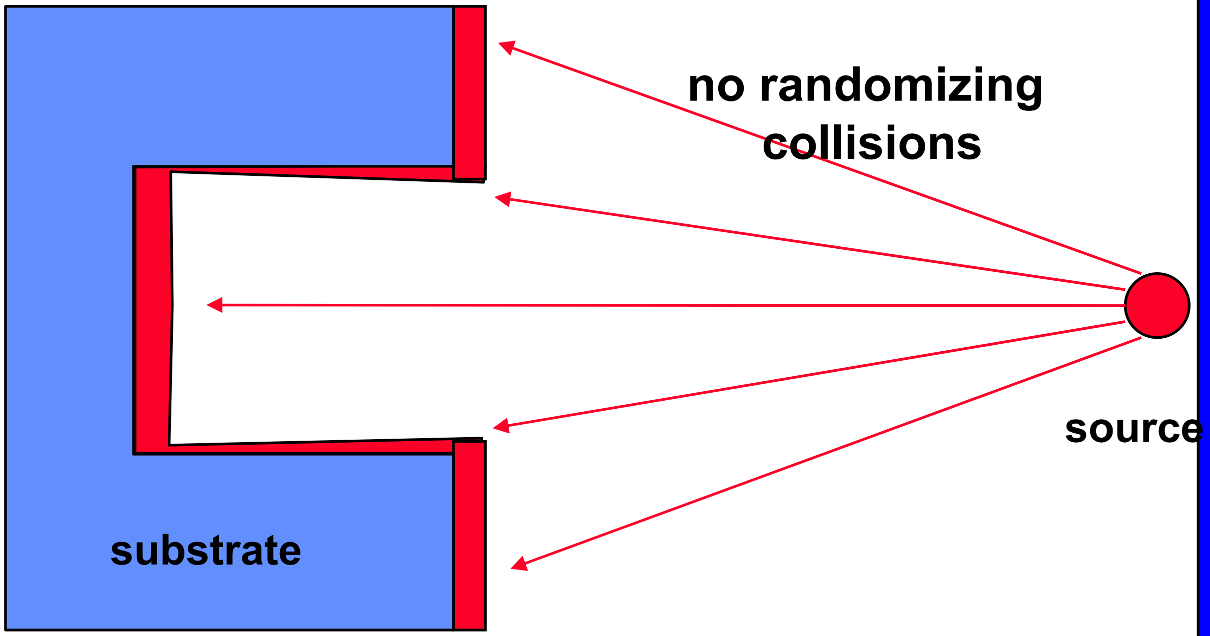


assumes material does NOT migrate after arrival!!

“vacuum” conditions: λ > system, λ >> step

- case III: 10^{-5} Torr ➡ λ = 5 meters
  - long compared to almost everything
- anisotropic arrival at all surfaces!
  - geometric “shadowing” dominates

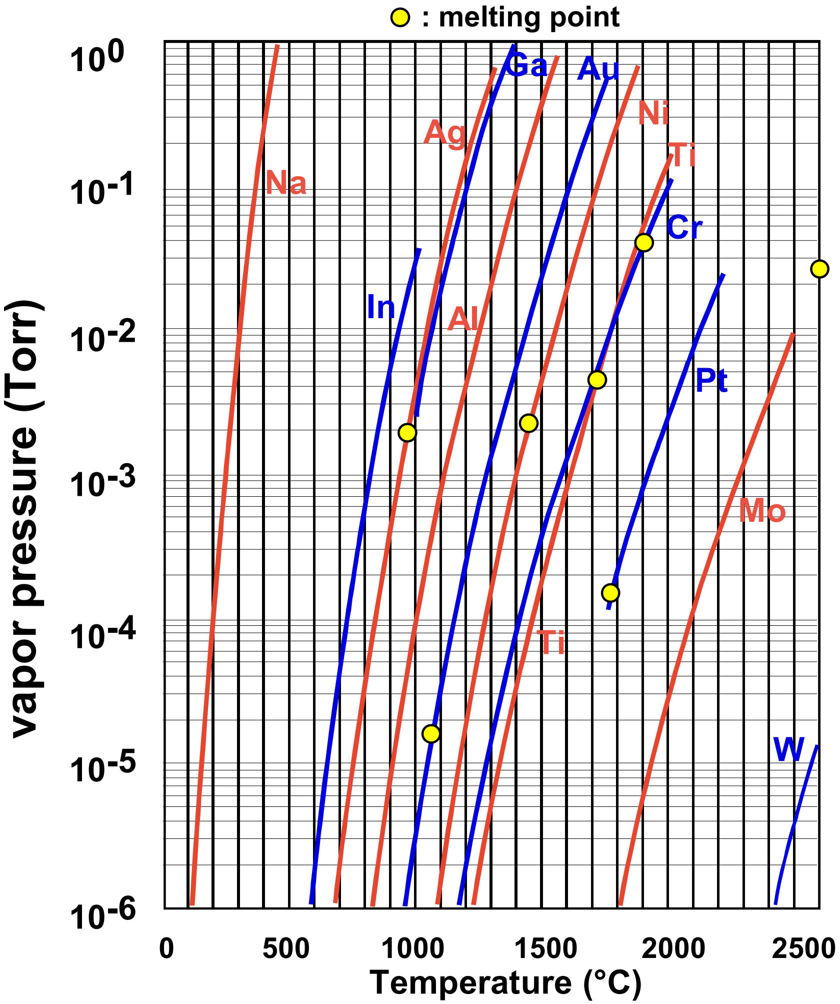
- anisotropic deposition
  - “line-of-sight” deposition
  - very thin on “side walls”
  - very dependent on source configuration relative to sample surface



