INTRODUCTION TO THIN FILMS LABORATORY

BY

DR. EMAN A. GAML

LECTURER OF EXPERIMENTAL PHYSICS

WHAT ARE THIN FILMS?

- A THIN FILM IS A LAYER OF MATERIAL ITS THICKNESS RANGING FROM FRACTIONS OF A NANOMETER (MONOLAYER) TO SEVERAL MICROMETERS IN THICKNESS.

METHODS OF FABRICATING THIN FILMS

- THERMAL EVAPORATION TECHNIQUE
- PHYSICAL VAPOR DEPOSITION
- CHEMICAL VAPOR DEPOSITION
- ELECTRODEPOSITION
- LANGMUIR-BLODGETT
- SOL-GEL METHOD
- SPUTTERING

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:

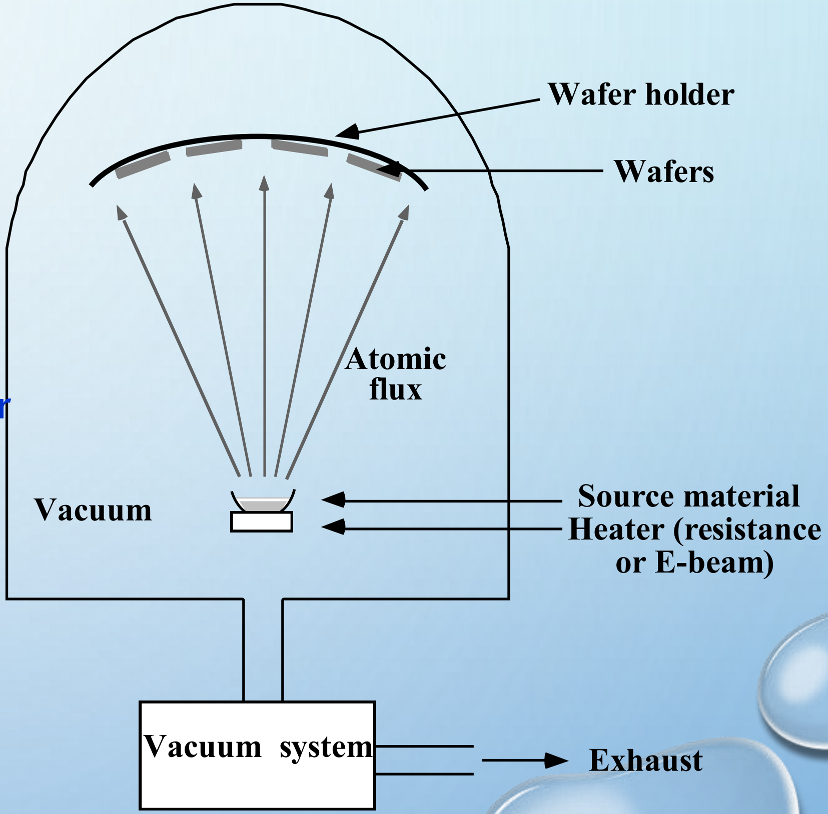
- Material source is heated to high temperature in vacuum either by thermal or e-beam methods.
- Material is vapor transported to target in vacuum.
- Film quality is often not as good as sputtered film (that involves energetic bombardment of ions to the as-deposited film, which makes the film denser).
- 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 (>1µm/min possible, but film quality may suffer. For R&D typical 0.1-1nm/sec).
- 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.

Evaporation: vacuum pressure and mean free path

Assume a particle of diameter σ, moving in speed v.

