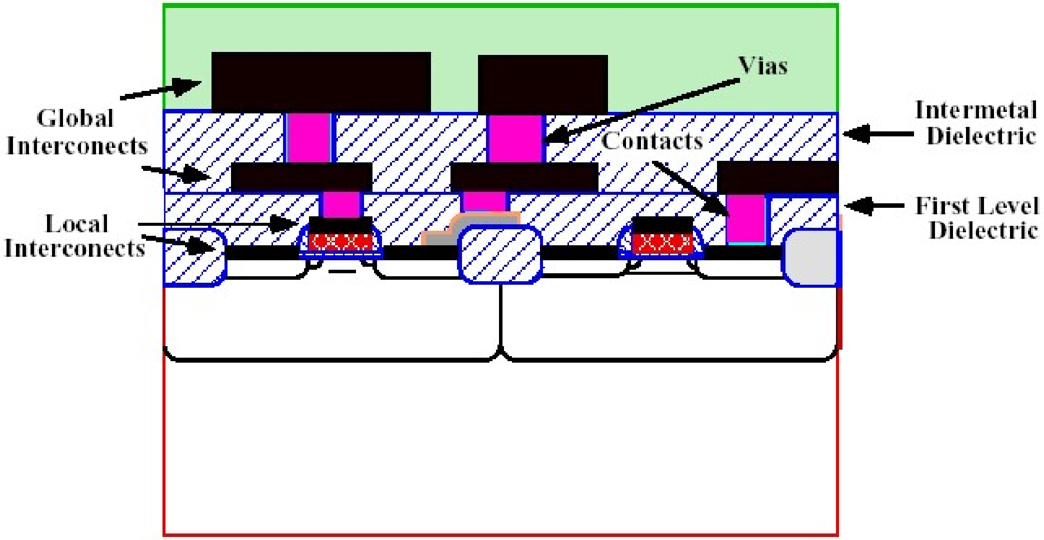
Thin film

Thin film: thickness typically <1000nm.

Typical steps in making thin films:

1. Emission of particles from source (heat, high voltage . . .)
2. Transport of particles to substrate
3. Condensation of particles on substrate



Lithography, thin film deposition and its etching are the three most important processes for micro-nano fabrication.

Thin film deposition methods

Two main deposition methods are used today:

Chemical Vapor Deposition (CVD)

Reactant gases introduced in the chamber, chemical reactions occur on wafer surface leading to the deposition of a solid film.

E.g. APCVD, LPCVD, PECVD, most commonly used for dielectrics and Si.

Physical Vapor Deposition (PVD) (no chemical reaction involved)

Vapors of constituent materials created inside the chamber, and condensation occurs on wafer surface leading to the deposition of a solid film.

E.g. evaporation, sputter deposition, most commonly used for metals.

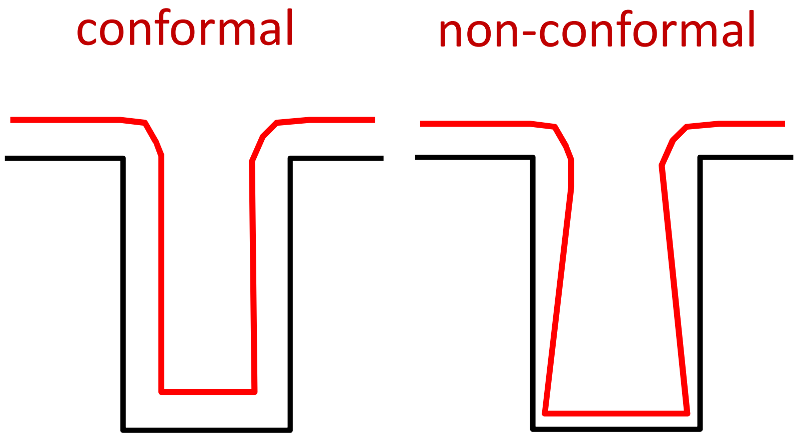
Other methods that are increasingly gaining importance in ULSI fabrication:

1. Coating with a liquid that becomes solid upon heating, e.g. spin-on-glass used for planarization.
2. Electro-deposition: coating from a solution that contains ions of the species to be coated. E.g. Cu electroplating for global interconnects.
3. Thermal oxidation.

General characteristics of thin film deposition

- Deposition rate
- Film uniformity:
  - Across wafer uniformity.
  - Run-to-run uniformity.
- Materials that can be deposited: metal, dielectric, polymer.
- Quality of film:
  - Physical and chemical properties
  - Electrical property, breakdown voltage
  - Mechanical properties, stress and adhesion to substrate
  - Optical properties, transparency, refractive index
  - Composition, stoichiometry
  - Film density, defect (pinhole…) density
  - Texture, grain size, boundary property, and orientation
  - Impurity level, doping
- Deposition directionality:
  - Directional - good for lift-off, trench filling
  - Non-directional - good for step coverage
- Cost of ownership and operation.

Step coverage



Poor (non-conformal) step coverage is good for liftoff.
Conformal film is good for electrical connection…

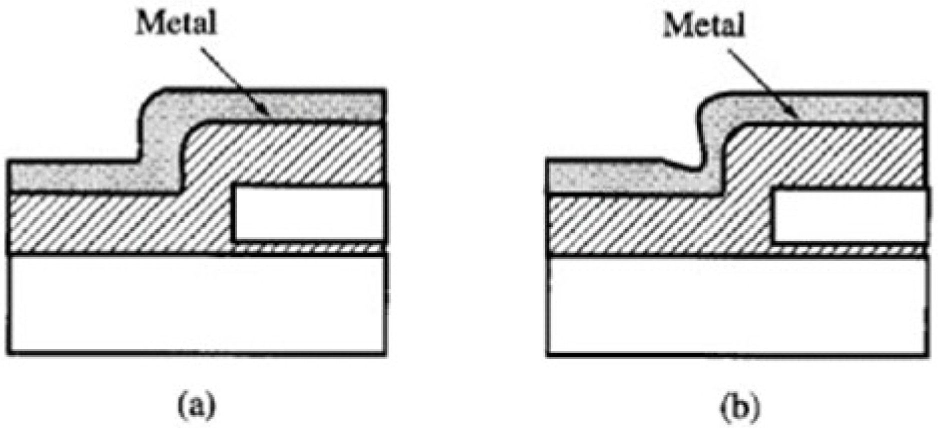
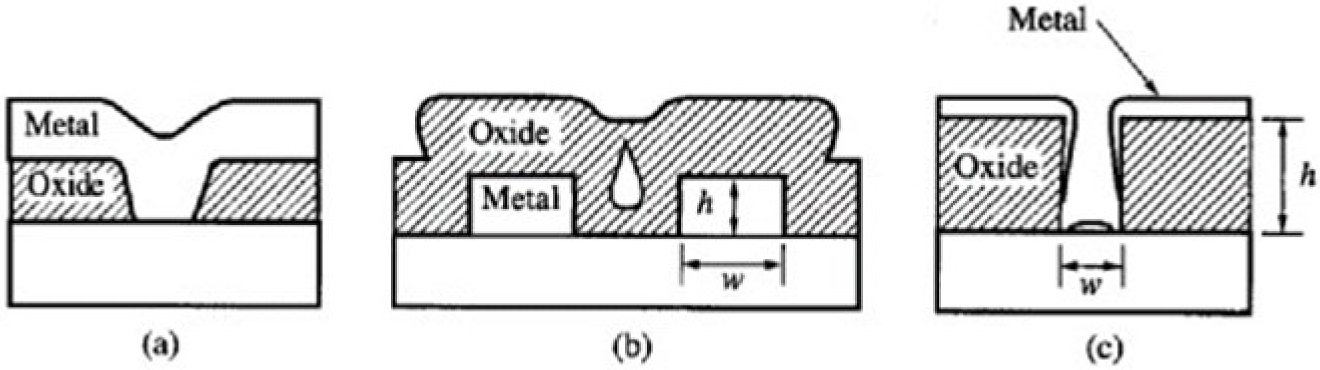


Figure 9-1 Step coverage of metal over non-planar topography.

(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.

(b) Poor step coverage, here thinner for vertical surfaces.

Thin film filling of holes/trenches



Aspect ratio (AR):
AR = feature height/width
AR = h/w

Figure 9-2 Thin film filling issues.

(a) Good metal filling of a via or contact in a dielectric layer.

(b) Silicon dioxide filling of the space between metal lines, with poor filling leading to void formation.

(c) Poor filling of the bottom of a via hole with a barrier or contact meal.

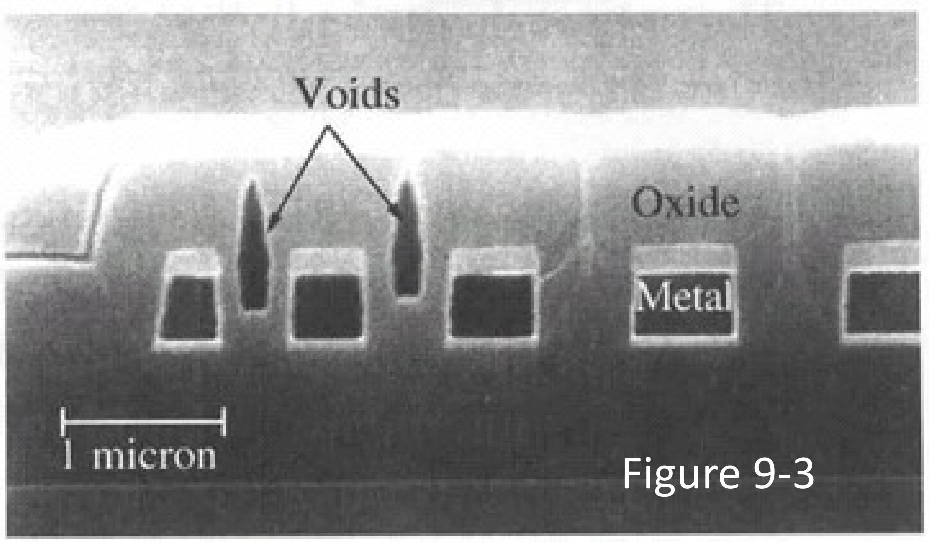
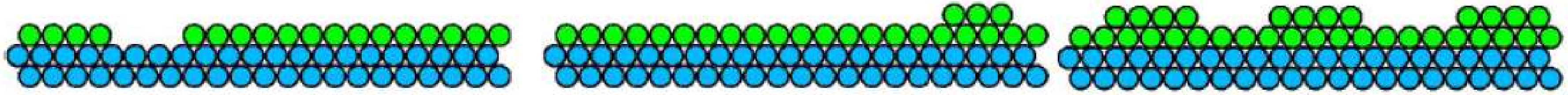


Figure 9-3

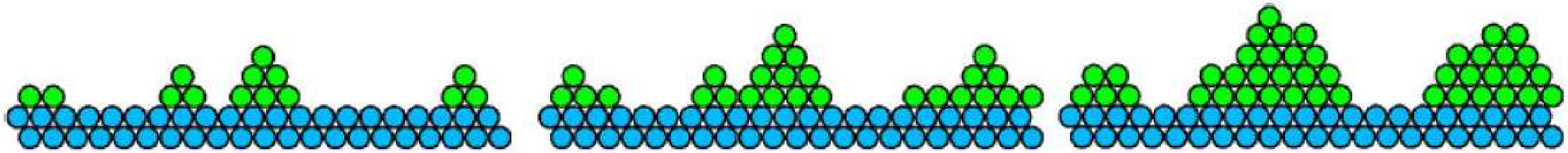
Voids in a chemical vapor deposition (CVD) oxide layer for narrow spaces between metal lines.
More difficult to fill without void for higher aspect ratio.

Four equilibrium growth/deposition modes

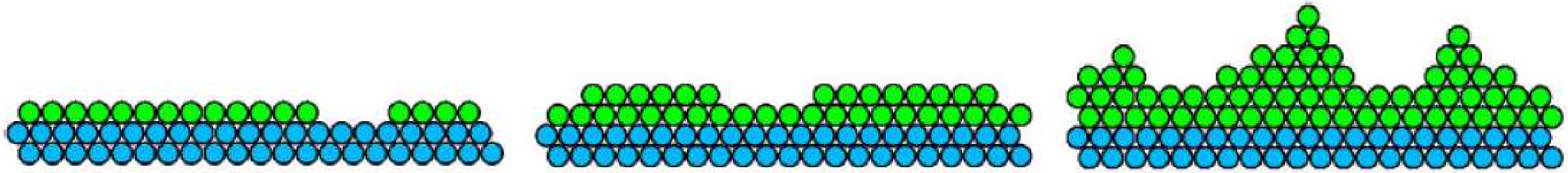
Epitaxy = crystal structure of film fits with the one of the substrate



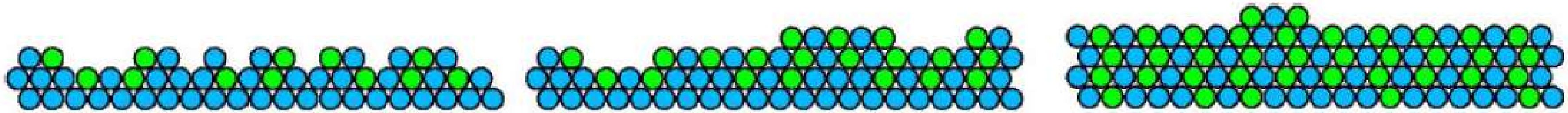
2D layer-by-layer growth (Frank-van der Merwe)   Si/Si, TiN/MgO



3D island growth (Volmer-Weber)   metals on SiO_2

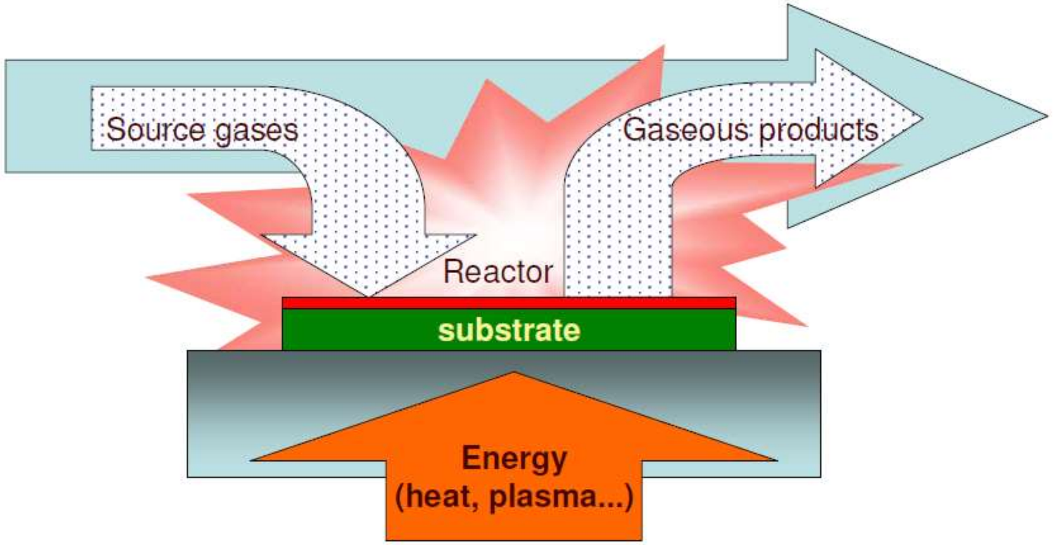


Stranski-Krastanov   In/Si, Ag/Si, Ge/Si, InP/GaAs, GaN/AlN



Reactive intermixing

Chemical Vapor Deposition (CVD)



CVD : deposit film through chemical reaction and surface absorption.

CVD steps:

1. Introduce reactive gases to the chamber.
2. Activate gases (decomposition) by heat or plasma.
3. Gas absorption by substrate surface .
4. Reaction take place on substrate surface.
5. Transport of volatile products away form substrate.
6. Exhaust waste.

Chemical vapor deposition (CVD) systems

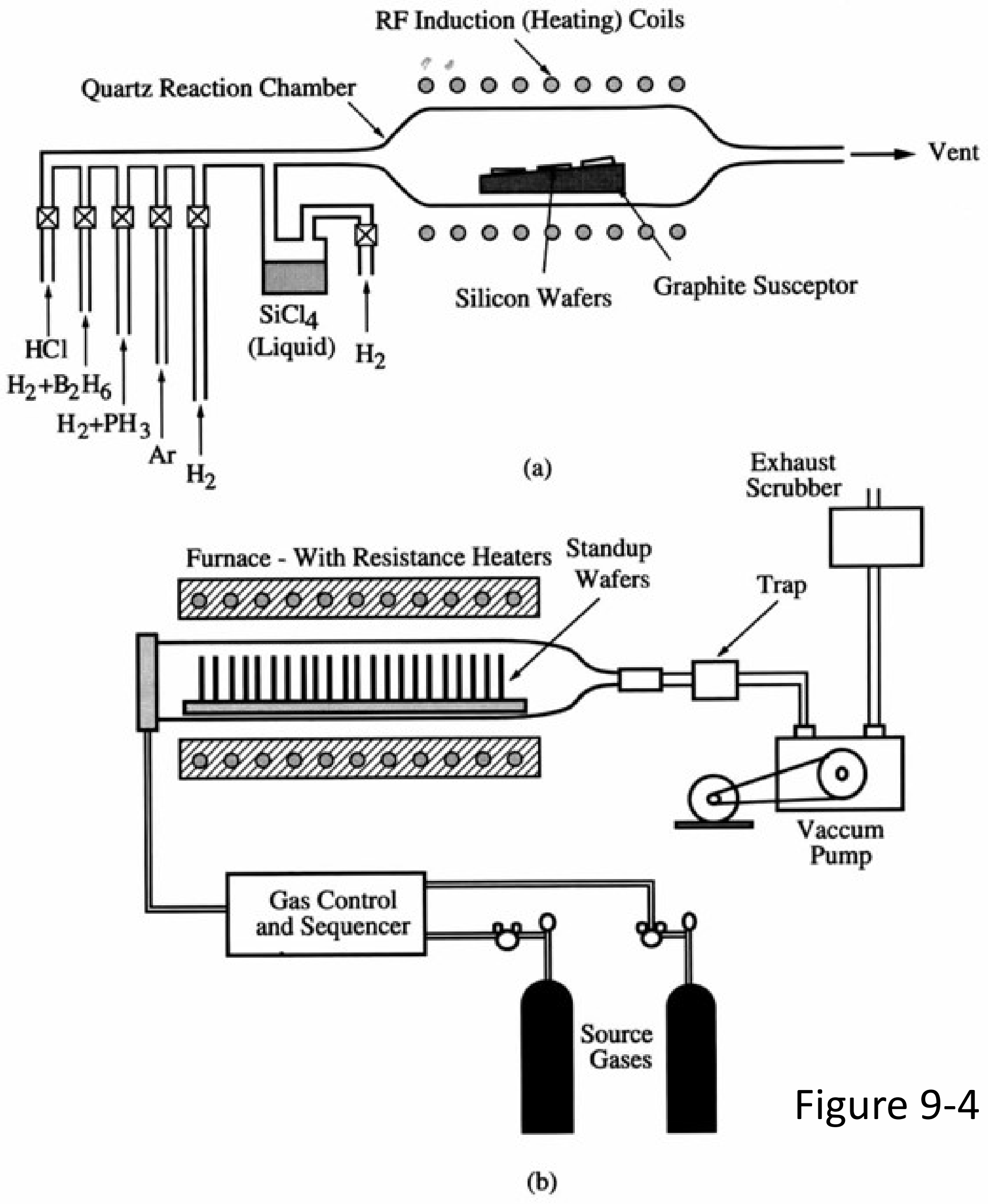


Figure 9-4

Atmospheric cold-wall system used for deposition of epitaxial silicon. ($SiCl_4 + 2H_2 \rightarrow Si + 4HCl$)

Low pressure hot-wall system used for deposition of polycrystalline and amorphous films, such as poly-silicon and silicon dioxide.