assumes material does NOT migrate after arrival!!

Physical vapor deposition: thermal evaporation

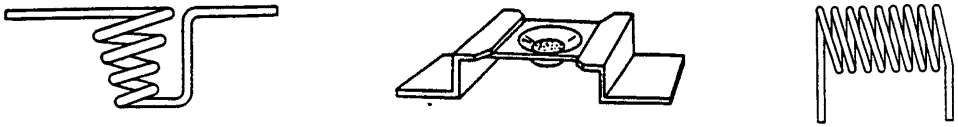
- high vacuum to avoid contamination
  - "line-of-sight" deposition, poor step coverage
- heating of source material
  - potential problem: thermal decomposition
- rates ~ 0.1- few nm/sec
  - typically $P_{vapor} \sim 10^{-4}$ Torr <u>immediately above source</u>
  - "pressure" at sample surface is much lower
    - few monolayers per sec ➡ $P_{equiv} \sim 10^{-6}$ Torr



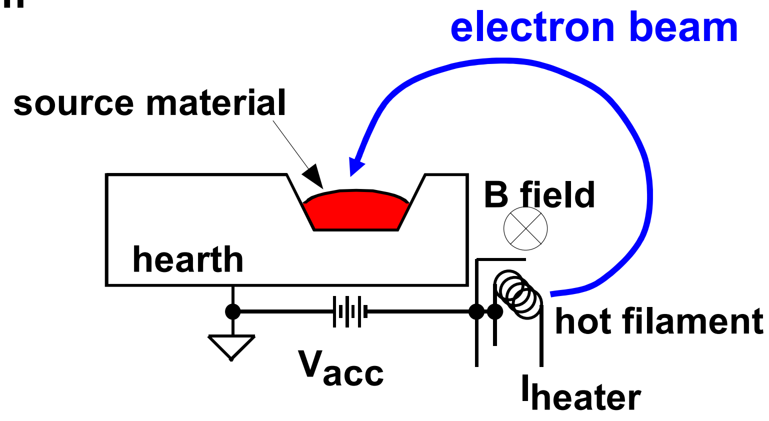
adapted from Campbell, p. 284.

Thermal evaporation

- main heating mechanisms
  - resistively heat “boat” containing material



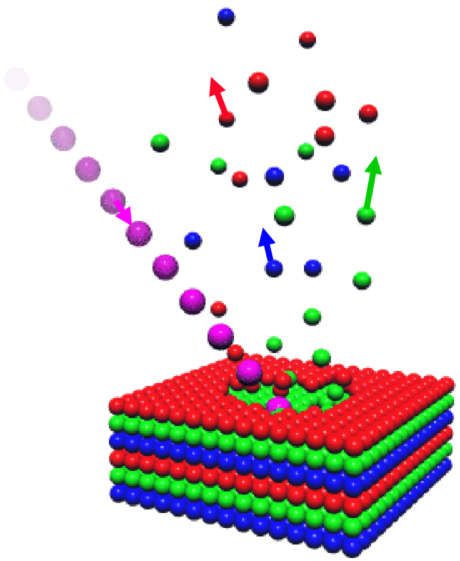
    - tungsten (mp 3410˚C), tantalum (mp 2996˚C), molybdenum (mp 2617˚C) very common “heater” materials
    - reaction with boat potential problem
  - electron beam evaporator