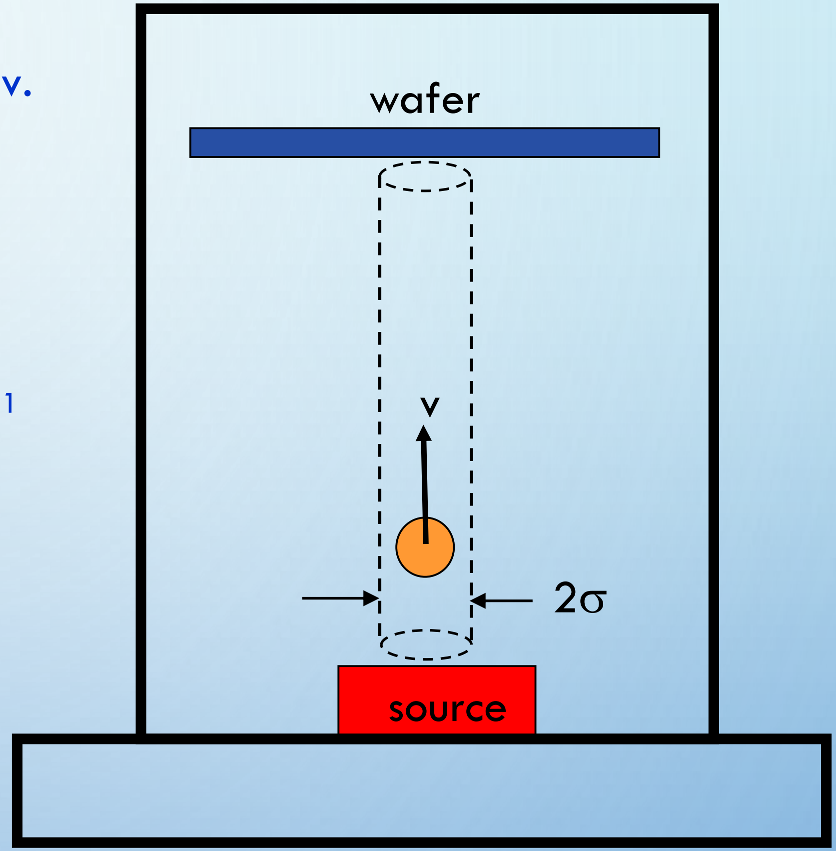
Collision cross-section = $\pi\sigma^2$

Collision volume swept during dt = $\pi\sigma^2$ vdt

# of collisions during dt = $(n/V)\,\pi\sigma^2$ vdt

Here n/V is number density.

Average mean free path λ = vdt/# = $[(n/V)\,\pi\sigma^2]^{-1}$



In more rigorous treatment, (PV=nkT)

$$\lambda = \left(\frac{n}{V}\pi\sigma^2\sqrt{2}\right)^{-1} = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