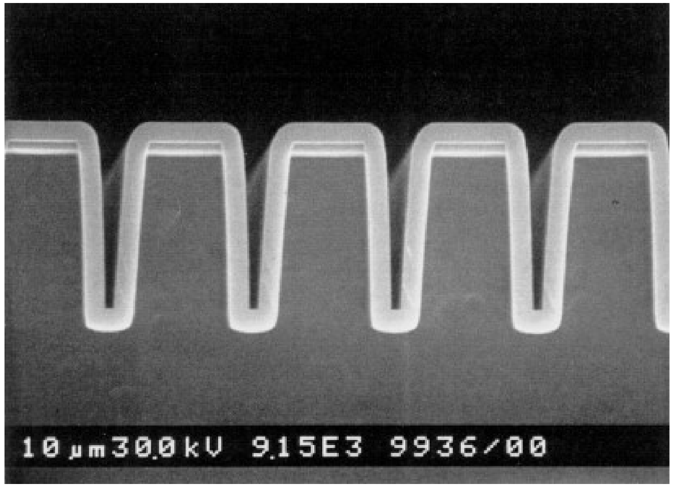
CVD advantages and disadvantages
(as compared to physical vapor deposition)

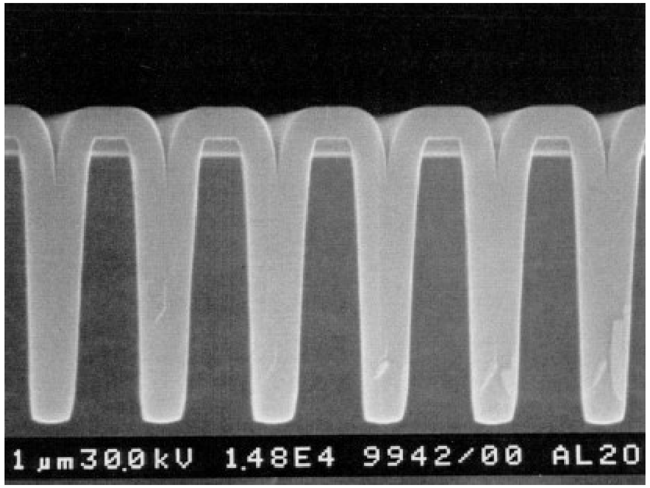
Advantages:

- High growth rates possible, good reproducibility.
- Can deposit wide variety of materials.
- Can grow epitaxial films.
- Generally better film quality, more conformal step coverage (see image below).

Disadvantages:

- High process temperatures.
- Complex processes, toxic and corrosive gasses.
- Film may not be pure (hydrogen incorporation…).





Types of CVD reactions

- **Thermal decomposition**

  AB(g) ---> A(s) + B(g)

  Si deposition from Silane at 650°C: $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

  $Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$ (180°C)

- **Reduction (using H_2)**

  $AX(g) + H_2(g) \rightarrow A(s) + HX(g)$

  W deposition at 300°C: $WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$

  $SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl$ (1200°C)

- **Oxidation (using O_2)**

  $AX(g) + O_2(g) \rightarrow AO(s) + [O]X(g)$

  SiO_2 deposition from silane and oxygen at 450°C (lower temp than thermal oxidation): $SiH_4(g) + O_2(g)$ ---> $SiO_2(s) + 2H_2(g)$

  $2AlCl_3(g) + 3H_2(g) + 3CO_2(g) \rightarrow Al_2O_3 + 3CO + 6HCl$ (1000°C)

  (O is more electronegative than Cl)

- **Compound formation (using NH_3 or H_2O)**

  $AX(g) + NH_3(g) \rightarrow AN(s) + HX(g)$ or $AX(g) + H_2O(g) \rightarrow AO(s) + HX(g)$

  Deposit wear resistant film (BN) at 1100°C: $BF_3(g) + NH_3(g) \rightarrow BN(s) + 3HF(g)$

  $(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4$ (650 – 750°C)

Types of CVD

APCVD (Atmospheric Pressure CVD), mass transport limited growth rate, leading to non-uniform film thickness.

LPCVD (Low Pressure CVD)

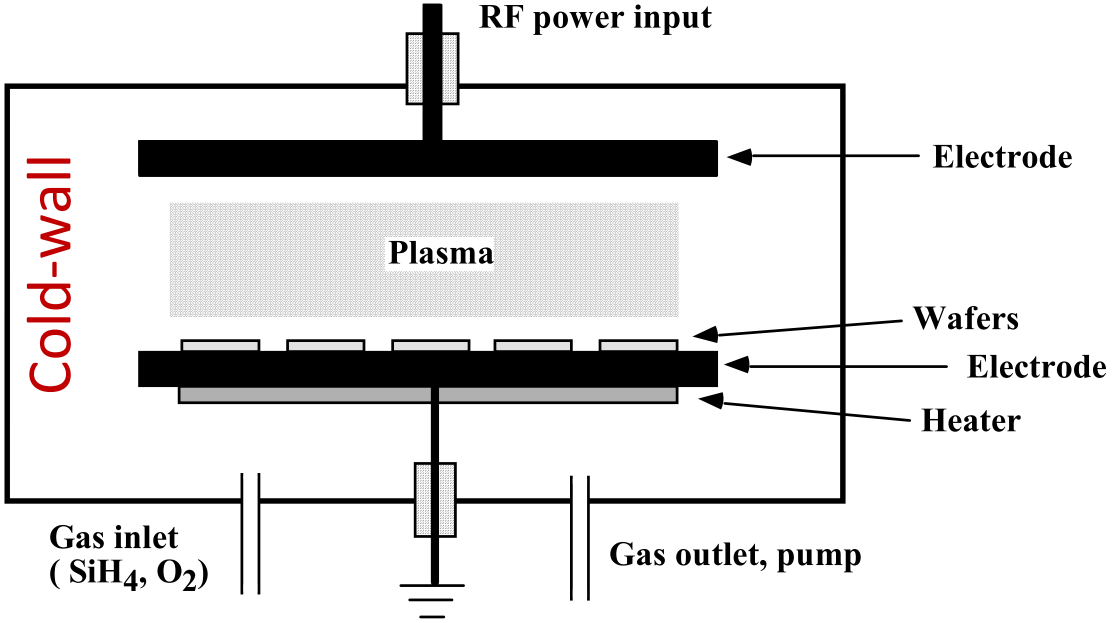
- Low deposition rate limited by surface reaction, so uniform film thickness
- Gas pressures around 1-1000mTorr (lower P => higher diffusivity of gas to substrate)
- Better film uniformity & step coverage and fewer defects
- Process temperature $\geq 500^{\circ}$C

PECVD (Plasma Enhanced CVD)

- Plasma helps to break up gas molecules: high reactivity, able to process at lower temperature and lower pressure (good for electronics on plastics).
- Pressure higher than in sputter deposition: more collision in gas phase, less ion bombardment on substrate
- Process temperature around 100 - 400°C.

MOCVD (Metal-organic CVD, also called OMVPE - organo metallic VPE), epitaxial growth for many optoelectronic devices with III-V compounds for solar cells, lasers, LEDs, photo-cathodes and quantum wells.

Plasma Enhanced CVD (PECVD)



"Good" quality films : energy supplied by plasma (i.e. ion bombardment of film) increases film density, composition, and step coverage.

- Use RF-induced plasma to transfer energy into the reactant gases, forming radicals that is very reactive.
- Low temperature process, as thermal energy is less critical when RF energy exists.
- Used for depositing film on metals (Al…) and other materials that cannot sustain high temperatures.

- Disadvantages: plasma damage, not pure film (often lots of H incorporated into film).

PECVD process parameter

Substrate temperature (100-300^{o}C, up to 1000^{o}C PECVD available)

- Control by external heater, very little heating from PECVD process

Gas flow (10s to 100s sccm – standard cubic centimeter per minute)

- Higher flow rates can increase deposition rate and uniformity

Pressure (P $\approx$ 50mTorr – 5Torr)

- Changes the energy of ions reaching electrodes
- Can change deposition rate
- Increases pressure may lead to chemical reactions in the gas

Power (10 -100 watts)

- Affects the number of electrons available for activation and the energy of those electrons
- Increased power may lead to chemical reactions in gas
- Increased power increases deposition rate

Frequency (mostly 13.56MHz, same for plasma etching and sputter deposition)

- Changes plasma characteristics
- Changes ion bombardment characteristics

Physical vapor deposition (PVD): evaporation and sputtering

In PVD, chemical reactions are not involved, except for reactive (add reactive gases into chamber) evaporation or reactive sputter deposition, which are not widely used.

Evaporation:

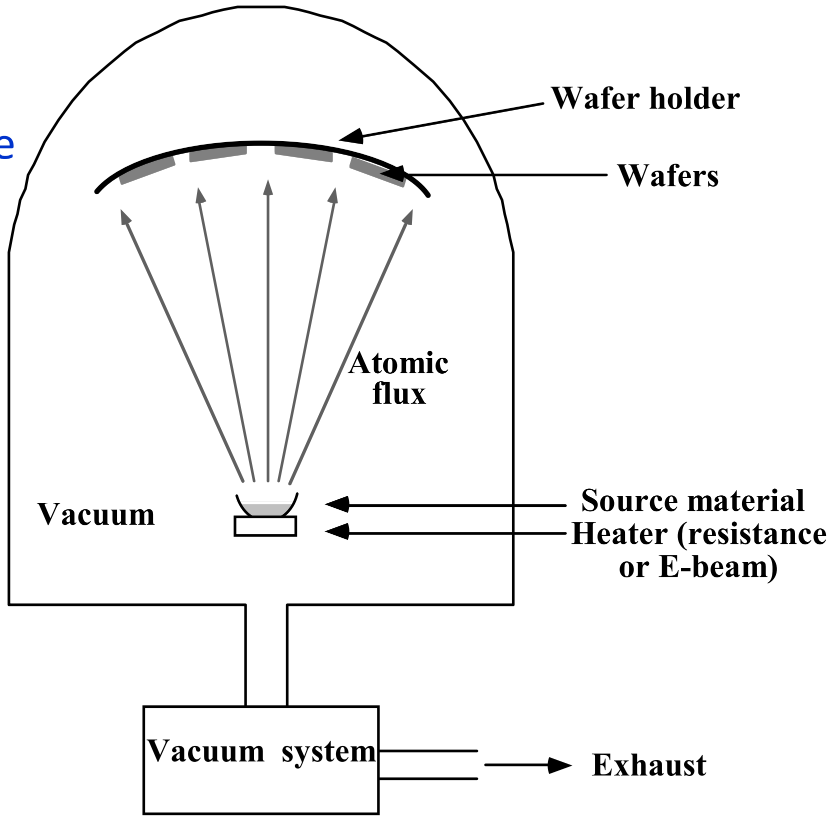
- Material source is heated to high temperature in vacuum either by thermal or e-beam methods.
- Material is vapor transported to target in vacuum.
- Film quality is often not as good as sputtered film (that involves energetic bombardment of ions to the as-deposited film, which makes the film denser).
- The film thickness can be monitored precisely using a quartz balance – this is necessary as the deposition is not reproducible (tiny change in T leads to large change of deposition rate. T is not monitored, power is).

Sputter *deposition*: (there is also sputter *etching*)

- Material is removed from target by momentum transfer.
- Gas molecules are ionized in a glow discharge (plasma), ions strike target and remove mainly neutral atoms.
- Sputtered atoms condense on the substrate.
- Not in vacuum, gas (Ar) pressure 5-50mTorr.

Evaporation (also called vacuum deposition)

- In evaporation, source material is heated in high vacuum chamber (P < 10^{-5} Torr), hence the name vacuum deposition.
- High vacuum is required to minimize collisions of source atoms with background species (light of site deposition)
- Heating is done by resistive or e-beam sources.
- Surface interactions are physical, can be very fast
- High sticking coefficient (at low T, adatom stays wherever it hits with limited surface migration), leading to poor conformal coverage/significant shadow. But this also makes evaporation the most popular thin film deposition for *nanofabrication* using liftoff process.



- Deposition rate is determined by emitted flux and by geometry of the source and wafer.
- Evaporation is not widely used by industry – sputter deposition is.
- For microfabrication R&D, evaporation is as important as sputter deposition.

Influence of background vacuum pressure

p (mbar)	Mean free path (cm)	Monolayers per sec
10^{0}	6.8×10^{-3}	3.3×10^{5}
10^{-3}	6.8×10^{0}	3.3×10^{2}
10^{-6}	6.8×10^{3}	3.3×10^{-1}
10^{-9}	6.8×10^{6}	3.3×10^{-4}

1bar=100000Pa (1atm=1.013bar)
1mbar=100Pa
1Torr=100000/760=132Pa=1.32mbar

Time to form a single complete layer of gas on a surface, assume sticking coefficient = 1.

Pressure (Torr)	Time
10^{-4}	0.02 s
10^{-5}	0.2 s
10^{-6}	2 s
10^{-7}	20 s
10^{-8}	3 min
10^{-9}	35 min
10^{-10}	6 hr
10^{-11}	3 days

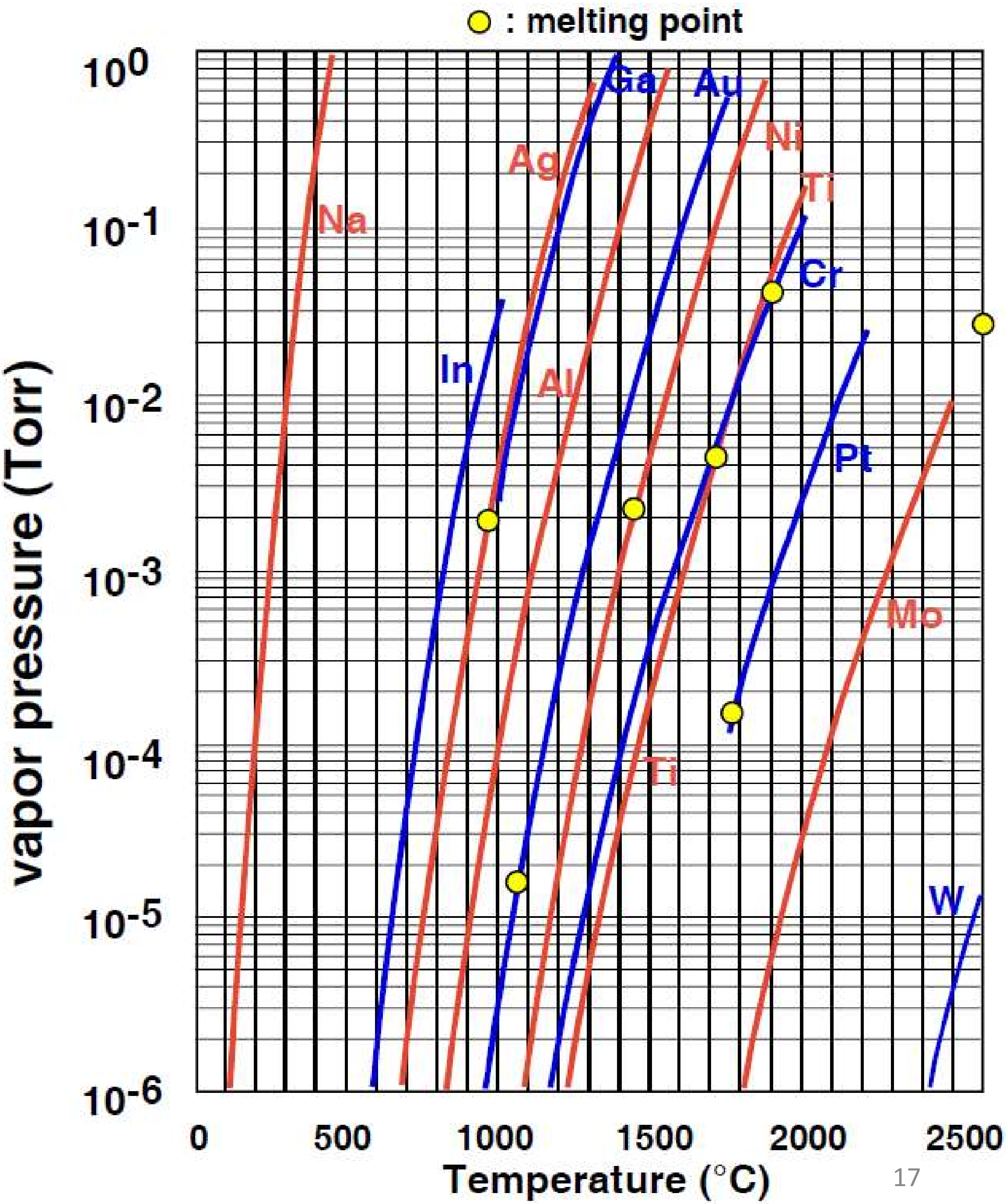
Vapor pressure of common materials

Vapor pressure of 1-10mTorr or more is required to achieve reasonable deposition rates of 0.1-1μm/min.