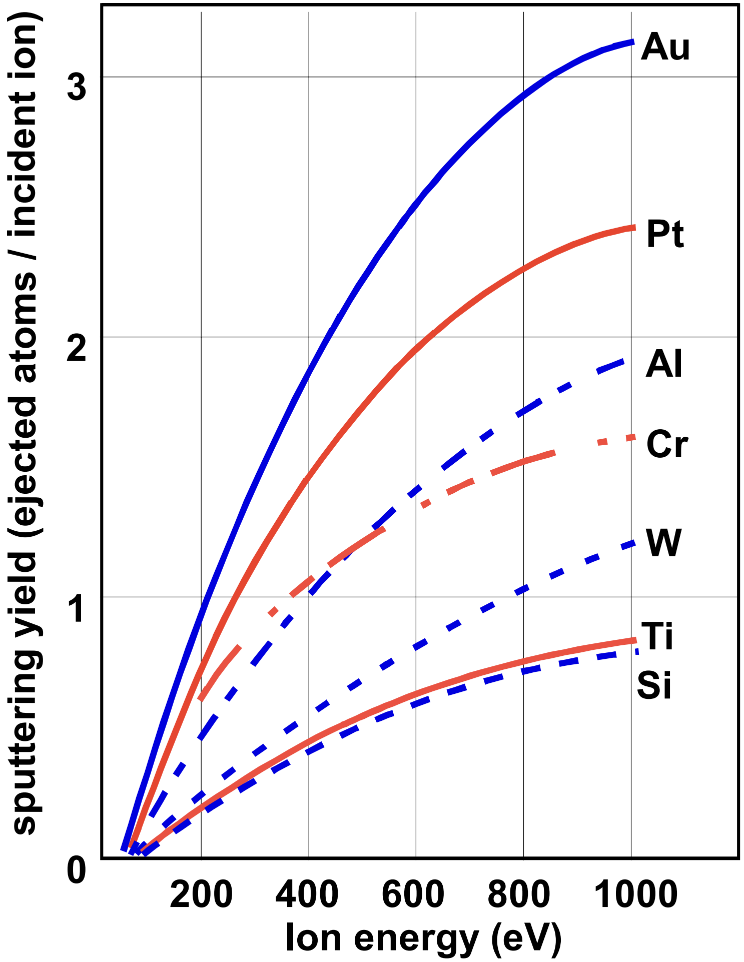
    - source material “directly” heated by electron bombardment
      - can generate x-rays, can damage substrate/devices
    - I_{beam} ~ 100 mA, V_{acc} ~ kV ➡ P ~ kWatts
  - inductively heat material (direct for metals)
    - essentially eddy current losses

Sputtering

- use moderate energy ion bombardment to eject atoms from target
- “purely” physical process
  - can deposit almost anything



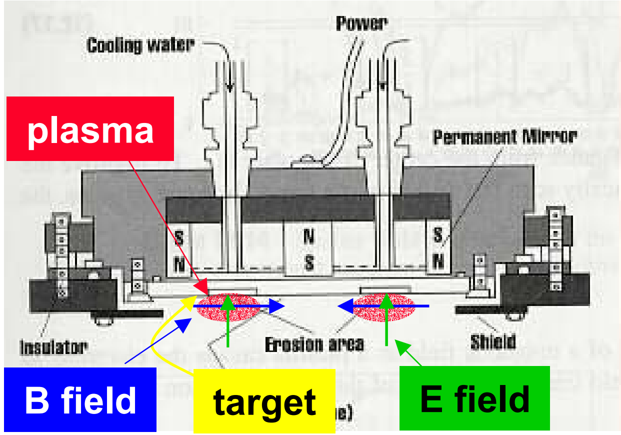
from the SIMS WWW server
http://www.simsworkshop.org/WWW/Siteinfo/gifstoshare/SIMSlogo1.gif