Assume σ = 3Å, T= 300K

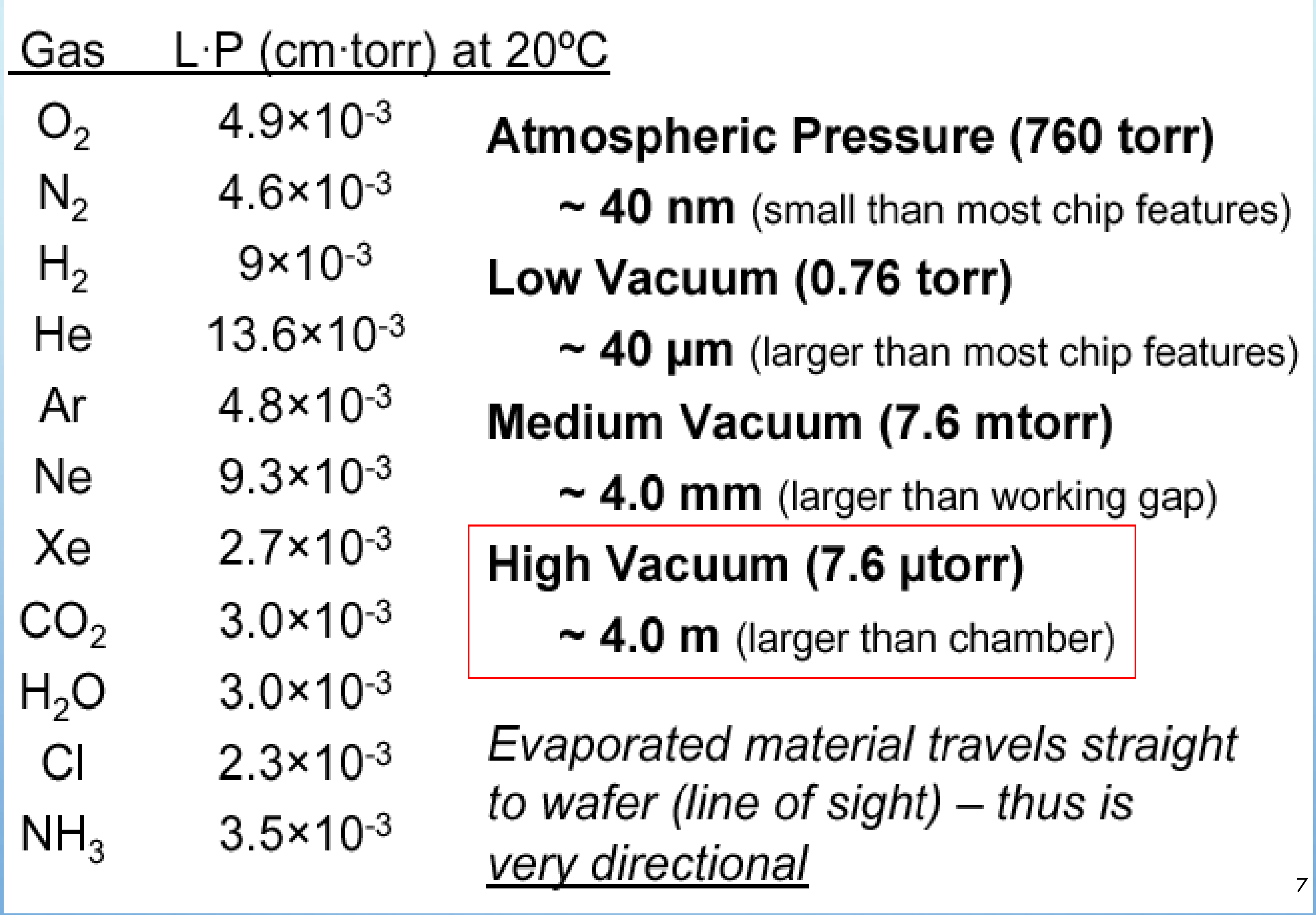
$$\boxed{P(\text{Torr}) \times \lambda(\text{cm}) = 7.8\text{x}10^{-3}}$$

1Torr = 1mmHg = 1/760atm

If λ=30 cm, then a pressure <$2.6\text{x}10^{-4}$ Torr is required.

Typical vacuum for evaporation <5×10^{-6}Torr

Mean-free path of varied gases



Gas	L·P (cm·torr) at 20°C
O_2	4.9×10^{-3}
N_2	4.6×10^{-3}
H_2	9×10^{-3}
He	13.6×10^{-3}
Ar	4.8×10^{-3}
Ne	9.3×10^{-3}
Xe	2.7×10^{-3}
CO_2	3.0×10^{-3}
H_2O	3.0×10^{-3}
Cl	2.3×10^{-3}
NH_3	3.5×10^{-3}

Atmospheric Pressure (760 torr)

~ 40 nm (small than most chip features)

Low Vacuum (0.76 torr)

~ 40 µm (larger than most chip features)

Medium Vacuum (7.6 mtorr)

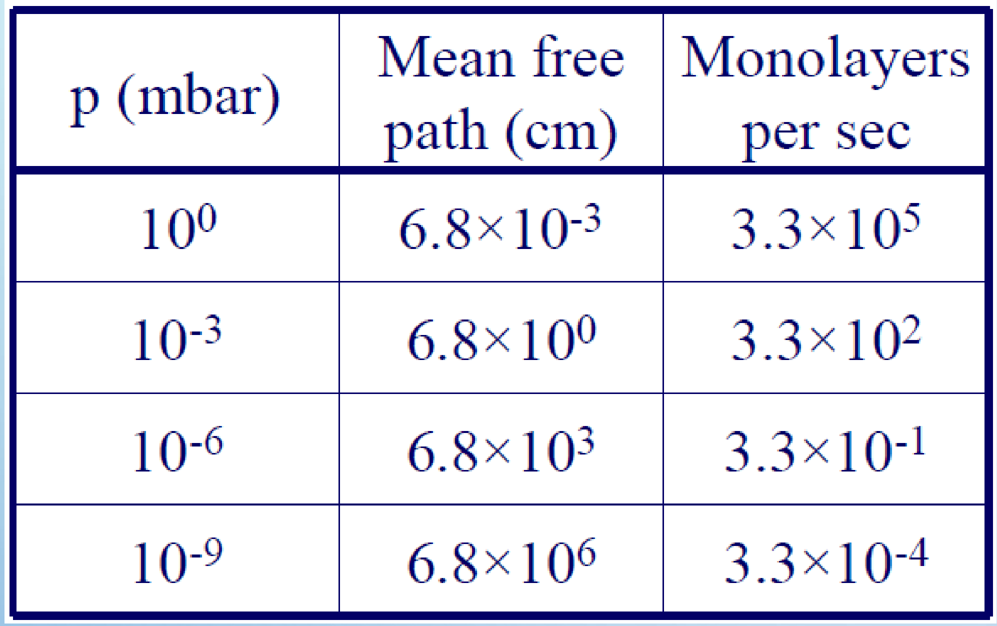
~ 4.0 mm (larger than working gap)