(? Seems the number doesn't match using the equations below)

$$v = \frac{R_{evap}}{\pi N r^2}\cos^n\theta_i \cdot \cos\theta_k$$

$$R_{evp} = 5.83\times10^{-2} A_s\left(\frac{m}{T}\right)^{1/2} P_e$$



Photos of source material for evaporation

Types of evaporation according to heating method

Three types:

Thermal evaporator – resistive heating, the only choice for evaporation of organic material.

Electron beam evaporator – heated by electron beam, most popular, more expensive than thermal evaporator.

Inductive heating (must be unpopular – I have never seen one).

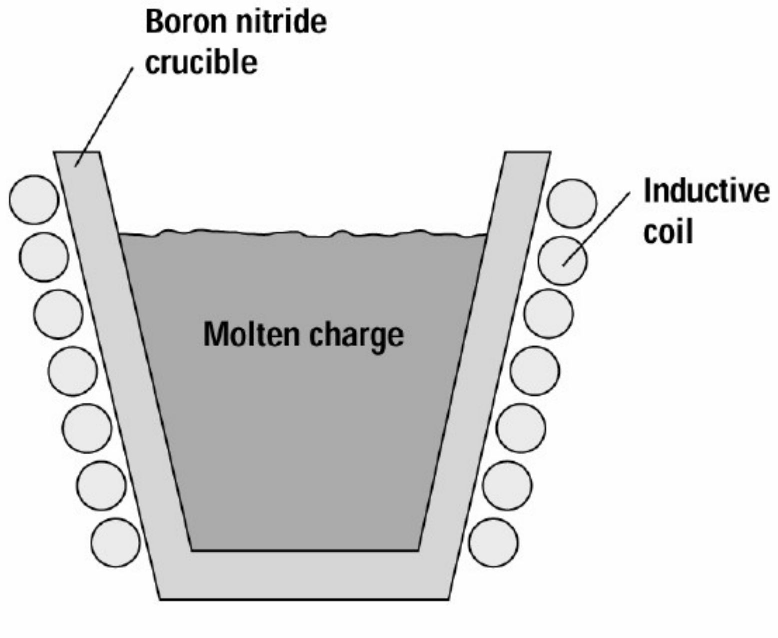
Inductive heating:

Metal element is wound around crucible and RF power is run through coil.

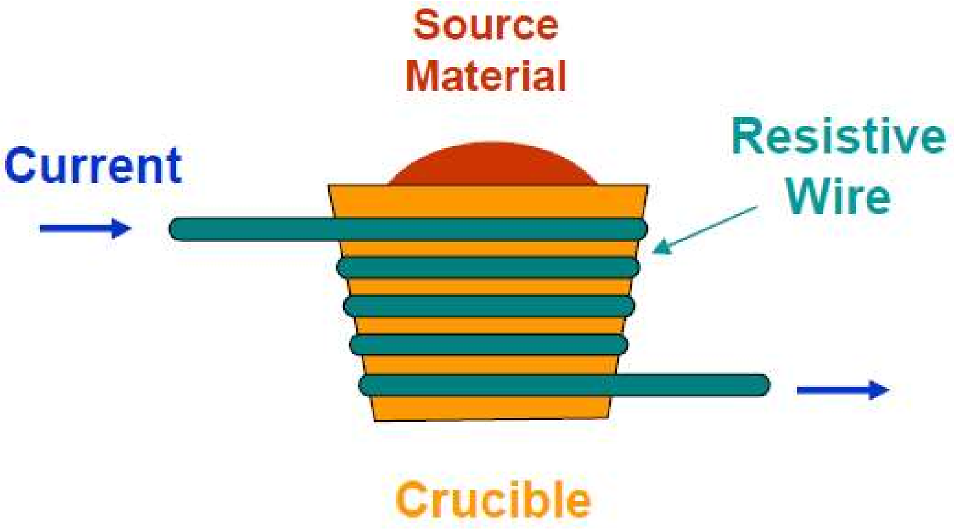
RF induces eddy currents in the charge causing it to heat.

Eddy current is caused when a conductor is exposed to a changing magnetic field due to relative motion of the field source and conductor; or due to variations of the field with time.

These circulating current create induced magnetic fields that oppose the change of the original magnetic field due to Lenz's law, causing repulsive or drag forces between the conductor and the magnet.



Thermal evaporation



Widespread use for materials whose vapor pressure can be reasonable at 1600°C or below.

Common evaporant materials:

Au, Ag, Al, Sn, Cr, Sb, Ge, In, Mg, Ga;

CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$.

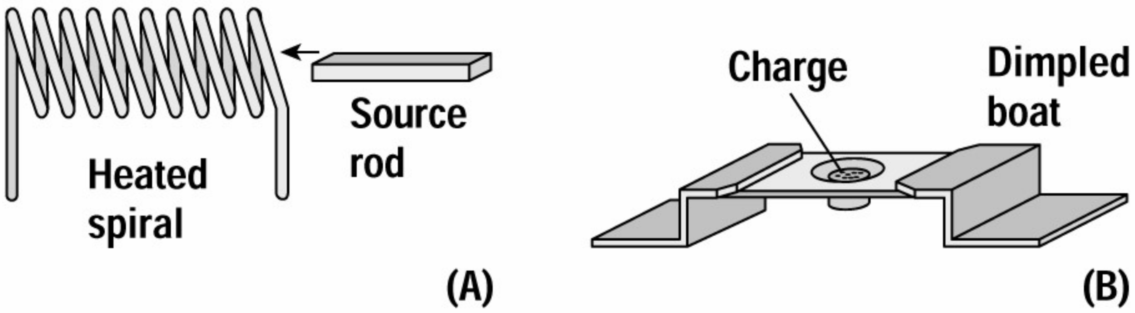
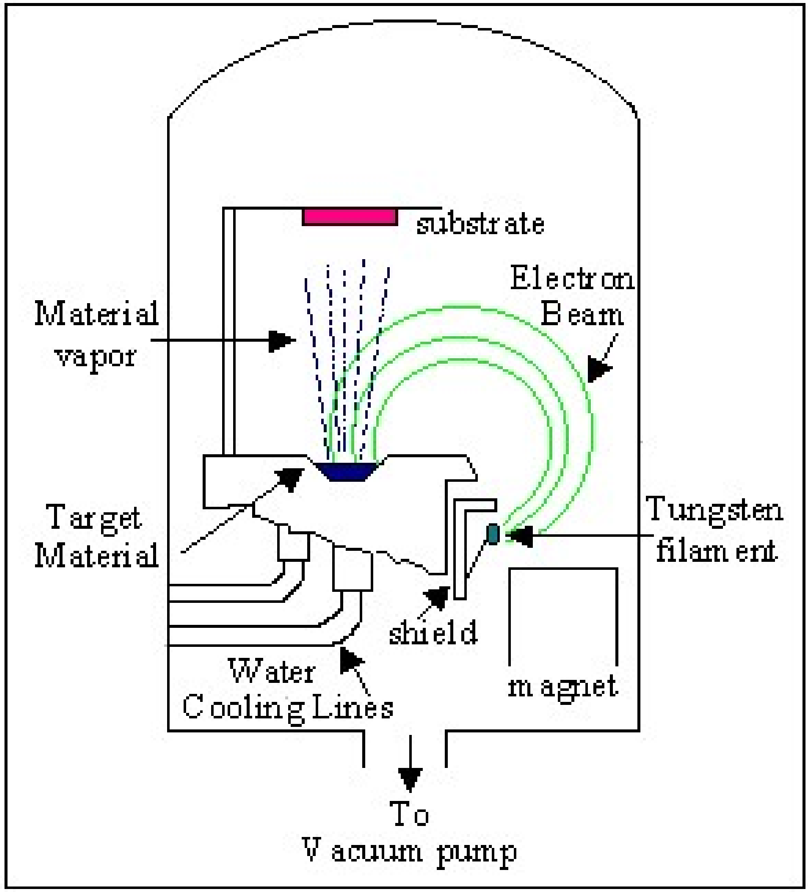
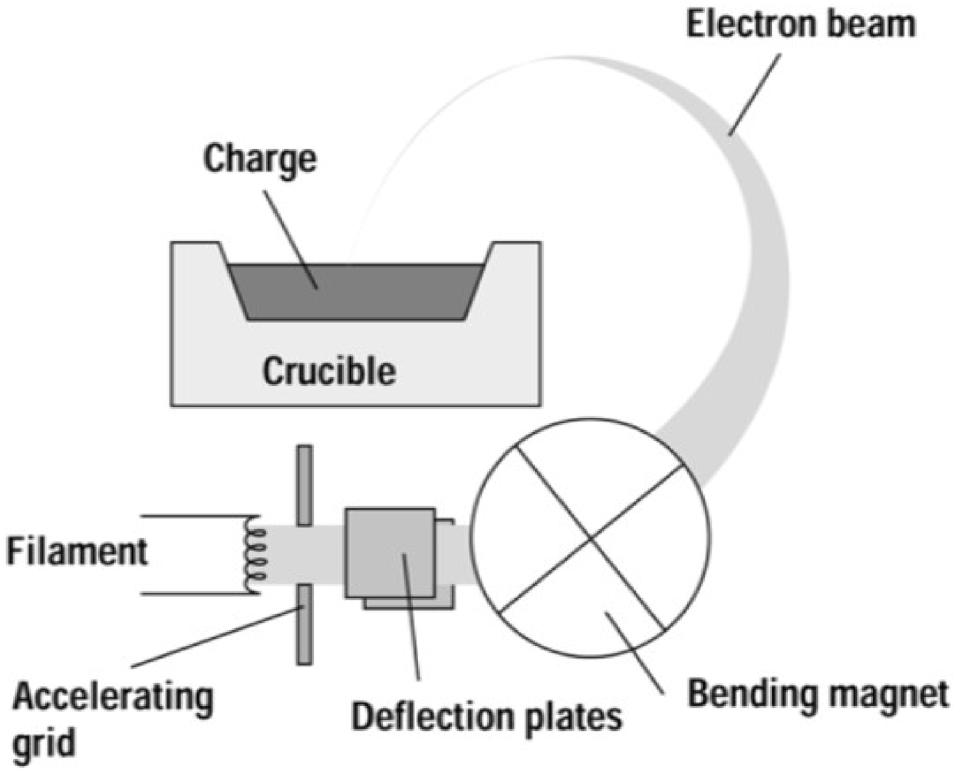


Figure 12.6 Resistive evaporator sources. (A) Simple sources including heating the charge itself and using a coil of refractory metal heater coil and a charge rod. (B) More standard thermal sources including a dimpled boat in a resistive media.

Electron beam evaporation



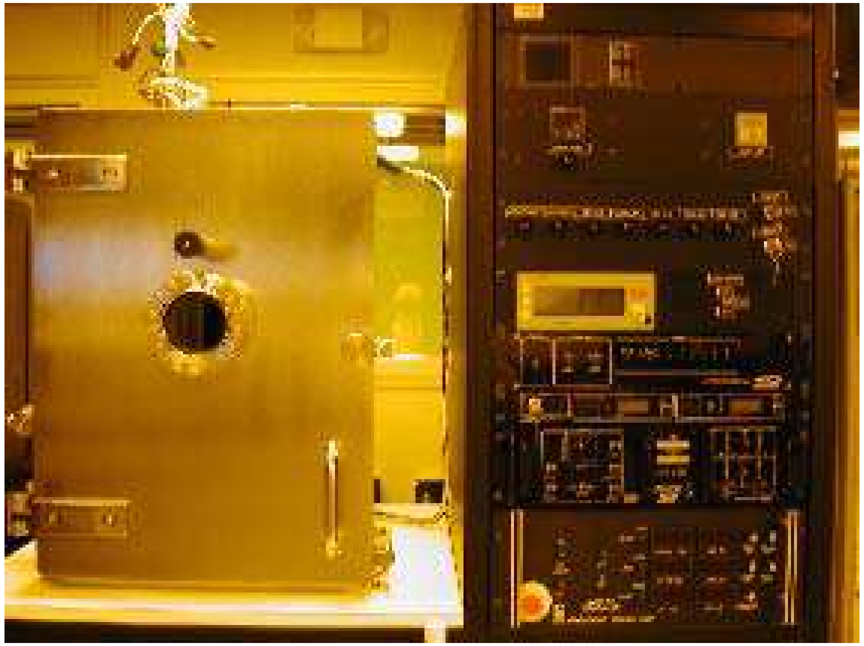


Deflection plates are to raster scan the beam across charge surface.

- Using a focused electron beam to heat and evaporate metals, electron temperature can be as high as 10,000 K. Electrons are accelerated by DC 10kV, and current 10s-100s of mA.
- Suitable for high T_{melt} metals like W, Ta, …
- Evaporation occurs at a highly localized point near the beam bombardment spot on the source surface , so little contamination from the crucible (not hot, water cooled).

Can one do e-beam evaporation of insulating materials like SiO_2?

Photos of e-beam evaporator

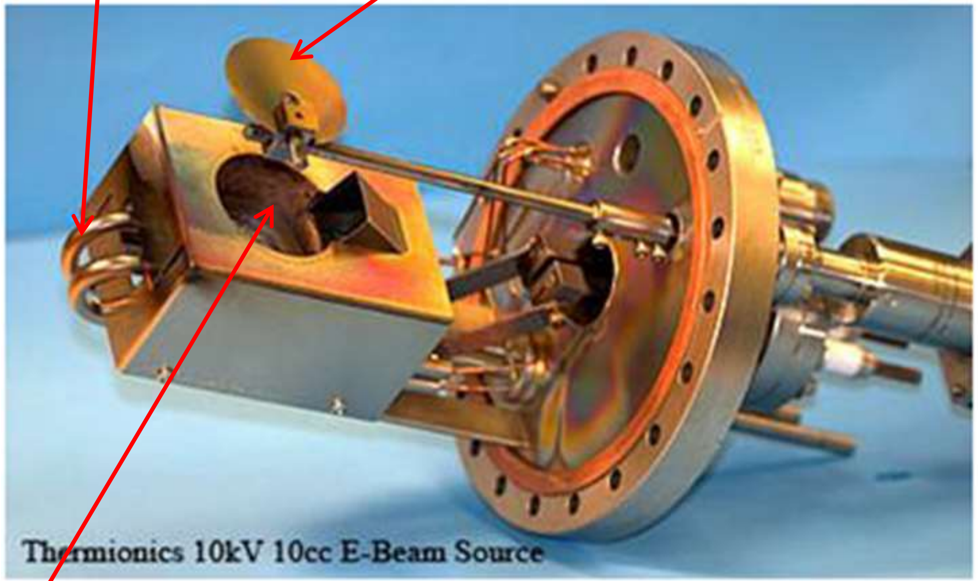


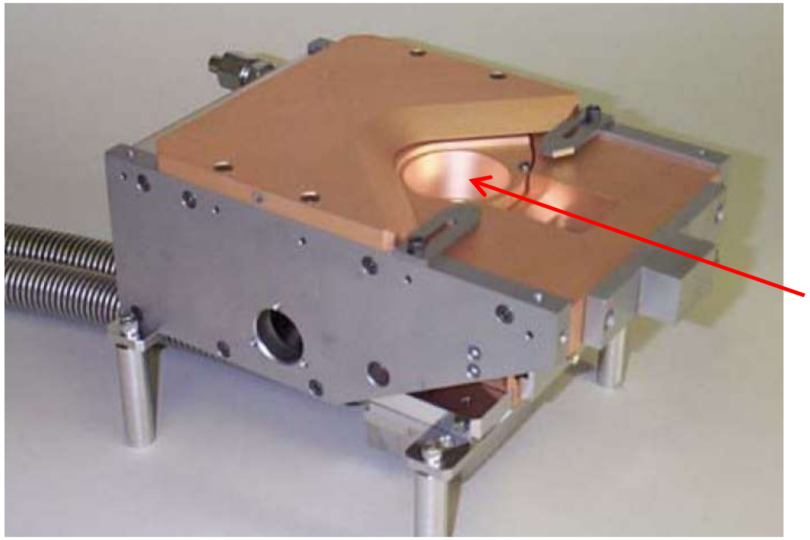
Mechanical shutter:

Evaporation rate is set by temperature of source, but this cannot be turned on and off rapidly.

Cooling water

Shutter





Put crucible here

Heat conduction of the hearth limits achievable temperature.

Power density: 10kV, up to 1.5A, 0.2-1cm^2 $\rightarrow$ 15-75kW/cm^2.

Comparison of thermal and e-beam evaporation

Deposition	Material	Typical Evaporant	Impurity	Deposition Rate	Temperature Range	Cost
Thermal	Metal or low melt-point materials	Au, Ag, Al, Cr, Sn, Sb, Ge, In, Mg, Ga CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$	High	1 ~ 20 A/s	~ 1800 ºC	Low
E-Beam	Both metal and dielectrics	Everything above, plus: Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo Al2O3, SiO, SiO2, SnO2, TiO2, ZrO2	Low	10 ~ 100 A/s	~ 3000 ºC	High

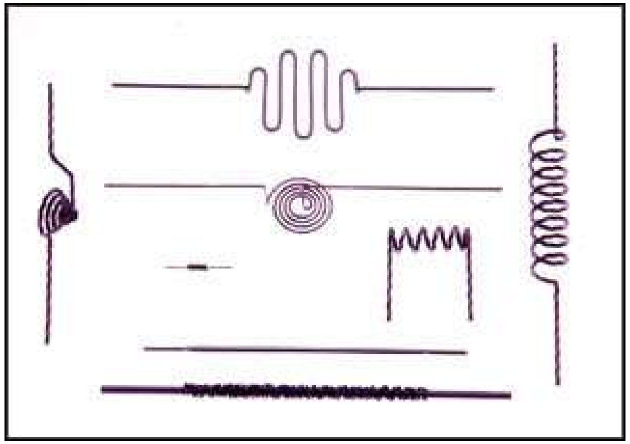
Thermal evaporation:

- Simple, robust, and in widespread use.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Contamination from heated boat/crucible.