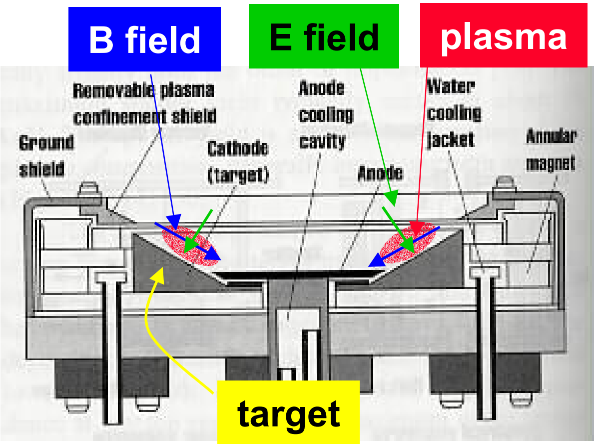
adapted from: Campbell, p. 295

Sputtering

- plasma generates high density, energetic incident particles
  - magnetic field used to confine plasma, electric field (“bias”) to accelerate
  - dc plasma: metals
    - rates up to ~1 µm / minute
  - rf plasma: dielectrics
- typically inert (noble) gas used to form incident ions
  - ion energies ~ few hundred eV ; ejected atoms ~ tens eV
  - ~10^{-2} Torr, λ ~ 5 mm
  - better step coverage than evaporation