High Vacuum (7.6 µtorr)

~ 4.0 m (larger than chamber)

Evaporated material travels straight to wafer (line of sight) – thus is very directional

Influence of background vacuum pressure



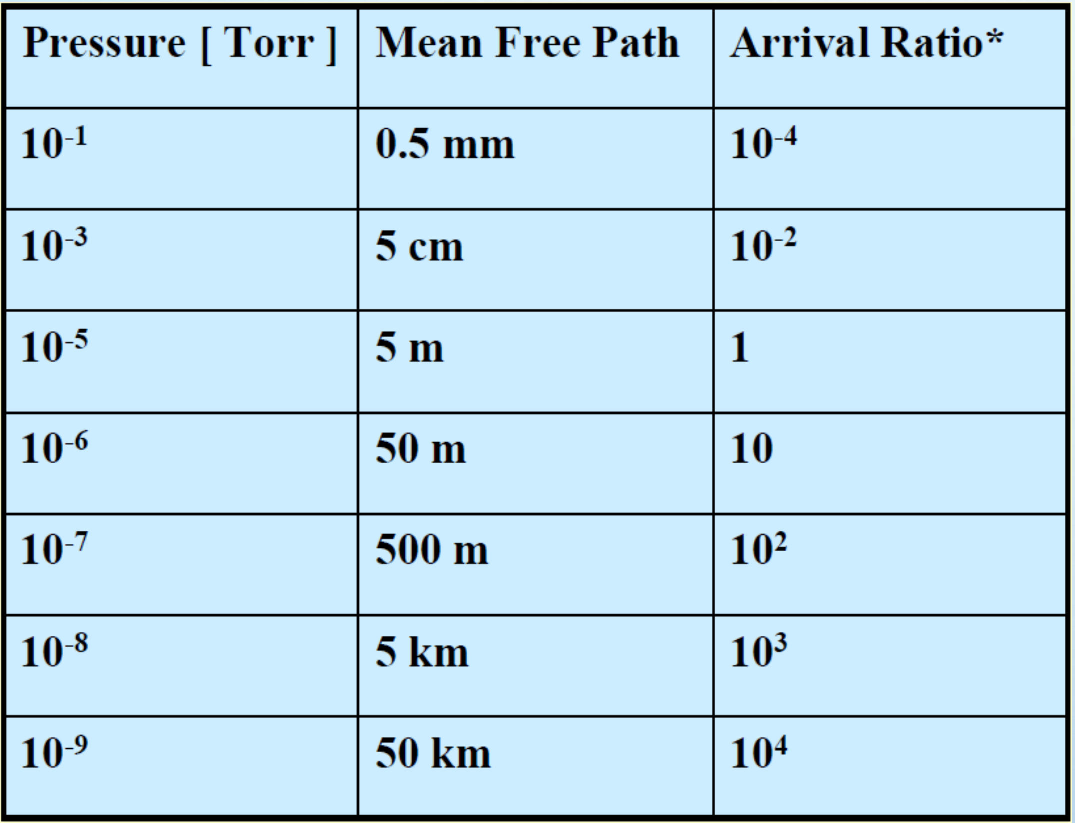
p (mbar)	Mean free path (cm)	Monolayers per sec
10^{0}	6.8×10^{-3}	3.3×10^{5}
10^{-3}	6.8×10^{0}	3.3×10^{2}
10^{-6}	6.8×10^{3}	3.3×10^{-1}
10^{-9}	6.8×10^{6}	3.3×10^{-4}