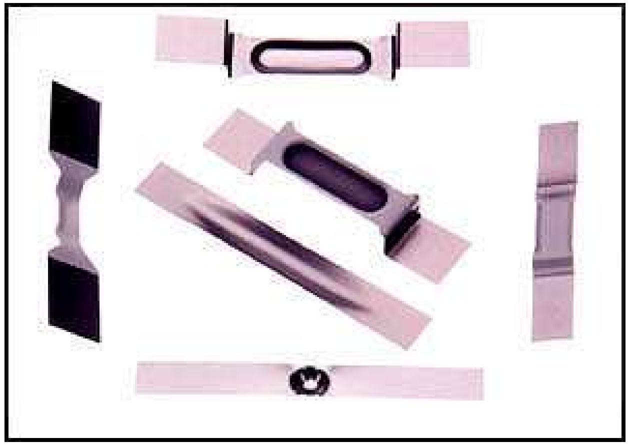
Electron beam evaporation:

- More complex, but extremely versatile, virtually any material.
- Less contamination, less heating to wafer (as only small source area heated to very high T).
- Exposes substrates to secondary electron radiation.
- X-rays can also be generated by high voltage electron beam.
- Since x-rays will damage substrate and dielectrics (leads to trapped charge), e-beam evaporators cannot be used in MOSFET.

Popular heating "containers" for evaporation source

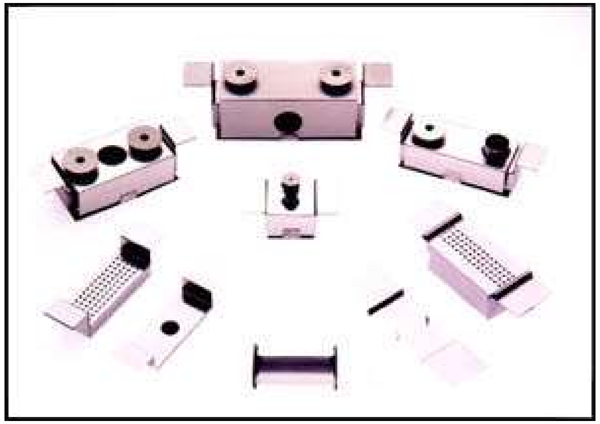


Resistors (put source rod inside coil)



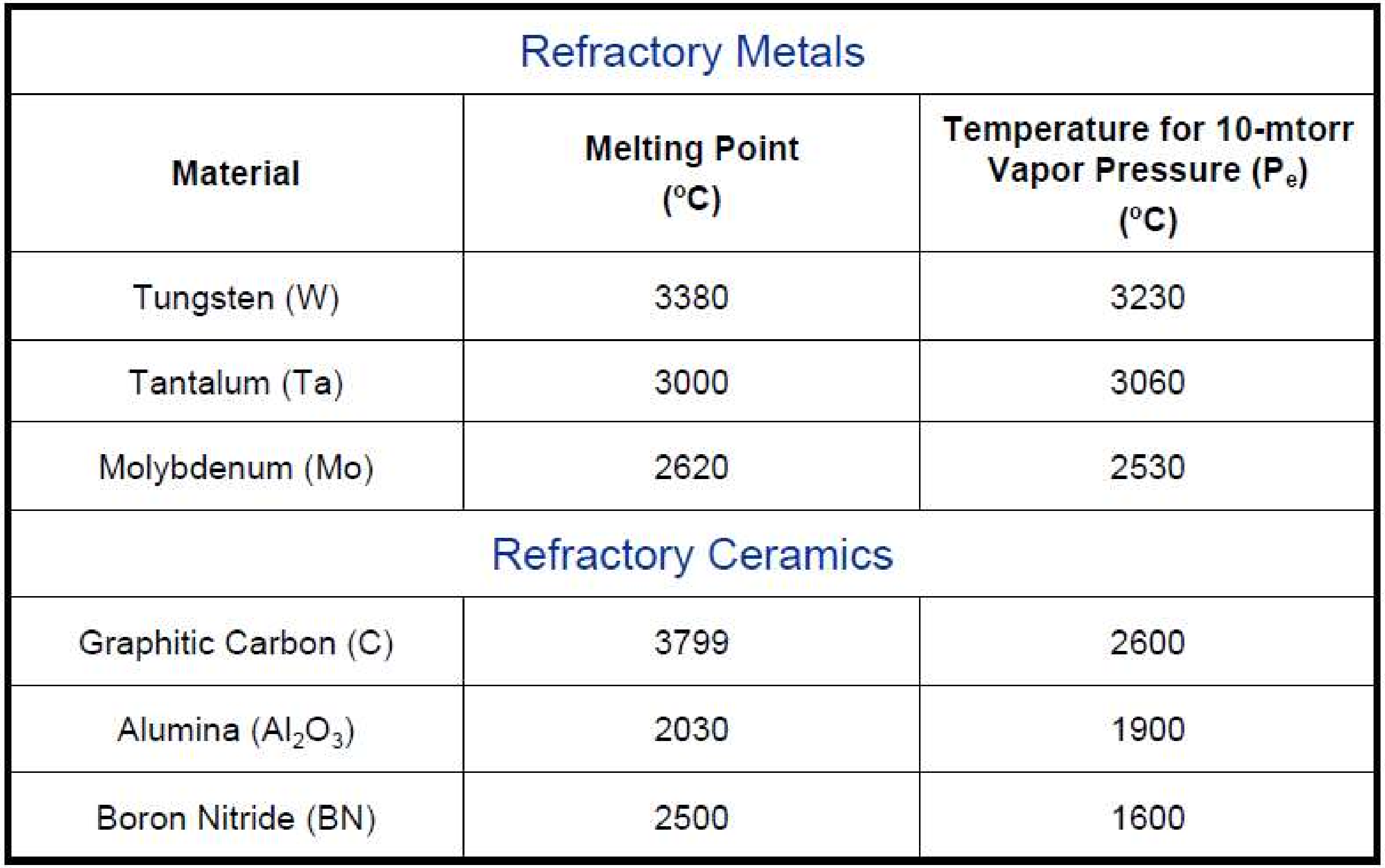
Heating boat (open top)

Crucibles
(only choice for e-beam evaporator)



Box with small opening
(Knudsen cell!)

Typical boat/crucible material



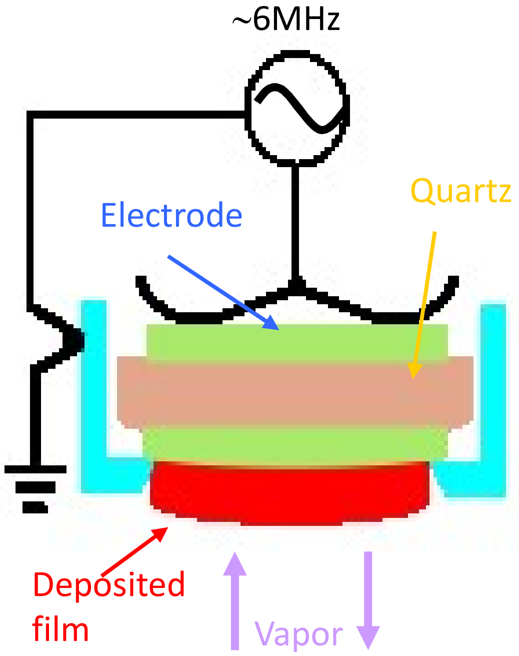
Material	Melting Point (°C)	Temperature for 10-mtorr Vapor Pressure (P_e) (°C)
Refractory Metals		
Tungsten (W)	3380	3230
Tantalum (Ta)	3000	3060
Molybdenum (Mo)	2620	2530
Refractory Ceramics		
Graphitic Carbon (C)	3799	2600
Alumina (Al_2O_3)	2030	1900
Boron Nitride (BN)	2500	1600

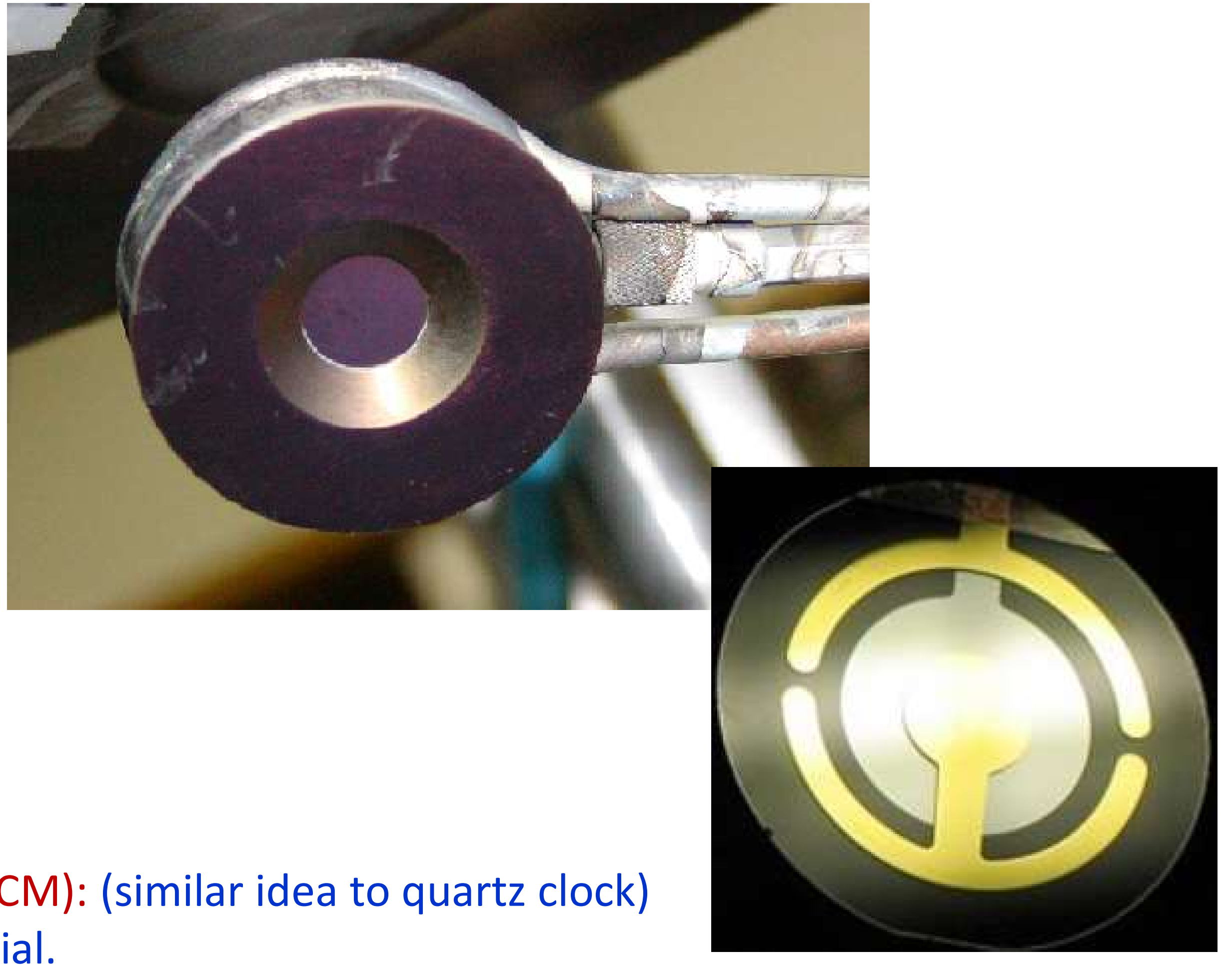
Considerations: thermal conductivity, thermal expansion, electrical conductivity, wetting and reactivity.

Graphite crucible is most popular, but avoid cracking the crucible due to stress/ temperature gradients (bad for materials that “wet” graphite such as Al and Ni).

Aluminum: tungsten dissolves in aluminum, so not quite compatible.

How to monitor film thickness during evaporation?





Quartz Crystal Micro-balance (QCM): (similar idea to quartz clock)

- Quartz is a piezoelectric material.
- With a high frequency AC voltage activation, the amplitude of vibration is maximum at resonance frequency.
- This resonance frequency will shift when film is deposited on its surface.
- Thus by measuring frequency shift Δf, one can measure film thickness with sub-Å accuracy.

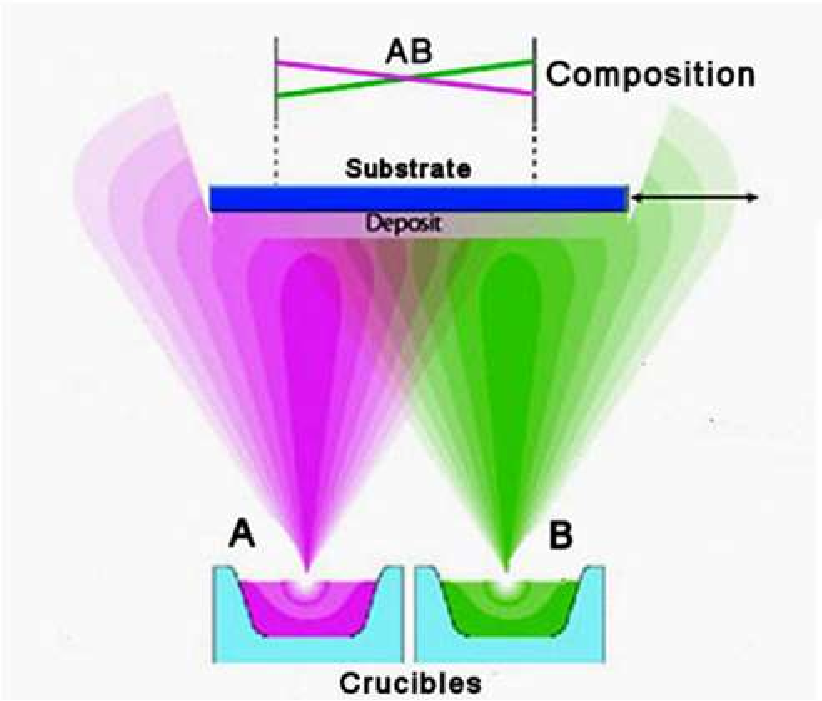
Evaporation issues: alloy evaporation

Stoichiometrical problem of evaporation:

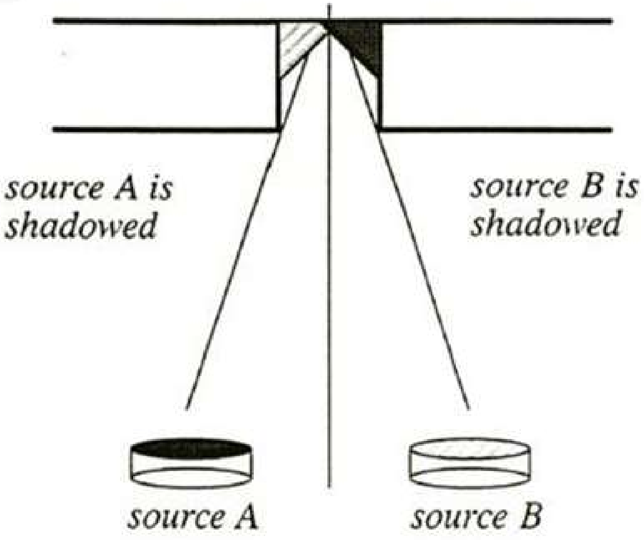
- Compound material breaks down at high temperature.
- Each component has different vapor pressure, therefore different deposition rate, resulting in a film with different stoichiometry compared to the source.

One solution is co-evaporation (use two e-beam guns).