planar magnetron



S-gun conical magnetron

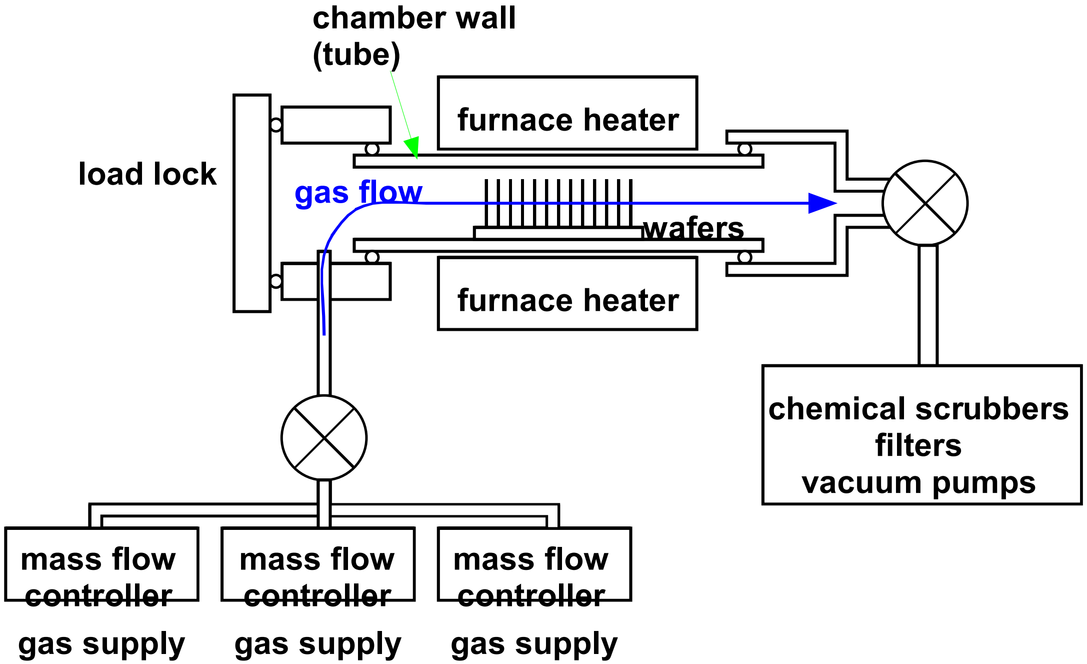
adapted from: Campbell, p. 298

Chemical vapor deposition

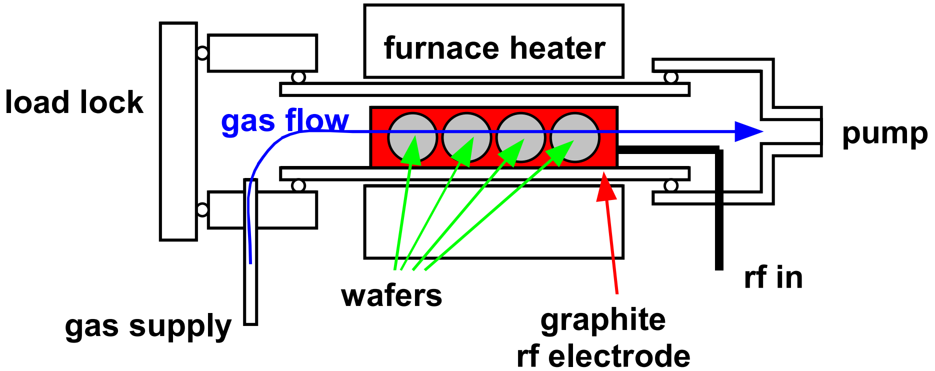
- **general characteristic of gas phase chemical reactions**
  - **pressures typically atmospheric to 50 mTorr**
    - **λ ranges from << 1 µm to ~ 1 mm**
  - **reactions driven by**
    - **thermal: temperatures 100˚ - 1000˚ C**
      - **higher temperature processes increase surface migration/mobility**
    - **plasma**
    - **optical**
- **example materials**
  - **polycrystalline silicon (poly)**
  - **silicon dioxide**
  - **phosphosilicate, borosilicate, borophosphosilicate glasses**
    - **PSG, BSG, BPSG**
  - **silicon nitride**

CVD system design: hot wall reactors

- **heat entire system:**
  thermally driven reactions
  - **requires leak-tight, sealed system**
    - **avoid unwanted contamination, escape of hazardous materials (the reactants)**
  - **atmospheric: high deposition rates**
  - **low pressure (LPCVD): lower rates, good uniformity**



plasma assisted CVD: PECVD

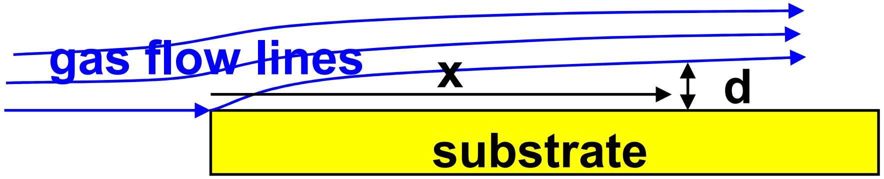


Cold wall reactors

- heat substrate “only” using
  - resistive heating (pass current through “susceptor”)
  - inductive heating (external rf fields create eddy currents in conductive susceptor)
  - optical heating(lamps generate IR, absorbed by susceptor)
- advantages
  - reduces contamination from hot furnace walls
  - reduces deposition on chamber walls
- disadvantages
  - more complex to achieve temperature uniformity
  - hard to measure temperature
    - inherently a non-isothermal system

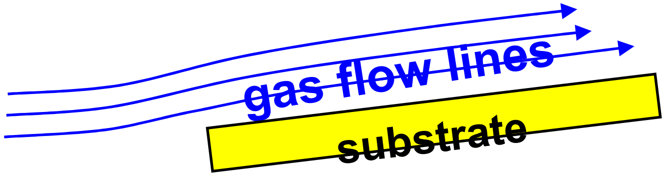
Gas flow in CVD systems

- purely "turbulent" flow
  - reactants are well mixed, no "geometric" limitations on supply of reactants to wafer surface
    - typical of LPCVD tube furnace design
- interaction of gas flow with surfaces
  - away from surfaces, flow is primarily laminar
  - friction forces velocity to zero at surfaces
    - causes formation of stagnant boundary layer



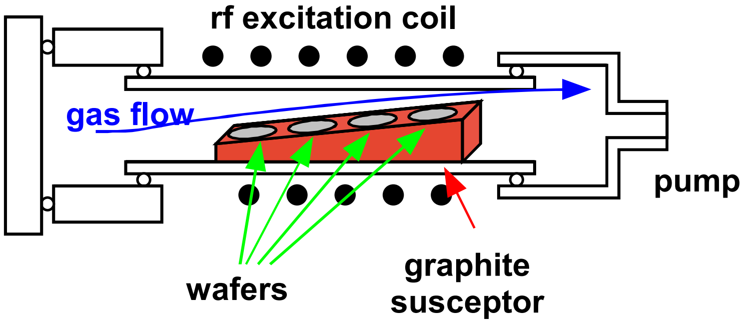
$$d = \sqrt{\frac{\mu \cdot x}{\rho \cdot v}}$$