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

Arrival ratio



Pressure [Torr]	Mean Free Path	Arrival Ratio*
10^{-1}	0.5 mm	10^{-4}
10^{-3}	5 cm	10^{-2}
10^{-5}	5 m	1
10^{-6}	50 m	10
10^{-7}	500 m	10^{2}
10^{-8}	5 km	10^{3}
10^{-9}	50 km	10^{4}

Arrival ratio:
Ratio of molecular vapor arrival at 1nm/sec deposition rate to molecular impact of residual gas.

Arrival ratio = 1 means the number of film molecules hitting the surface per second is the same as the number of gas molecules.

For materials that is very reactive with the gas (such as Ti to O_2), the film can be very impure when arrival ration ~1.

In fact, Ti is used as a pump for ultrahigh vacuum (called Ti pump, where Ti vapor is produced to trap gas in vacuum chamber).

Evaporation characteristics of materials

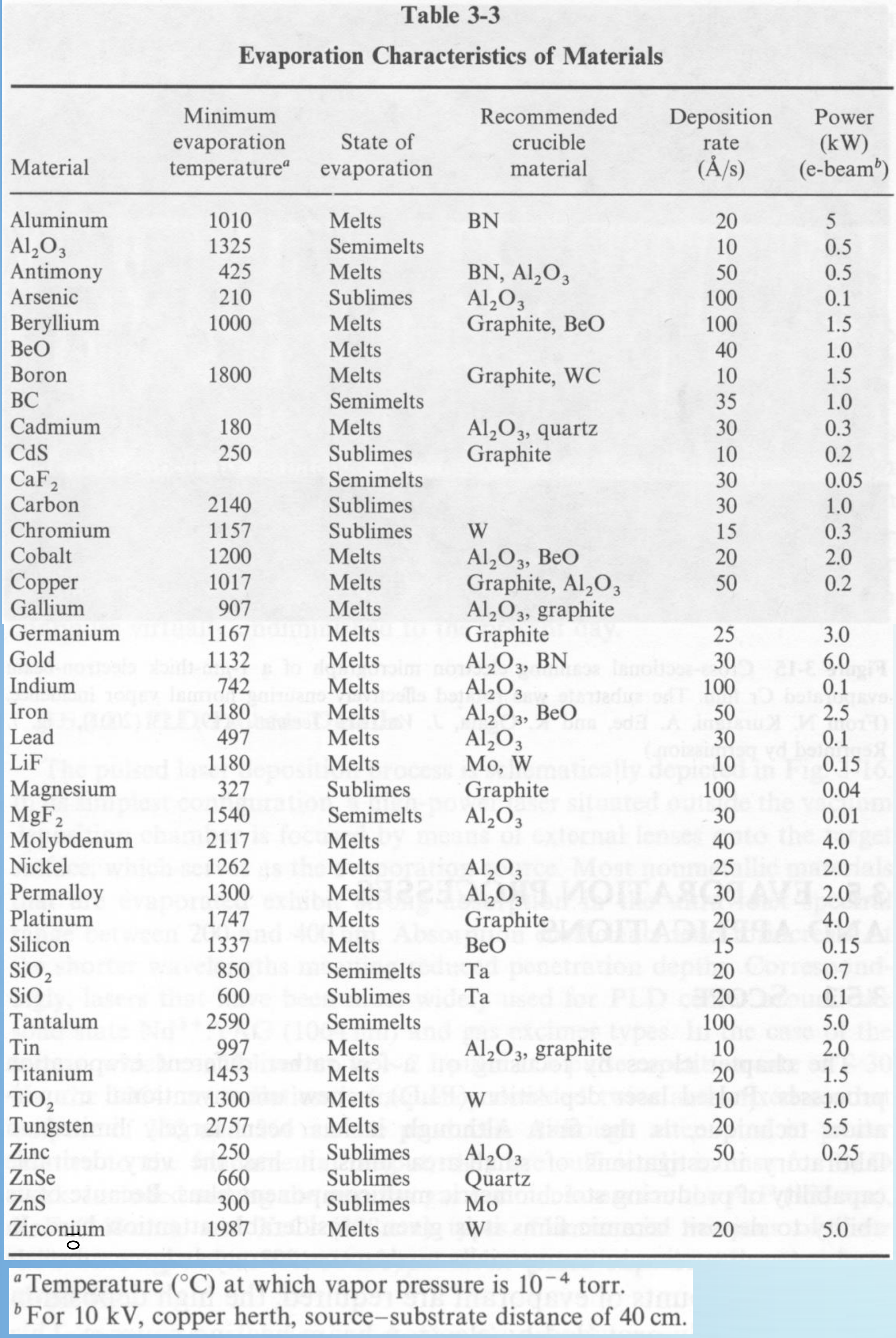


Table 3-3

Evaporation Characteristics of Materials

Material	Minimum evaporation temperature[a]	State of evaporation	Recommended crucible material	Deposition rate (Å/s)	Power (kW) (e-beam[b])
Aluminum	1010	Melts	BN	20	5
Al_2O_3	1325	Semimelts		10	0.5
Antimony	425	Melts	BN, Al_2O_3	50	0.5
Arsenic	210	Sublimes	Al_2O_3	100	0.1
Beryllium	1000	Melts	Graphite, BeO	100	1.5
BeO		Melts		40	1.0
Boron	1800	Melts	Graphite, WC	10	1.5
BC		Semimelts		35	1.0
Cadmium	180	Melts	Al_2O_3, quartz	30	0.3