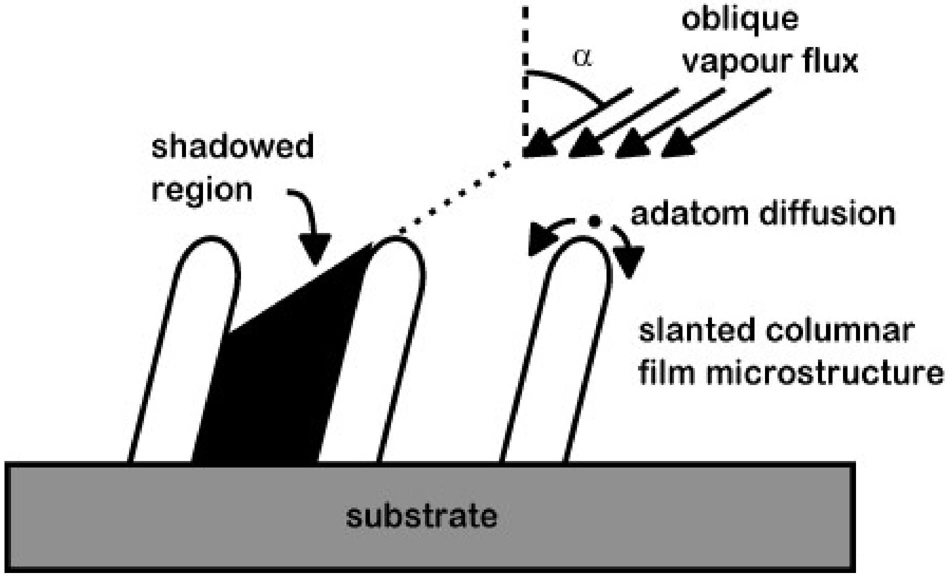
Lateral composition change

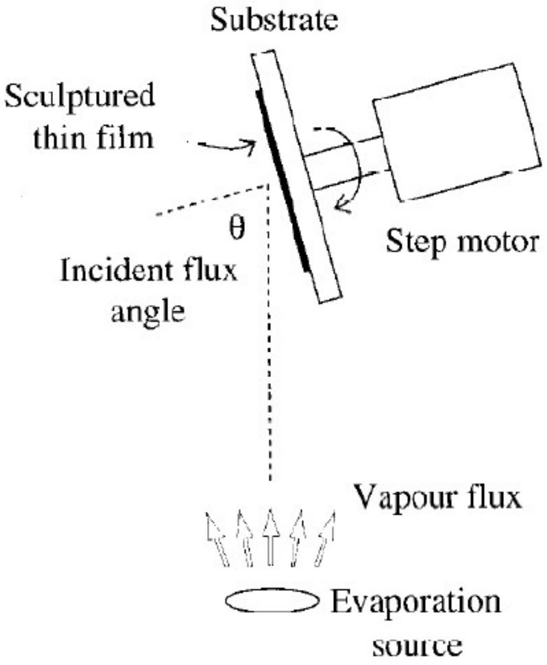


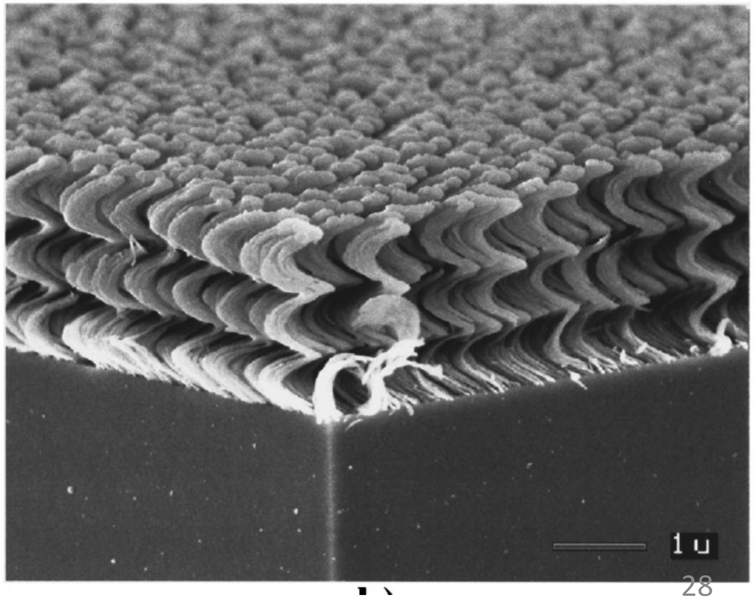
shadow problems...



GLAD (glancing angle deposition): self assembly of film



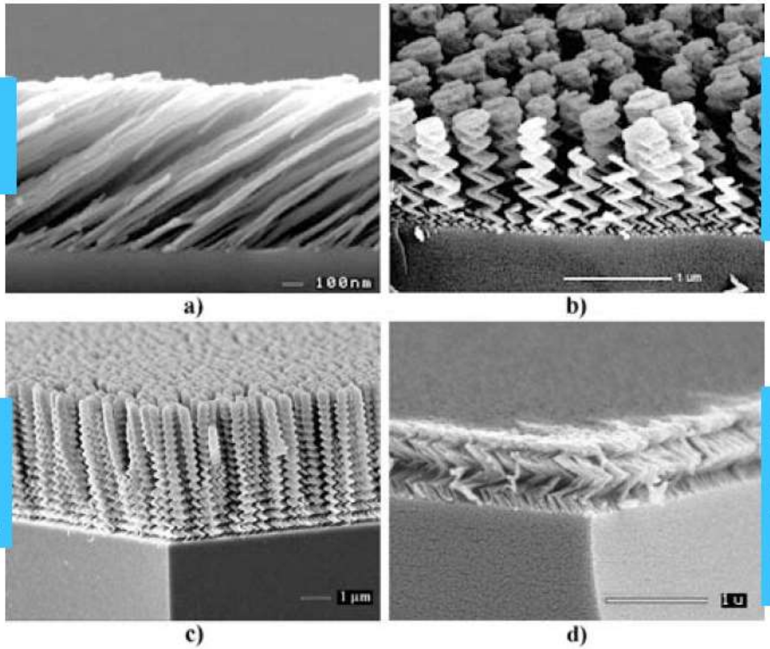




Angle >80^o, with (or without) substrate rotation.
Self assembly mainly due to shadowing effect that magnifies the otherwise grain structures.

Invented by Michael Brett from University of Alberta
http://www.ece.ualberta.ca/~glad/lab.html

Various nanostructures obtained in GLAD thin films

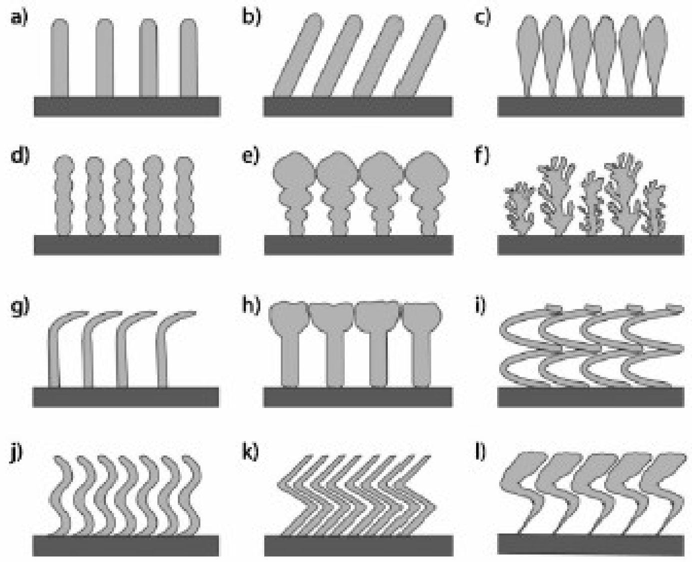


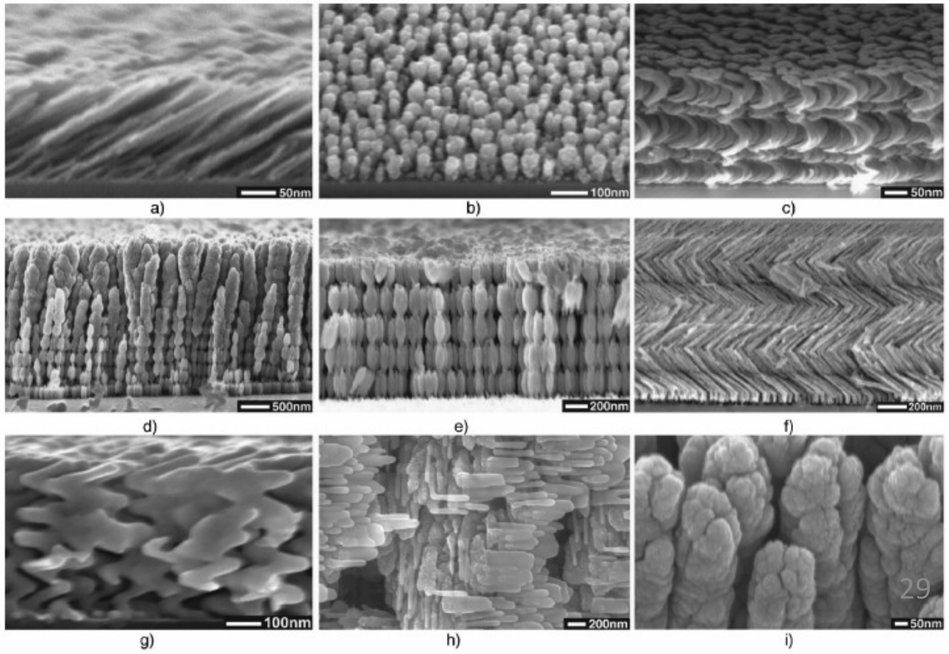
flux arrived from the right for the entire deposition

the direction of arriva of the flux was alternated from the left and right 12 times during deposition

the substrate was rotated continuously during deposition

a combination of the techniques used in b) and c). The substrate was rotated in 90 degree steps during deposition.





Evaporation: a quick summary

Evaporation advantages:

- Films can be deposited at high rates (e.g., 1µm/min, though for research typically < 0.1µm/min).
- Low energy atoms (~0.1 eV) leave little surface damage.
- Little residual gas and impurity incorporation due to high vacuum conditions.
- No or very little substrate heating.

Limitations:

- Accurately controlled alloy compounds are difficult to achieve.
- No in-situ substrate cleaning.
- Poor step coverage (but this is good for liftoff).
- Variation of deposit thickness for large/multiple substrates – has to rely on quartz crystal micro-balance for thickness monitoring.
- X-ray damage.

Sputtering process

- Sputtering process can be run in DC or RF mode (insulator must be run in RF mode)
- Major process parameters:
  - Operation pressure (~1-100mTorr)
  - Power (few 100W)
  - For DC sputtering, voltage -2 to -5kV.
  - Additional substrate bias voltage.
  - Substrate temperature (20-700°C)

In addition to IC industry, a wide range of industrial products use sputtering: LCD, computer hard drives, hard coatings for tools, metals on plastics.

It is more widely used for industry than evaporator, partly because that, for evaporation:

- There are very few things (rate and substrate temperature) one can do to tailor film property.
- The step coverage is poor.
- It is not suitable for compound or alloy deposition.
- Considerable materials are deposited on chamber walls and wasted.

Targets for sputter deposition.

Sputter deposition advantages

Advantages:

- Able to deposit a wide variety of metals, insulators, alloys and composites.
- Replication of target composition in the deposited films.
- Capable of in-situ cleaning prior to film deposition by reversing the potential on the electrodes .
- Better film quality and step coverage than evaporation.
- This is partly because adatoms are more energetic, and film is ‘densified’ by in-situ ion bombardment, and it is easier to heat up to high T than evaporation that is in vacuum.
- More reproducible deposition control – same deposition rate for same process parameters (not true for evaporation), so easy film thickness control via time.
- Can use large area targets for uniform thickness over large substrates.
- Sufficient target material for many depositions.
- No x-ray damage.

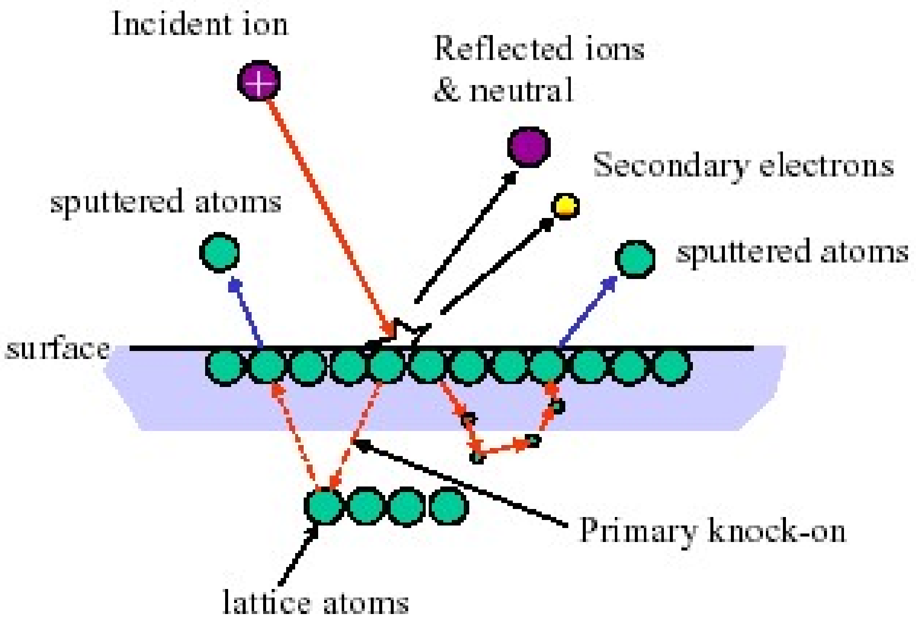
Disadvantages:

- Substrate damage due to ion bombardment or UV generated by plasma.
- Higher pressures 1 –100 mtorr (< 10^{-5} torr in evaporation), more contaminations unless using ultra clean gasses and ultra clean targets.
- Deposition rate of some materials quite low.
- Some materials (e.g., organics) degrade due to ionic bombardment.
- Most of the energy incident on the target becomes heat, which must be removed.

Mechanisms of sputtering and alloy sputtering

The ion impact may set up a series of collisions between atoms of the target, possibly leading to the ejection of some of these atoms. This ejection process is known as sputtering.

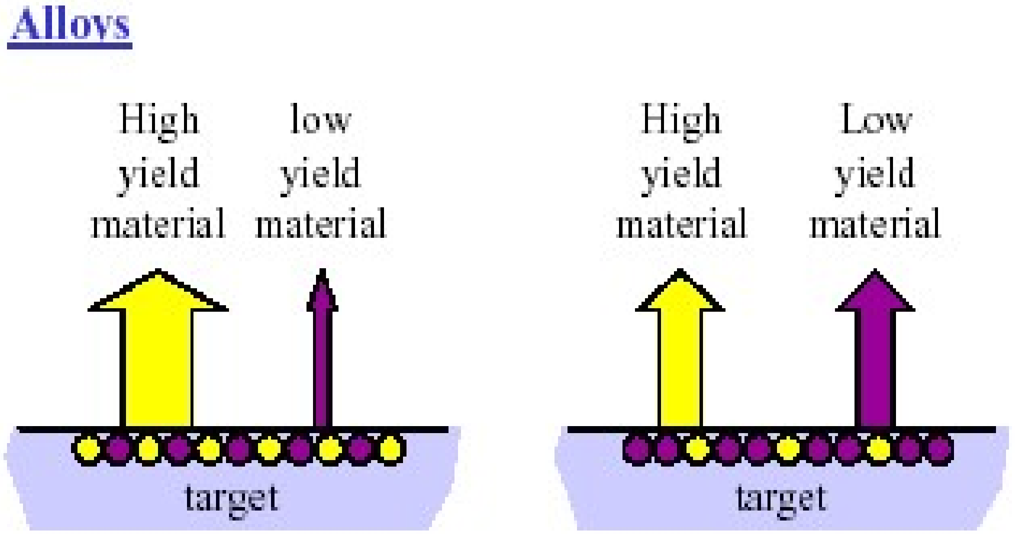
Here we are interested in sputter deposition. Of course sputter can also be used as an etching method (the substrate to be etched will be the 'target'), which is called sputter etching.



Unlike evaporation, composition of alloy film is approximately the same as target.

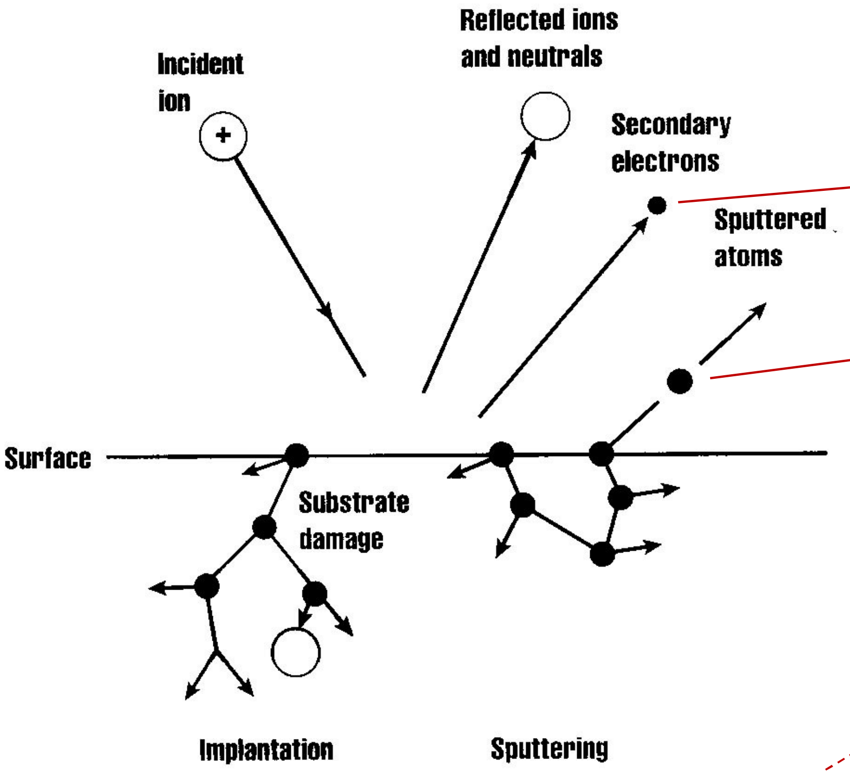
Target NOT melted, slow *diffusion* (no material flow) mixing.

When target reaches steady state, surface composition balances sputter yield.



Before surface equilibrium After surface equilibrium

Sputtering process



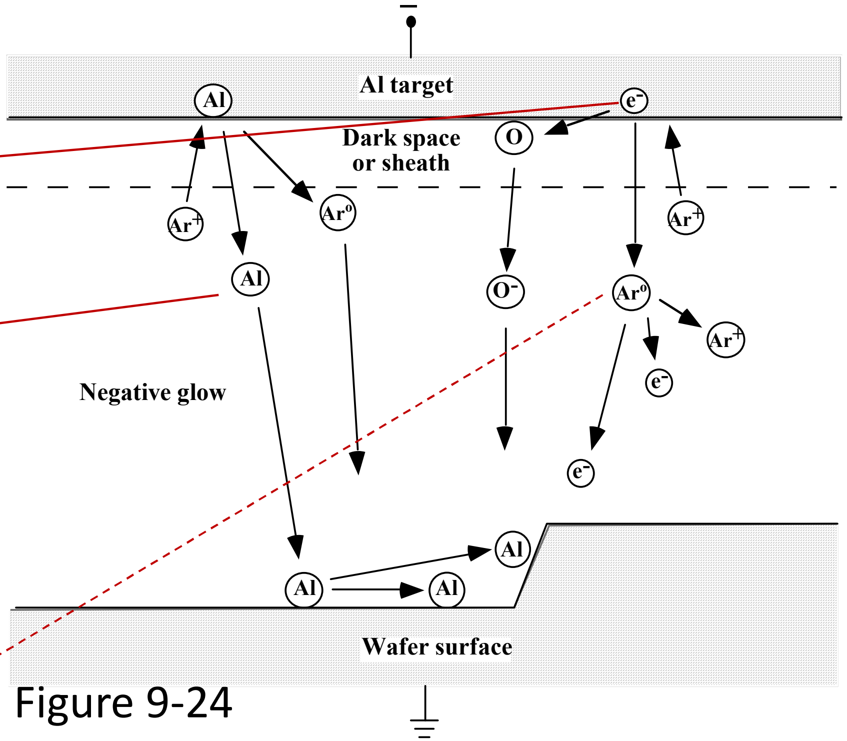


Figure 9-24

After collision ionization, there are now TWO free electrons.
This doubles the available electrons for ionization.
This ongoing doubling process is called "impact ionization”, which sustains a plasma.