      - v: velocity; ρ: density; μ: viscosity
    - reactant supply limited by diffusion across boundary layer
    - geometry of wafers relative to gas flow critical for film thickness uniformity
      - to improve boundary layer uniformity can tilt wafer wrt gas flow

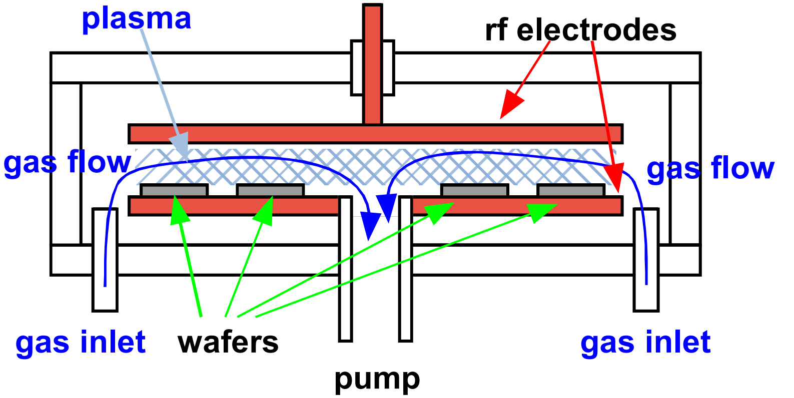


Basic configurations

- horizontal tube reactor


rf excitation coil
gas flow
pump
wafers
graphite susceptor

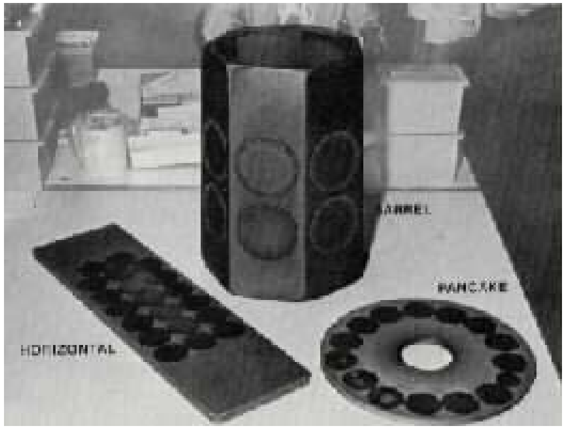
- parallel plate plasma reactor


plasma
rf electrodes
gas flow
gas flow
gas inlet
wafers
gas inlet
pump

  – "pancake" configuration is similar

- barrel reactor
- single wafer systems

from: http://www.appliedmaterials.com/products/pdd.html



Material examples: polysilicon

- uses
  - gates, high value resistors, “local” interconnects
- deposition
  - silane pyrolysis: 600˚-700˚ C $SiH_4 \rightarrow Si + 2H_2$
    - atmospheric, cold wall, 5% silane in hydrogen, ~1/2 µm/min
    - LPCVD (~1 Torr), hot wall, 20-100% silane, ~hundreds nm/min
  - grain size dependent on growth temperature, subsequent processing
    - 950˚ C phosphorus diffusion, 20 min: ~1 µm grain size
    - 1050˚ C oxidation: ~1-3 µm grain size
- in-situ doping
  - p-type: diborane B_2H_6: $\rho \sim 0.005\ \Omega$-cm (B/Si ~ 2.5×10^{-3})
    - can cause substantial increase in deposition rate
  - n-type: arsine AsH_3, phosphine PH_3 : $\rho \sim 0.02\ \Omega$-cm
    - can cause substantial decrease in deposition rate
- dope after deposition (implant, diffusion)

Metal CVD

- tungsten
  - $WF_6 + 3H_2 \leftrightarrows W + 6HF$
  - cold wall systems
  - ~300˚C
  - can be selective
  - adherence to SiO_2 problematic
    - TiN often used to improve adhesion
    - causes long “initiation” time before W deposition begins
  - frequently used to fill deep (“high aspect ratio”) contact vias
- aluminum
  - tri-isobutyl-aluminum (TIBA)
  - LPCVD
  - ~200˚-300˚ C, tens nm/min deposition rate
- copper
  - Cu β-diketones, ~100˚-200˚ C