CdS	250	Sublimes	Graphite	10	0.2
CaF_2		Semimelts		30	0.05
Carbon	2140	Sublimes		30	1.0
Chromium	1157	Sublimes	W	15	0.3
Cobalt	1200	Melts	Al_2O_3, BeO	20	2.0
Copper	1017	Melts	Graphite, Al_2O_3	50	0.2
Gallium	907	Melts	Al_2O_3, graphite		
Germanium	1167	Melts	Graphite	25	3.0
Gold	1132	Melts	Al_2O_3, BN	30	6.0
Indium	742	Melts	Al_2O_3	100	0.1
Iron	1180	Melts	Al_2O_3, BeO	50	2.5
Lead	497	Melts	Al_2O_3	30	0.1
LiF	1180	Melts	Mo, W	10	0.15
Magnesium	327	Sublimes	Graphite	100	0.04
MgF_2	1540	Semimelts	Al_2O_3	30	0.01
Molybdenum	2117	Melts		40	4.0
Nickel	1262	Melts	Al_2O_3	25	2.0
Permalloy	1300	Melts	Al_2O_3	30	2.0
Platinum	1747	Melts	Graphite	20	4.0
Silicon	1337	Melts	BeO	15	0.15
SiO_2	850	Semimelts	Ta	20	0.7
SiO	600	Sublimes	Ta	20	0.1
Tantalum	2590	Semimelts		100	5.0
Tin	997	Melts	Al_2O_3, graphite	10	2.0
Titanium	1453	Melts		20	1.5
TiO_2	1300	Melts	W	10	1.0
Tungsten	2757	Melts		20	5.5
Zinc	250	Sublimes	Al_2O_3	50	0.25
ZnSe	660	Sublimes	Quartz		
ZnS	300	Sublimes	Mo		
Zirconium	1987	Melts	W	20	5.0

---

[a] Temperature (°C) at which vapor pressure is 10^{-4} torr.

[b] For 10 kV, copper herth, source–substrate distance of 40 cm.

. From “Materials science of thin films” by Ohring, 2002.

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).

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.