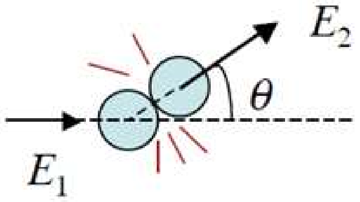
On the left side, sputter off an Al atom.
On the right side, generate secondary electrons, which are accelerated across the sheath region and 1) ionize/excite an Ar; or 2) ionize an impurity atom, here O, to generate O^- (for Ar, always positive ion Ar^+). This O^- is accelerated toward substrate and may go into the film (bad).

Sputtering process

- Energy of each incoming ion is 500-1000eV. Energy of sputtered atoms is 3-10eV.
- Thus, the sputtering process is very inefficient from the energy point of view, 95% of incoming energy goes to target heating & secondary electron.
- High rate sputter processes need efficient cooling techniques to avoid target damage from overheating (serious problem).
- The sputtered species, in general, are predominantly neutral.
- The energy of the ejected atoms shows a Maxwellian distribution with a long tail toward higher energies.
- The energies of the atoms or molecules sputtered at a given rate are about one order of magnitude higher than those thermally evaporated at the same rate, which often lead to better film quality.
- However, since sputtering yields are low and the ion currents are limited, sputter-deposition rates are invariably one to two orders of magnitude lower compared to thermal evaporation rates under normal conditions.

Sputtering yield

Elastic energy transfer



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

E_2 is greatest for $M_1 = M_2$.
There is also inelastic energy transfer, which leads to secondary electrons emission…

$$Y = \frac{\text{sputtered atoms}}{\text{bombing ions}} = \alpha \frac{\mathrm{Mm}}{(\mathrm{M}+\mathrm{m})^2} \frac{\mathrm{E_m}}{\mathrm{U_M}}$$

M : mass of target atom

m : mass of bombing ion

$\mathrm{E_m}$: kinetic energy of bombing ion

$\mathrm{U_M}$: Bonding energy of target metal

α : depends on striking /incident angle

- Sputter yield Y: the number of sputtered atoms per impinging ion.
- Obviously, the higher yield, the higher sputter deposition rate.
- Sputter yield is 1-3: not too much difference for different materials.
- The sputter yield depends on: (a) the energy of the incident ions; (b) the masses of the ions and target atoms; (c) the binding energy of atoms in the solid; and (d) the incident angle of ions.
- The yield is rather insensitive to the target temperature except at very high temperatures where it show an apparent rapid increase due to the accompanying thermal evaporation.

Dependence of sputter yield on ion energy

A threshold energy for the release of an atom from the target exists, below which the atom is not “sputtered”.
This threshold energy is:

$$E_{threshold} = \frac{Heat\ of\ Vaporization}{\gamma(1-\gamma)}$$

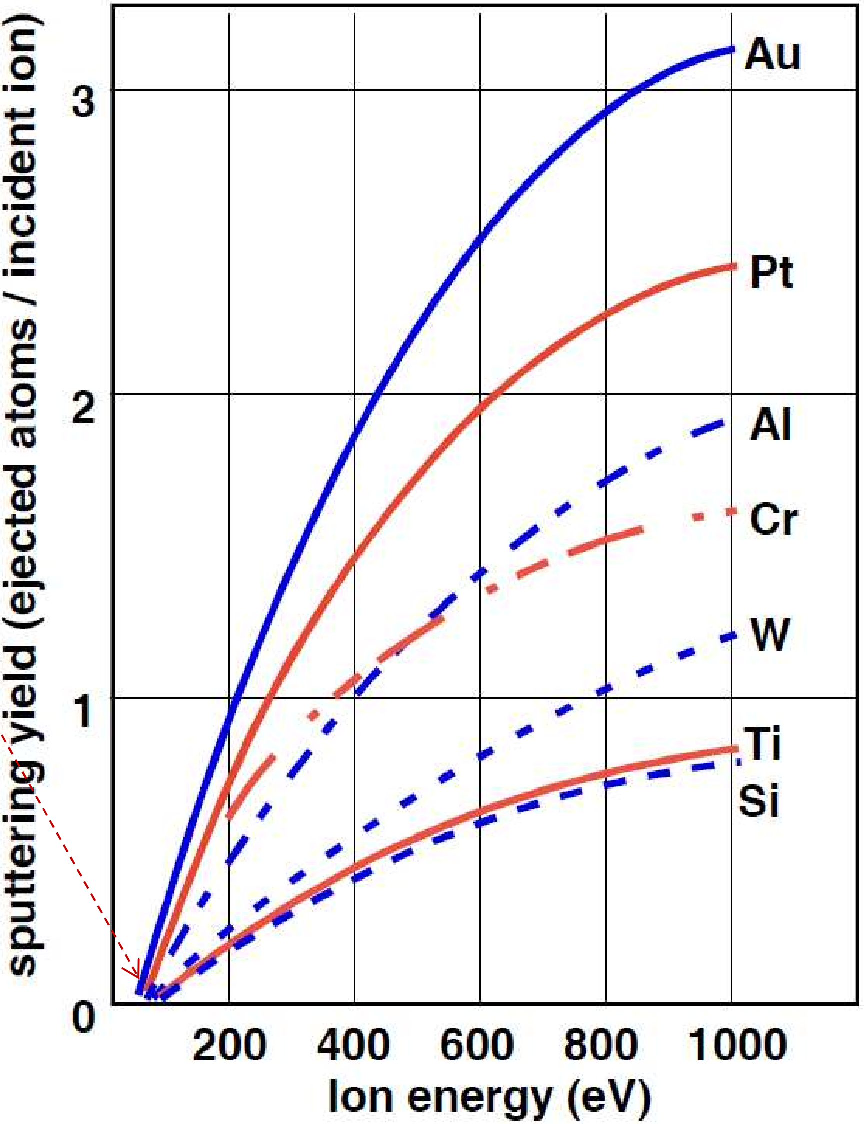
$$where\ \ \gamma = \frac{4M_1M_2}{(M_1+M_2)^2}$$

(E_{th} very high when $M_1 \approx M_2$ or they are very different?)

The yield increases with the energy.

For higher energies, the yield approaches saturation, which occurs at higher energies for heavier bombarding particles.
e.g.: Xe^+ ~100keV and Ar^+ ~20KeV for saturation.

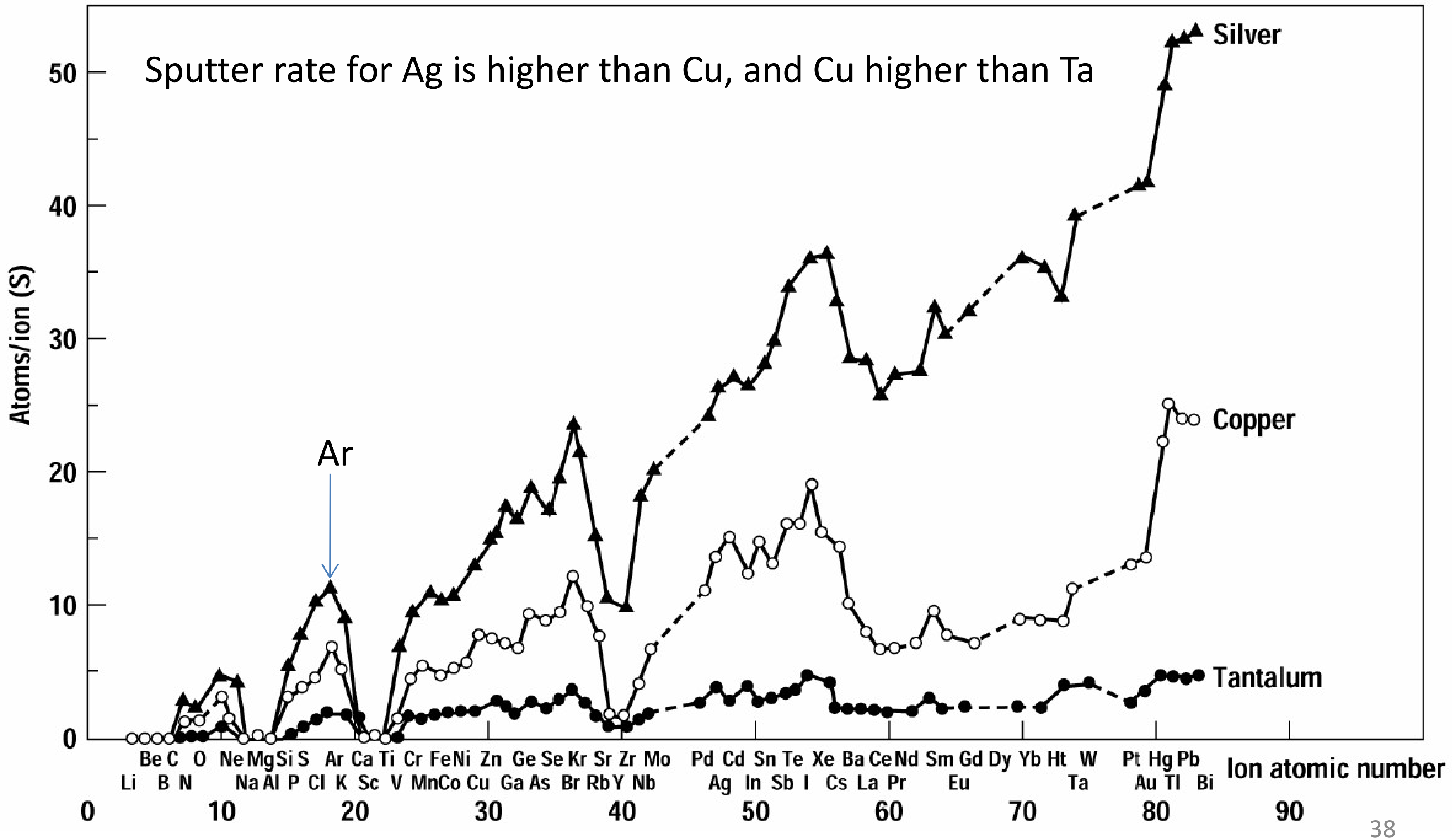
Sometimes, at very high energies, the yield decreases because of the increasing penetration depth and hence increasing energy loss below the surface, i.e. not all the affected atoms are able to reach the surface to escape.



Dependence of sputter yield on ion mass

Sputter increases with ion mass.

Sputter yield is a maximum for ions with full valence shells: noble gasses such as Ar, Kr, Xe have large yields.



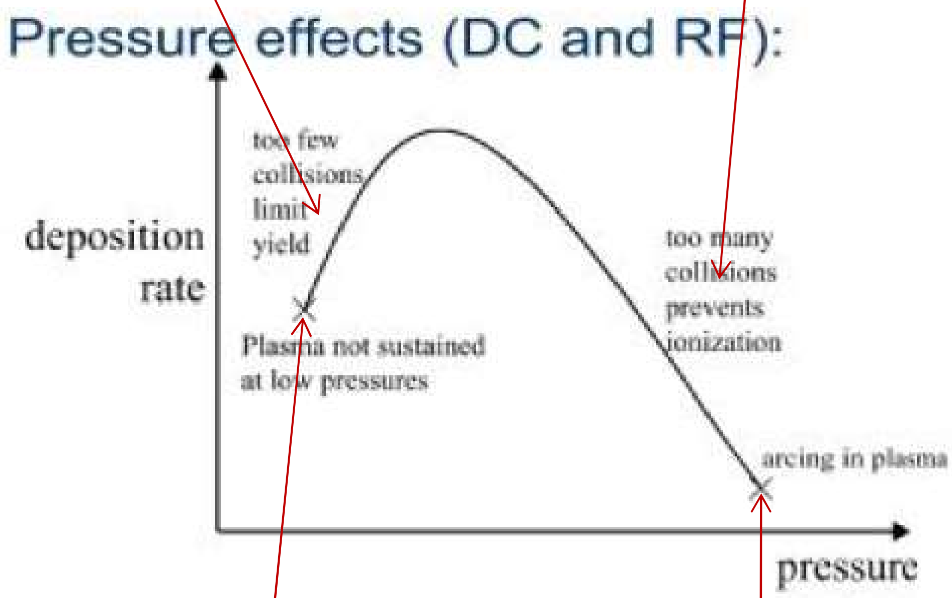
Sputter rate for Ag is higher than Cu, and Cu higher than Ta

Ar

Dependence of deposition rate on chamber pressure

Too few collisions limit yield

Too many collisions prevent ionization



Plasma not sustained at low pressure

Arcing in plasma (?)

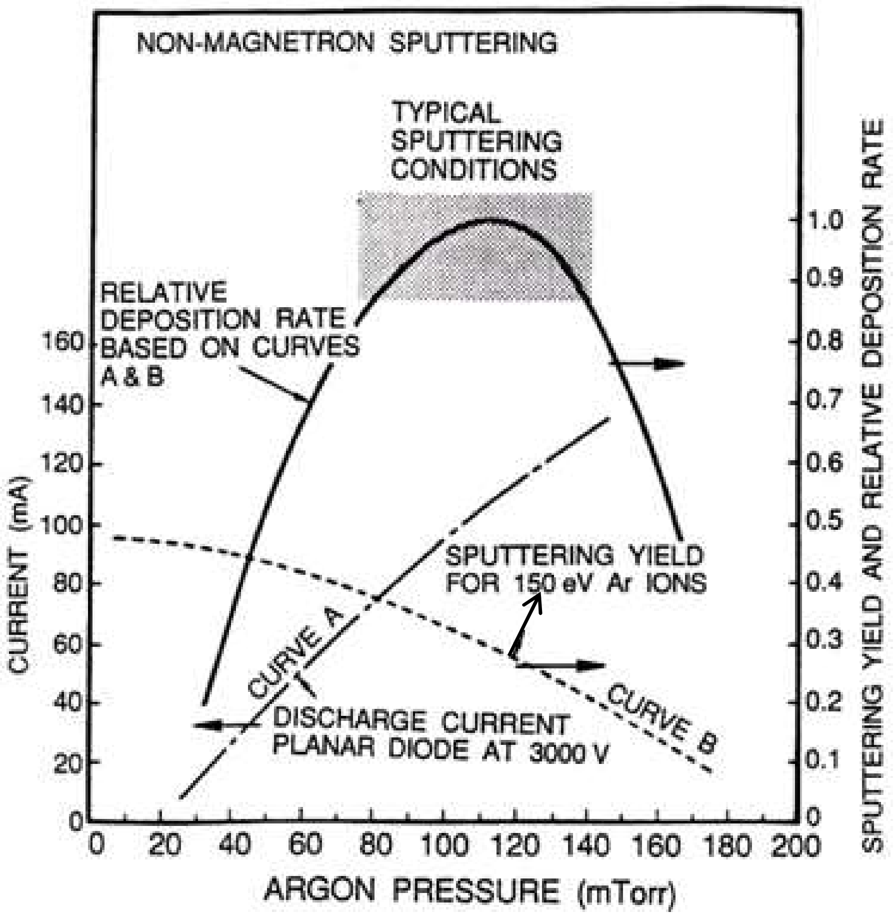
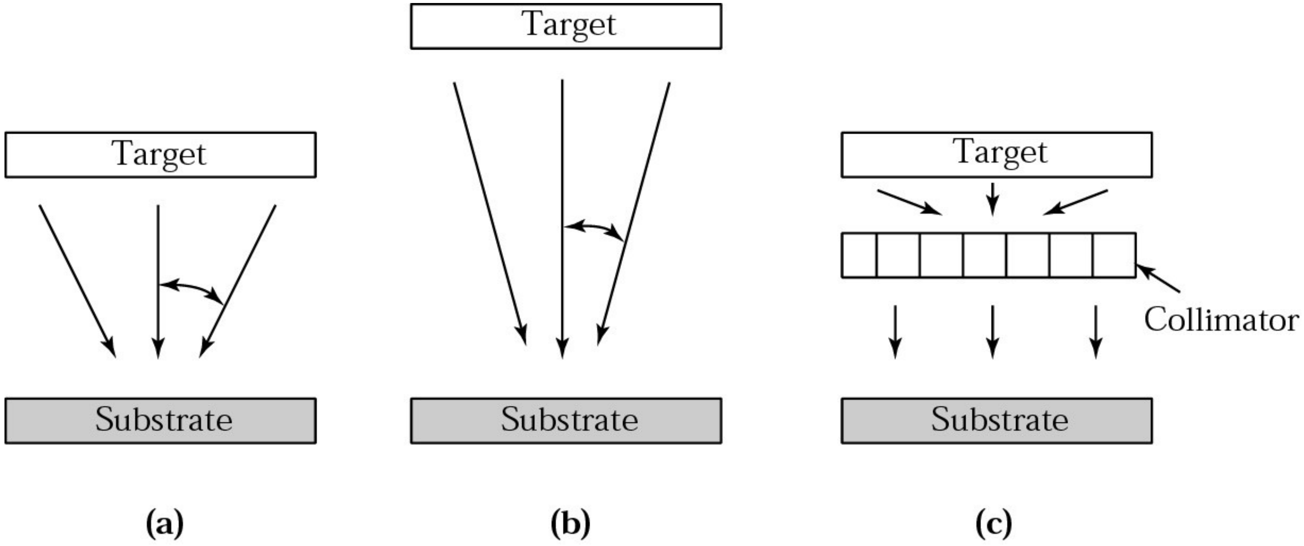


Figure 3-18 Influence of working pressure and current on deposition rate for non-magnetron sputtering.