CVD silicon dioxide

- thermally driven reaction
  - mid-temperature: ~ 500˚C
    - “LTO” (low-temp. oxide) T < ~500˚C
  - $SiH_4 + O_2 \rightarrow SiO_2 + H_2$
  - cold-wall, atmospheric, ~0.1 µm/min
  - hot-wall, LPCVD, ~0.01 µm/min
- plasma-enhanced reaction (PECVD)
  - low temperature: ~250˚C
- high temperature: ~700˚C
  - tetraethyl orthosilicate (TEOS)
    - $Si(OC_2H_5)_4 \rightarrow SiO_2$ + by-products
- new materials
  - low “k” dielectrics
    - interlevel insulation with lower dielectric constants (k < ~3)
      - fluorinated oxides, spin-on glasses, organics
  - high k dielectrics: k > ~25-100’s
    - gate insulators, de-coupling caps

summary of SiO_2 characteristics

	plasma	$SiH_4 + O_2$	TEOS	thermal
temperature	~200°C	~450°C	~700°C	~1000°C
composition	$SiO_{1.9}$ (H)	SiO_2 (H)	SiO_2	SiO_2
step coverage	non-conformal	non-conformal	conformal	"conformal"
thermal stability	loses H	densifies	stable	stable
density (g/cm^3)	2.3	2.1	2.2	2.2
stress (Mdyne/cm^2)	3C - 3T	3T	1C	3C
dielectric strength (MV/cm)	3-6	8	10	11
index of refraction (632.8 nm)	1.47	1.44	1.46	1.46
ε_r (low freq.)	4.9	4.3	4.0	3.9

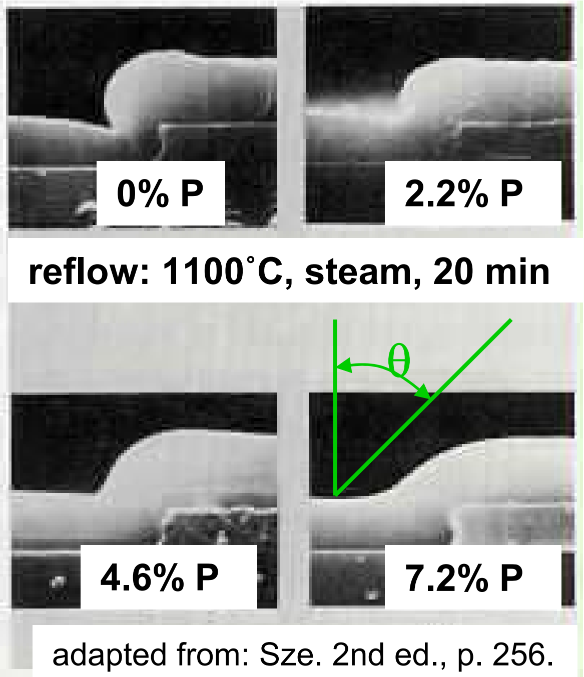
adapted from Sze, 2nd, p. 259.

Phosphosilicate glass (PSG)

- good barrier to sodium migration
- can be used to “planarize” topography using “glass reflow”
  - plastic flow of PSG at T > ~1000˚C
- deposition
  - add phosphine during pyrolysis of silane
    $4PH_3 + 5O_2 \rightarrow 2P_2O_5 + 6H_2$
    - P_2O_5 incorporated in SiO_2
- problems / limitations
  - for reflow, need high P content to get appreciable flow at “reasonable” time/temps
  - P_2O_5 is VERY hygroscopic
  - for > ~ 8% P_2O_5 can cause corrosion of Al
    - normally limit to < ~ 6%

Glass reflow process

- to "even out" step edges can use plastic flow of overcoating dielectric
- usually last "high" temperature step
  - "first fusion"
    - wet, high T ambient
    - densifies, prepares layer for window etch
    - only small reflow if T < 1000˚C
  - second fusion
    - after contact windows are etched
    - can be wet or dry ambient