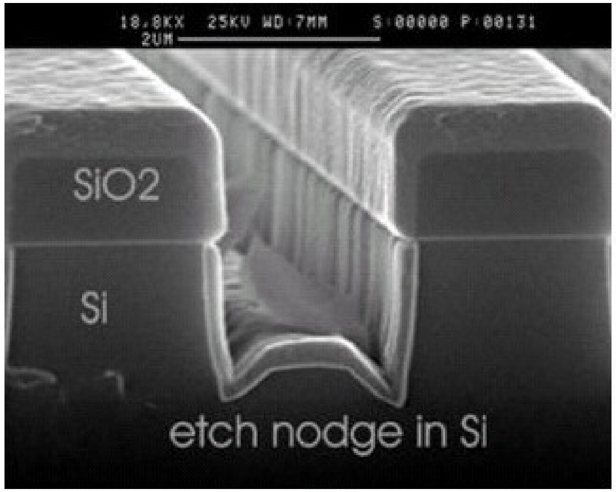
For same power P=I×V=constant, high current (ion number) comes with low voltage (ion energy)

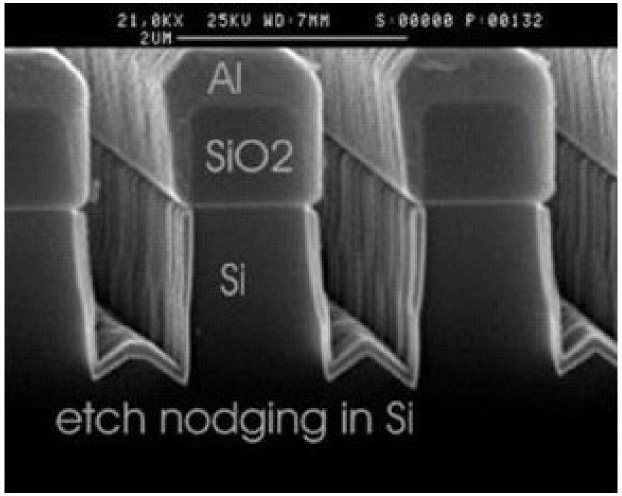
Arrival angle can be tailored to some degree



(a) Standard sputtering.
(b) Long-throw sputtering.
(c) Sputtering with a collimator.

However, when the mean free path of the *target* atom (determined by gas pressure, order 10cm for 1mTorr pressure/1cm for 10mTorr) is much shorter than target-substrate separation, many collisions will occur, which broaden the arrival angle distribution.





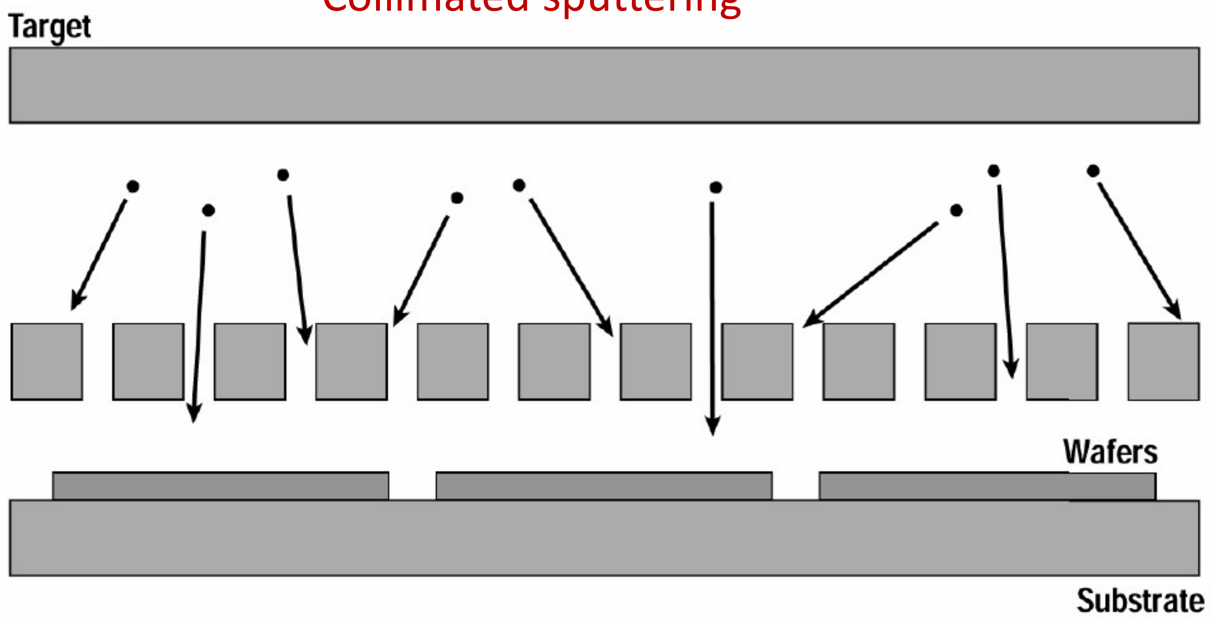
More deposition on top surface.

Collimated sputtering

The goal is to fill high aspect ratio holes by more directional sputtering with narrow arrival angle distribution.

The long throw sputtering (previous slide) is one kind of “collimated” sputtering, but also with low efficiency.

Collimated sputtering



- Insert a plate with high-aspect-ratio holes.
- Sputter at low pressure, mean path is long enough that few collisions occur between collimator and wafer.
- Species with velocities nearly perpendicular to wafer surface pass through the holes.
- Reduce deposition rate considerably (most sputtered atoms cannot reach the substrate).

Reactive sputtering

Sputtering metallic target in the presence of a reactive gas mixed with inert gas (Ar).

- Sputtering a compound target may not give what one wants.
- This doesn't mean reactive sputtering will give what one wants – it is just one more thing to try with.
- Certainly reactive sputtering can be done using DC sputtering, whereas compound target (insulating) can only be used for RF sputtering.
- Chemical reaction takes place on substrate and target.
- Can "poison" target if chemical reactions are faster than sputter rate.
- Need to adjust reactive gas flow to get good composition (e.g. SiO_2 rather than SiO_{2-x}) without incorporating excess gas into film.

A mixture of inert + reactive gases used for sputtering:

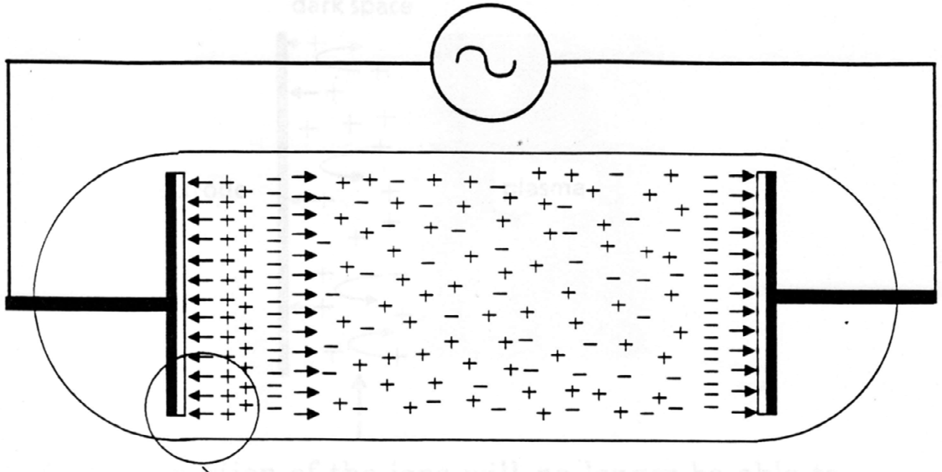
Oxides – Al_2O_3, SiO_2, Ta_2O_5 (O_2 mixed with Ar)

Nitrides – TaN, TiN, Si_3N_4 (N_2, NH_3, mixed with Ar)

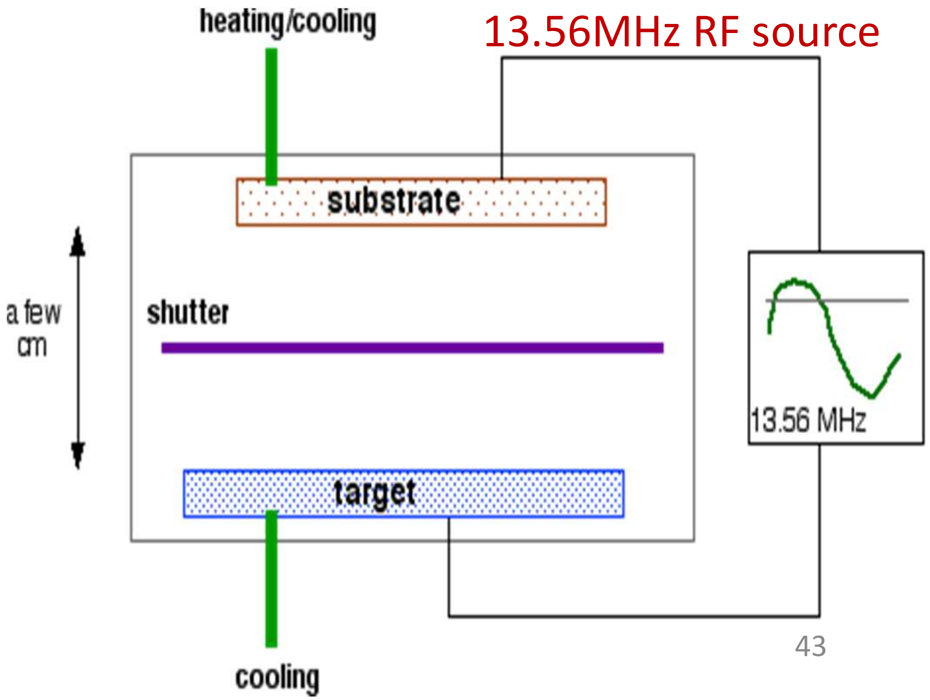
Carbides – TiC, WC, SiC (CH_4, C_2H_4, C_3H_8, mixed with Ar)

RF (radio frequency) sputter deposition

- Good for insulating materials because, positive charge (Ar^+) build up on the cathode (target) in DC sputtering systems. Alternating potential can avoid charge buildup
- When frequencies less than ~50kHz, both electrons and ions can follow the switching of the anode and cathode, basically DC sputtering of both surfaces.
- When frequencies well above ~50kHz, ions (heavy) can no longer follow the switching, and electrons can neutralize positive charge buildup on each electrode during each half cycle.
- As now electrons gain energy directly from RF powder (no need of secondary electrons to maintain plasma), and oscillating electrons are more efficient to ionize the gas, RF sputter is capable of running in lower pressure (1-15 mTorr), so fewer gas collisions and more line of sight deposition.

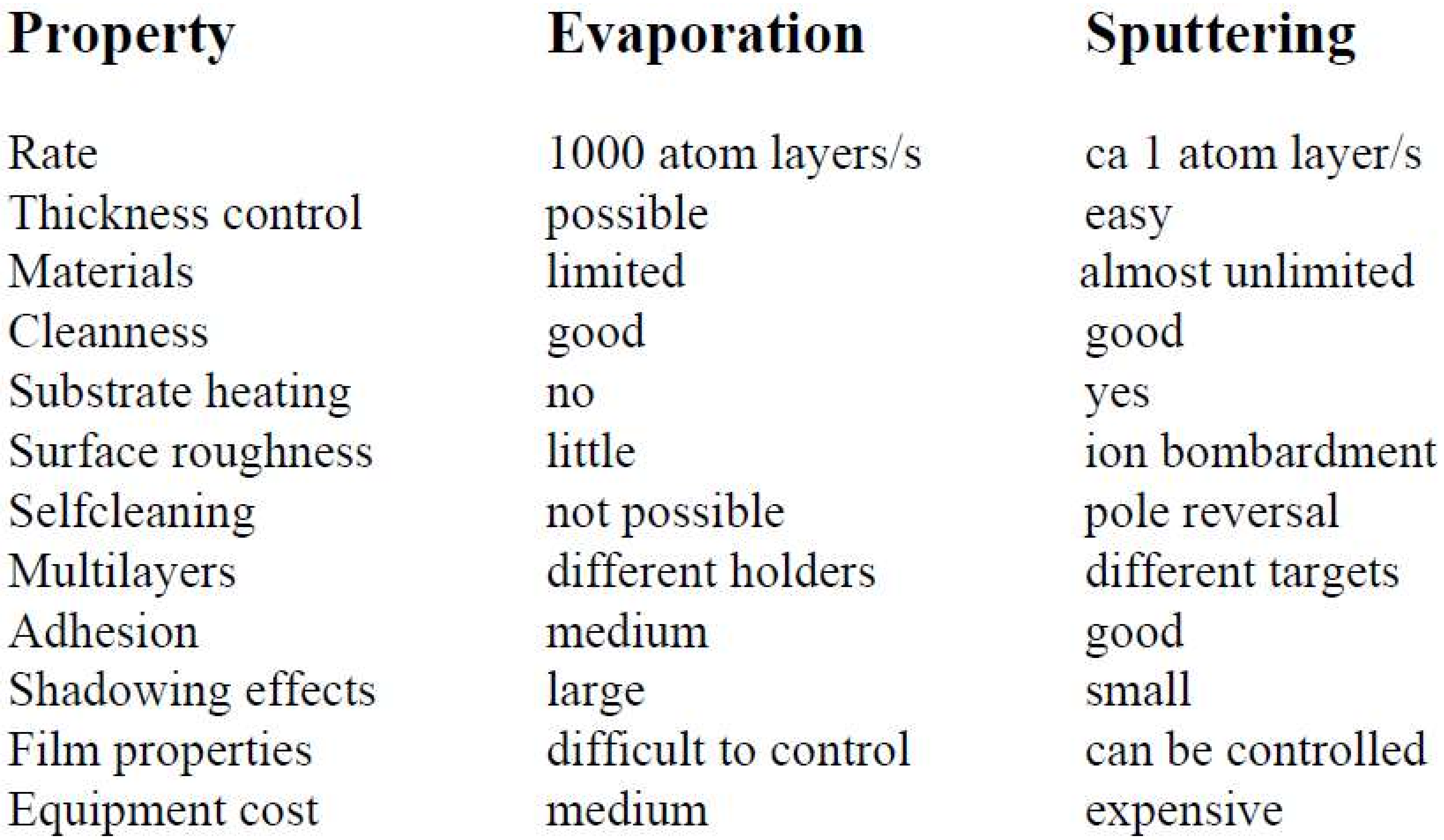


Switch polarities before the target surface saturates with ions.



13.56MHz RF source

Comparison of evaporation and sputtering

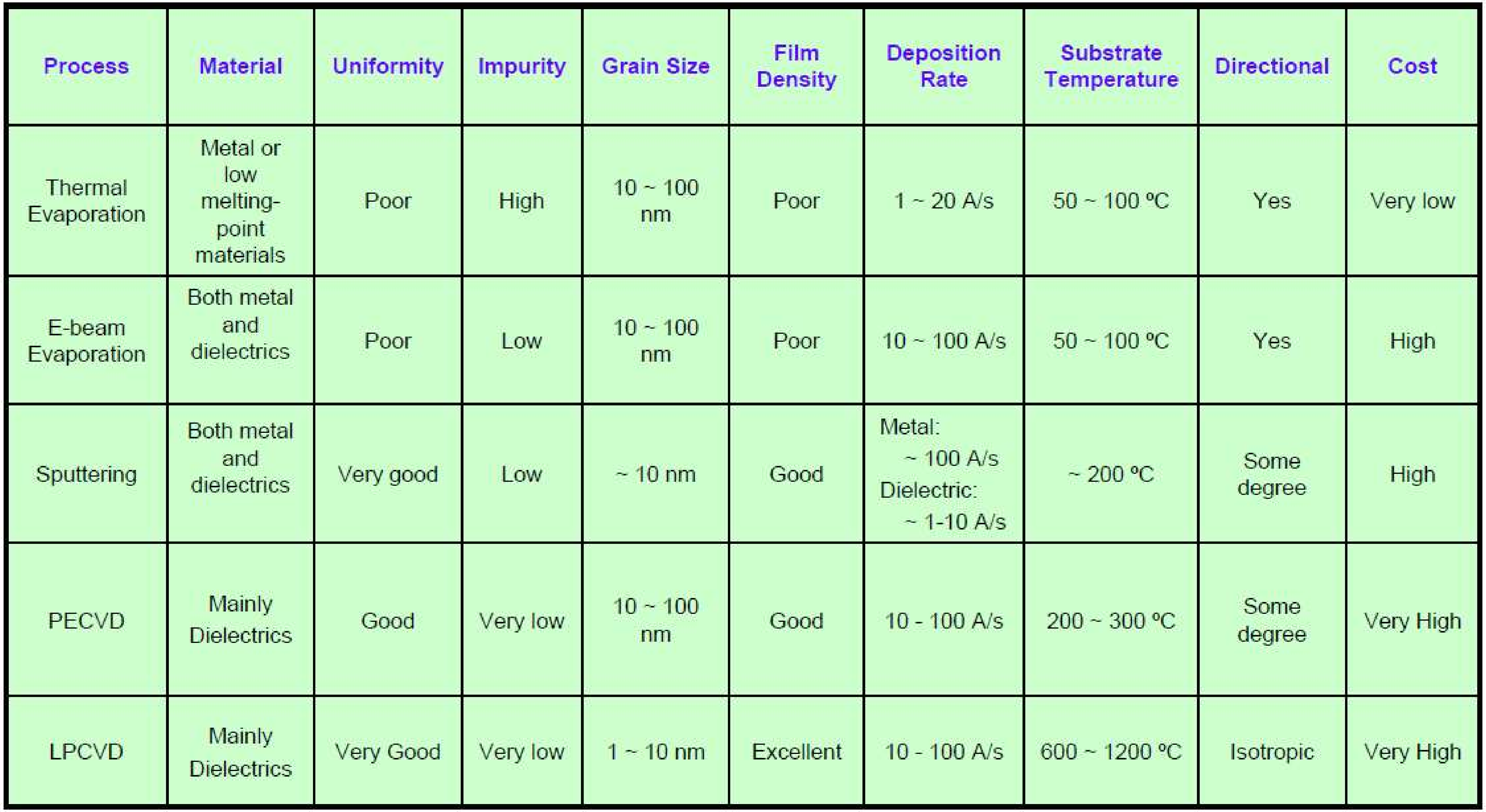


Property	**Evaporation**	**Sputtering**
Rate	1000 atom layers/s	ca 1 atom layer/s
Thickness control	possible	easy
Materials	limited	almost unlimited
Cleanness	good	good
Substrate heating	no	yes
Surface roughness	little	ion bombardment
Selfcleaning	not possible	pole reversal
Multilayers	different holders	different targets
Adhesion	medium	good
Shadowing effects	large	small
Film properties	difficult to control	can be controlled
Equipment cost	medium	expensive

Comparison of evaporation and sputtering

EVAPORATION	SPUTTERING
low energy atoms	higher energy atoms
high vacuum path • few collisions • line of sight deposition • little gas in film	low vacuum, plasma path • many collisions • less line of sight deposition • gas in film
larger grain size	smaller grain size
fewer grain orientations	many grain orientations
poorer adhesion	better adhesion

Comparison of typical thin film deposition technology



Process	Material	Uniformity	Impurity	Grain Size	Film Density	Deposition Rate	Substrate Temperature	Directional	Cost
Thermal Evaporation	Metal or low melting-point materials	Poor	High	10 ~ 100 nm	Poor	1 ~ 20 A/s	50 ~ 100 ºC	Yes	Very low
E-beam Evaporation	Both metal and dielectrics	Poor	Low	10 ~ 100 nm	Poor	10 ~ 100 A/s	50 ~ 100 ºC	Yes	High
Sputtering	Both metal and dielectrics	Very good	Low	~ 10 nm	Good	Metal: ~ 100 A/s Dielectric: ~ 1-10 A/s	~ 200 ºC	Some degree	High
PECVD	Mainly Dielectrics	Good	Very low	10 ~ 100 nm	Good	10 - 100 A/s	200 ~ 300 ºC	Some degree	Very High
LPCVD	Mainly Dielectrics	Very Good	Very low	1 ~ 10 nm	Excellent	10 - 100 A/s	600 ~ 1200 ºC	Isotropic	Very High

Common deposition methods for thin films in IC fabrication

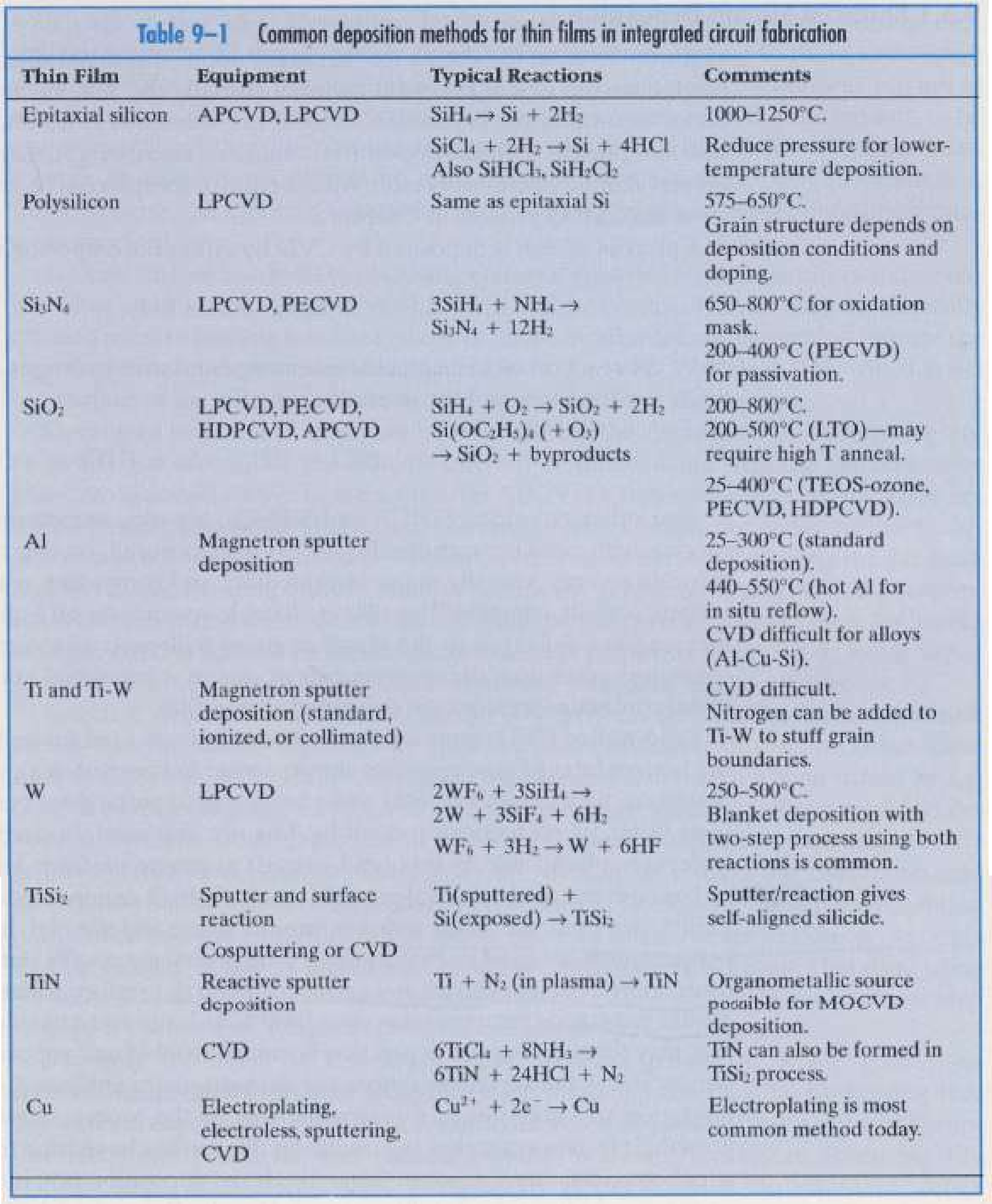


Table 9–1 Common deposition methods for thin films in integrated circuit fabrication

Thin Film	Equipment	Typical Reactions	Comments
Epitaxial silicon	APCVD, LPCVD	$SiH_4 \rightarrow Si + 2H_2$ $SiCl_4 + 2H_2 \rightarrow Si + 4HCl$ Also $SiHCl_3$, SiH_2Cl_2	1000–1250°C. Reduce pressure for lower-temperature deposition.
Polysilicon	LPCVD	Same as epitaxial Si	575–650°C. Grain structure depends on deposition conditions and doping.
Si_3N_4	LPCVD, PECVD	$3SiH_4 + NH_4 \rightarrow Si_3N_4 + 12H_2$	650–800°C for oxidation mask. 200–400°C (PECVD) for passivation.
SiO_2	LPCVD, PECVD, HDPCVD, APCVD	$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$ $Si(OC_2H_5)_4\ (+O_3) \rightarrow SiO_2$ + byproducts	200–800°C. 200–500°C (LTO)—may require high T anneal. 25–400°C (TEOS-ozone, PECVD, HDPCVD).
Al	Magnetron sputter deposition		25–300°C (standard deposition). 440–550°C (hot Al for in situ reflow). CVD difficult for alloys (Al-Cu-Si).
Ti and Ti-W	Magnetron sputter deposition (standard, ionized, or collimated)		CVD difficult. Nitrogen can be added to Ti-W to stuff grain boundaries.
W	LPCVD	$2WF_6 + 3SiH_4 \rightarrow 2W + 3SiF_4 + 6H_2$ $WF_6 + 3H_2 \rightarrow W + 6HF$	250–500°C. Blanket deposition with two-step process using both reactions is common.
$TiSi_2$	Sputter and surface reaction Cosputtering or CVD	Ti(sputtered) + Si(exposed) $\rightarrow TiSi_2$	Sputter/reaction gives self-aligned silicide.
TiN	Reactive sputter deposition CVD	$Ti + N_2$ (in plasma) $\rightarrow TiN$ $6TiCl_4 + 8NH_3 \rightarrow 6TiN + 24HCl + N_2$	Organometallic source possible for MOCVD deposition. TiN can also be formed in $TiSi_2$ process.
Cu	Electroplating, electroless, sputtering, CVD	$Cu^{2+} + 2e^- \rightarrow Cu$	Electroplating is most common method today.

Silicon nitride deposition

- Application:
  - Masks to prevent oxidation for LOCOS process
  - Final passivation barrier for moisture and sodium contamination
  - Etch stop for Cu damascene process
  - Popular membrane material by Si backside through-wafer wet etch.
- PECVD

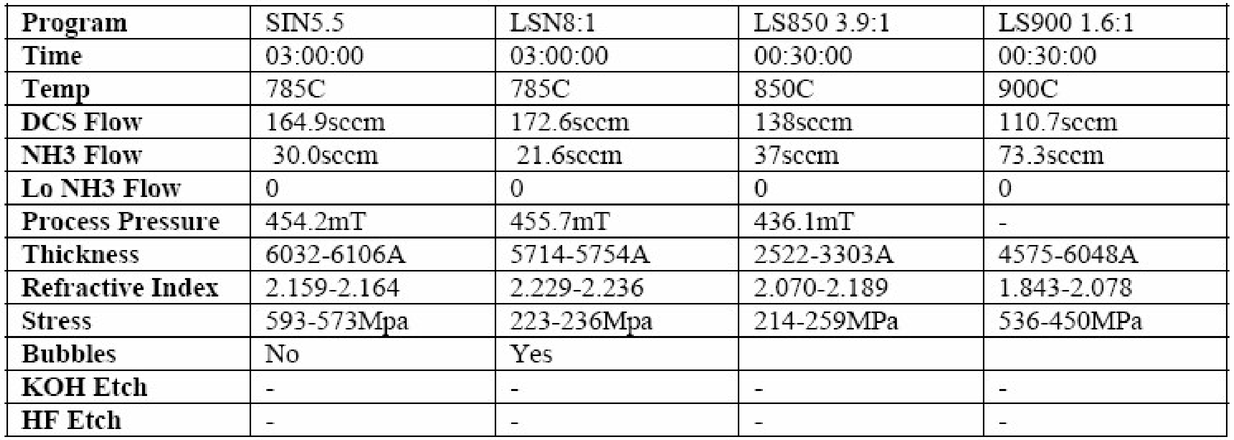
$$SiH_4 + NH_3 \xrightarrow{200\text{–}400°C} SiN_xH_y + H_2$$

- LPCVD

$$3SiH_4 + 4NH_3 \xrightarrow{650\text{–}800°C} Si_3N_4 + 12H_2$$

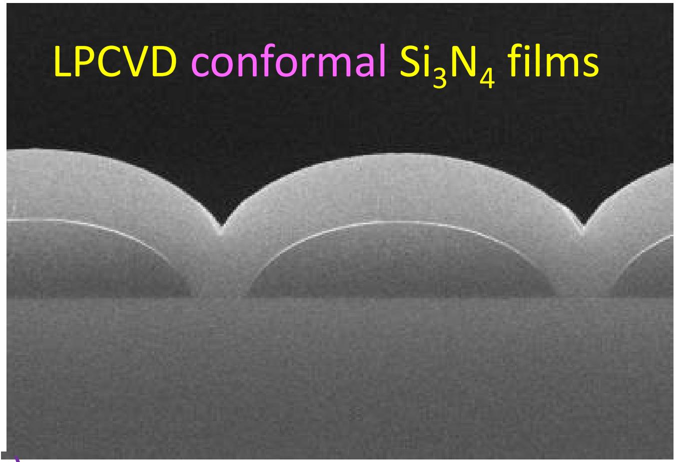
$$3SiCl_2H_2 + 4NH_3 \xrightarrow{650\text{–}800°C} Si_3N_4 + 6HCl + 6H_2$$

- Can also deposit nitride using silane at 700-900°C by APCVD; or use N_2 gas instead of NH_3.



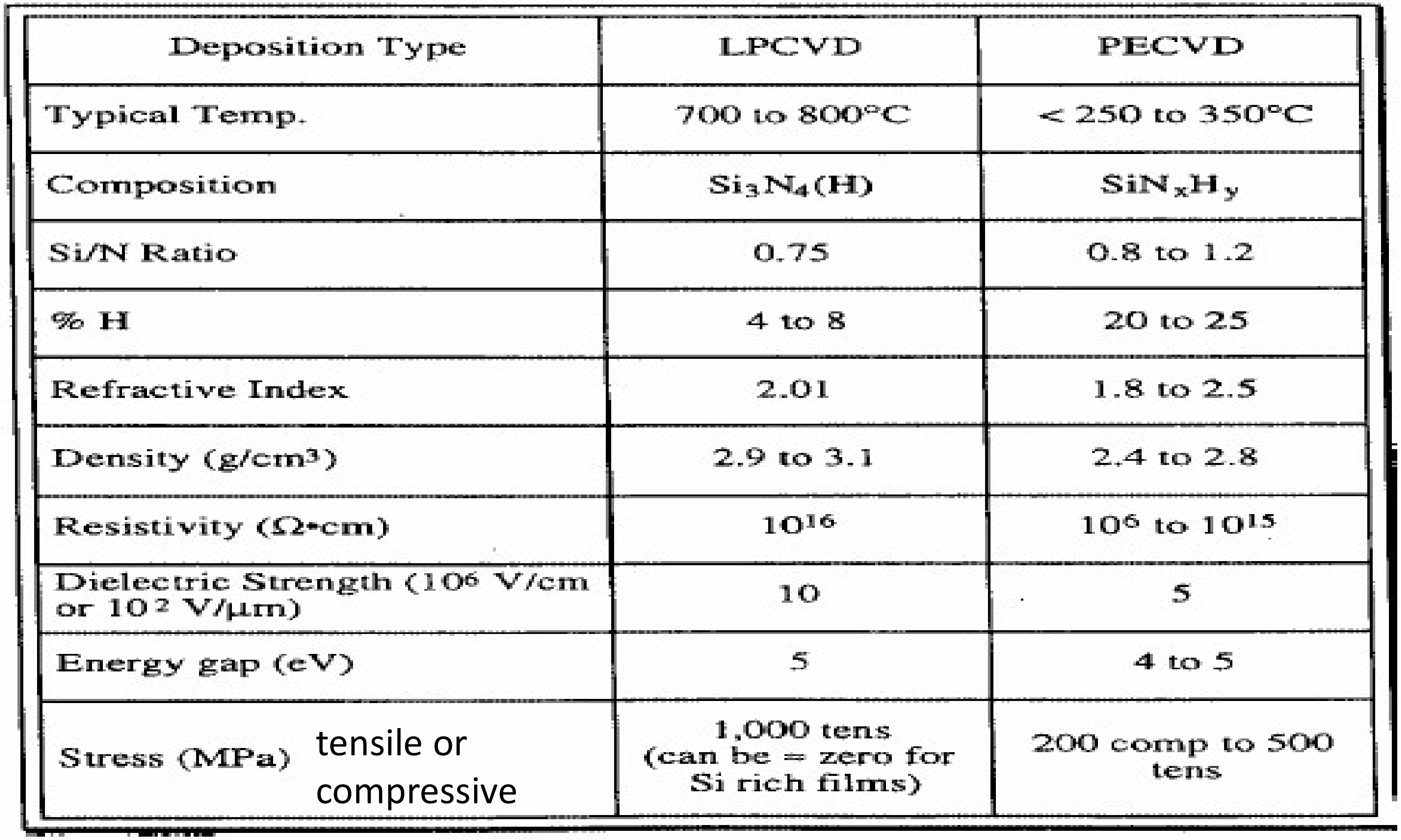
Program	SIN5.5	LSN8:1	LS850 3.9:1	LS900 1.6:1
Time	03:00:00	03:00:00	00:30:00	00:30:00
Temp	785C	785C	850C	900C
DCS Flow	164.9sccm	172.6sccm	138sccm	110.7sccm
NH3 Flow	30.0sccm	21.6sccm	37sccm	73.3sccm
Lo NH3 Flow	0	0	0	0
Process Pressure	454.2mT	455.7mT	436.1mT	-
Thickness	6032-6106A	5714-5754A	2522-3303A	4575-6048A
Refractive Index	2.159-2.164	2.229-2.236	2.070-2.189	1.843-2.078
Stress	593-573Mpa	223-236Mpa	214-259MPa	536-450MPa
Bubbles	No	Yes		
KOH Etch	-	-	-	-
HF Etch	-	-	-	-

Low-stress nitride deposition using DCS (dichloro-silane $SiCl_2H_2$)



LPCVD conformal Si_3N_4 films

Silicon nitride properties



Deposition Type	LPCVD	PECVD
Typical Temp.	700 to 800°C	< 250 to 350°C
Composition	$Si_3N_4(H)$	SiN_xH_y
Si/N Ratio	0.75	0.8 to 1.2
% H	4 to 8	20 to 25
Refractive Index	2.01	1.8 to 2.5
Density (g/cm³)	2.9 to 3.1	2.4 to 2.8
Resistivity (Ω•cm)	10^{16}	10^6 to 10^{15}
Dielectric Strength (10^6 V/cm or 10^2 V/μm)	10	5
Energy gap (eV)	5	4 to 5
Stress (MPa) tensile or compressive	1,000 tens (can be = zero for Si rich films)	200 comp to 500 tens

LPCVD film quality is much better than PECVD in almost every aspect.