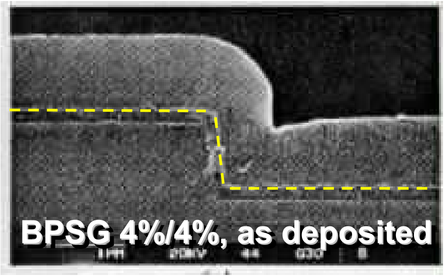


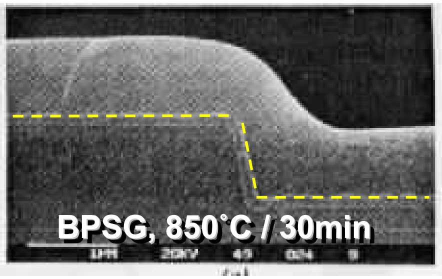
reflow: 1100˚C, steam, 20 min

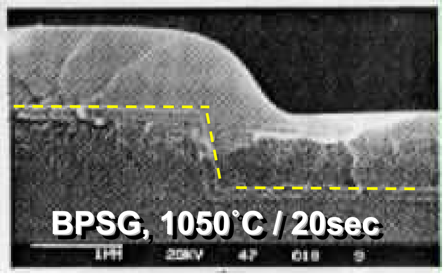
adapted from: Sze. 2nd ed., p. 256.

Rapid flow and BPSG

- can add both phosphorus and boron to glass
  - ~4% P and ~4% B
    - avoids hygroscopicity problems, lowers glass transition temperature
  - examples
    - PSG, 8% P, 950°C / 30 min: no appreciable reflow
    - BPSG, 4% each, 830°C / 30min: 30° flow angle
- can also use rapid thermal process for heating







from: J. S. Mercier, Rapid flow of doped glasses for VLSI fabrication, Solid State Technology, July 1987, p. 87.

Silicon nitride Si_3N_4

- uses
  - diffusivity of O_2, H_2O is very low in nitride
    - mask against oxidation
    - protect against water/corrosion
  - diffusivity of Na also very low
    - protect against mobile ion contamination
- deposition
  - stoichiometric formulation is Si_3N_4
    - in practice Si/N ratio varies from 0.7 (N rich) to 1.1 (Si rich)
  - LPCVD: ~700˚C - 900˚C
    - $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$; can also use $Si_2Cl_2H_2$ as source gas
    - Si/N ratio 0.75, 4-8% H
    - $\rho \sim 3$ g/cm^3 ; n ~ 2.0; k ~ 6-7
    - stress: ~10 Gdyne/cm^2, tensile
  - PECVD: ~250˚C - 350˚C
    - $aSiH_4 + bNH_3 \rightarrow Si_xN_yH_z + cH_2$
    - $aSiH_4 + bN_2 \rightarrow Si_xN_yH_z + cH_2$
    - Si/N ratio 0.8-1.2, ~20% H
    - $\rho \sim 2.4$-2.8 g/cm^3 ; n ~ 1.8-2.5; k ~ 6-9
    - stress: ~2C - 5T Gdyne/cm^2

Safety issues in CVD

- most gases used are toxic, pyrophoric, flammable, explosive, or some combination of these
  - silane, SiH_4
    - toxic, burns on contact with air
  - phosphine
    - very toxic, flammable
  - ammonia
    - toxic, corrosive
- how to deal with this?
  - monitor!
  - limit maximum flow rate from gas sources
    - helps with dispersal problem associated with gases
  - double walled tubing, all welded distribution networks

Epitaxy

- growth of thin crystalline layers upon a crystalline substrate
  - heteroepitaxy
    - dissimilar film and substrate
  - autoepitaxy
    - same film and substrate composition
- techniques
  - Vapor-Phase Epitaxy (VPE)
    - CVD: Metal-organic VPE (MOCVD, OMVPE, ...)
    - PVD: Molecular Beam Epitaxy (MBE)
  - Liquid-Phase Epitaxy (LPE)
    - mainly for compound semiconductors
  - Solid-Phase Epitaxy
    - recystallization of amorphized or polycrystalline layers
- applications
  - bipolar, BiCMOS IC's
    - 2-5 µm in high speed digital
    - 10-20 µm in linear circuits
  - special devices
    - SOI, SOS
    - HEMT, MODFET, HBT

Summary Slide

- Deposited thin films
- Kinetic theory of gases
- Physical vapor deposition: thermal evaporation
- Sputtering
- Chemical vapor deposition
- next topic: epitaxy