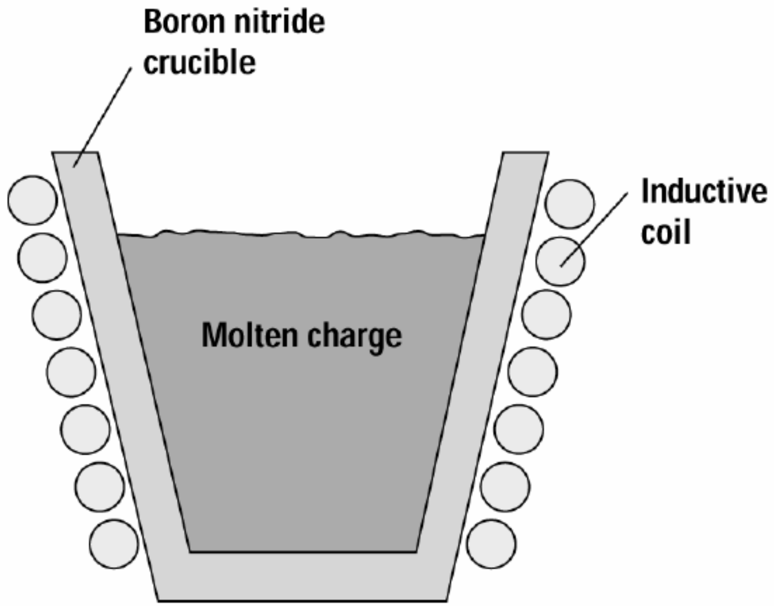
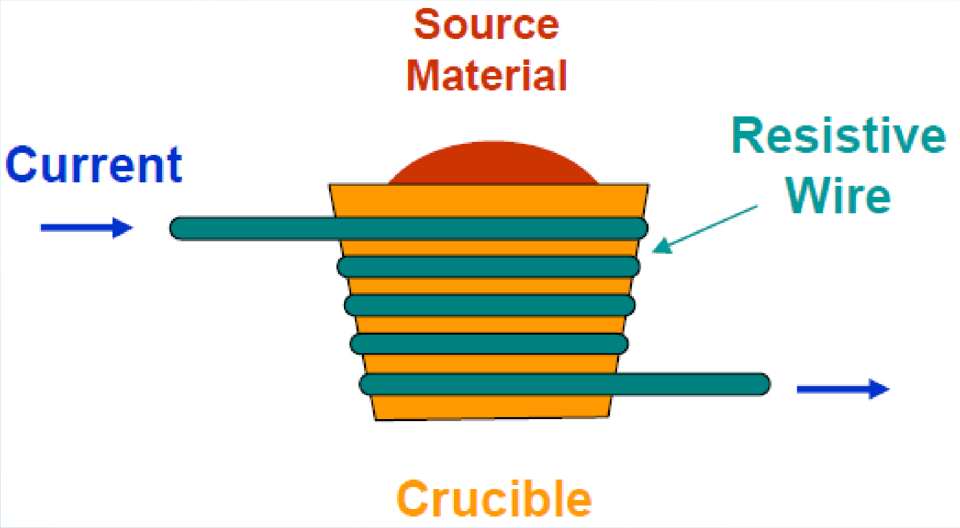


Figure 12.7 Example of an inductively heated crucible used to create moderately charged temperatures.

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, $PbCl_2$.

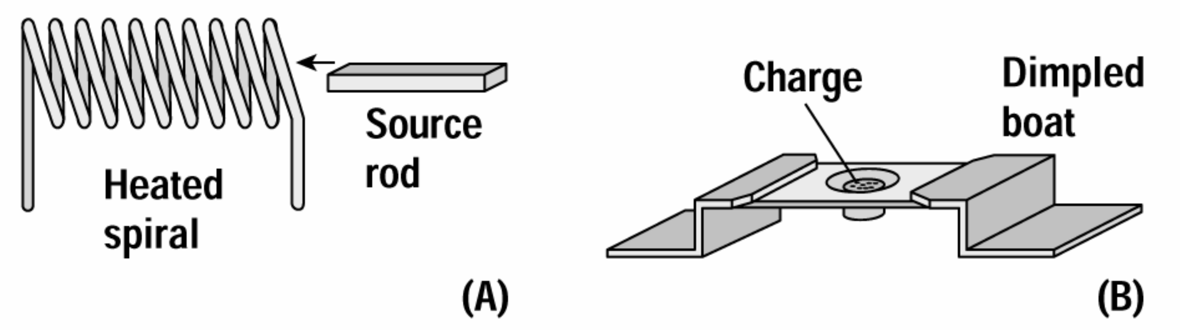
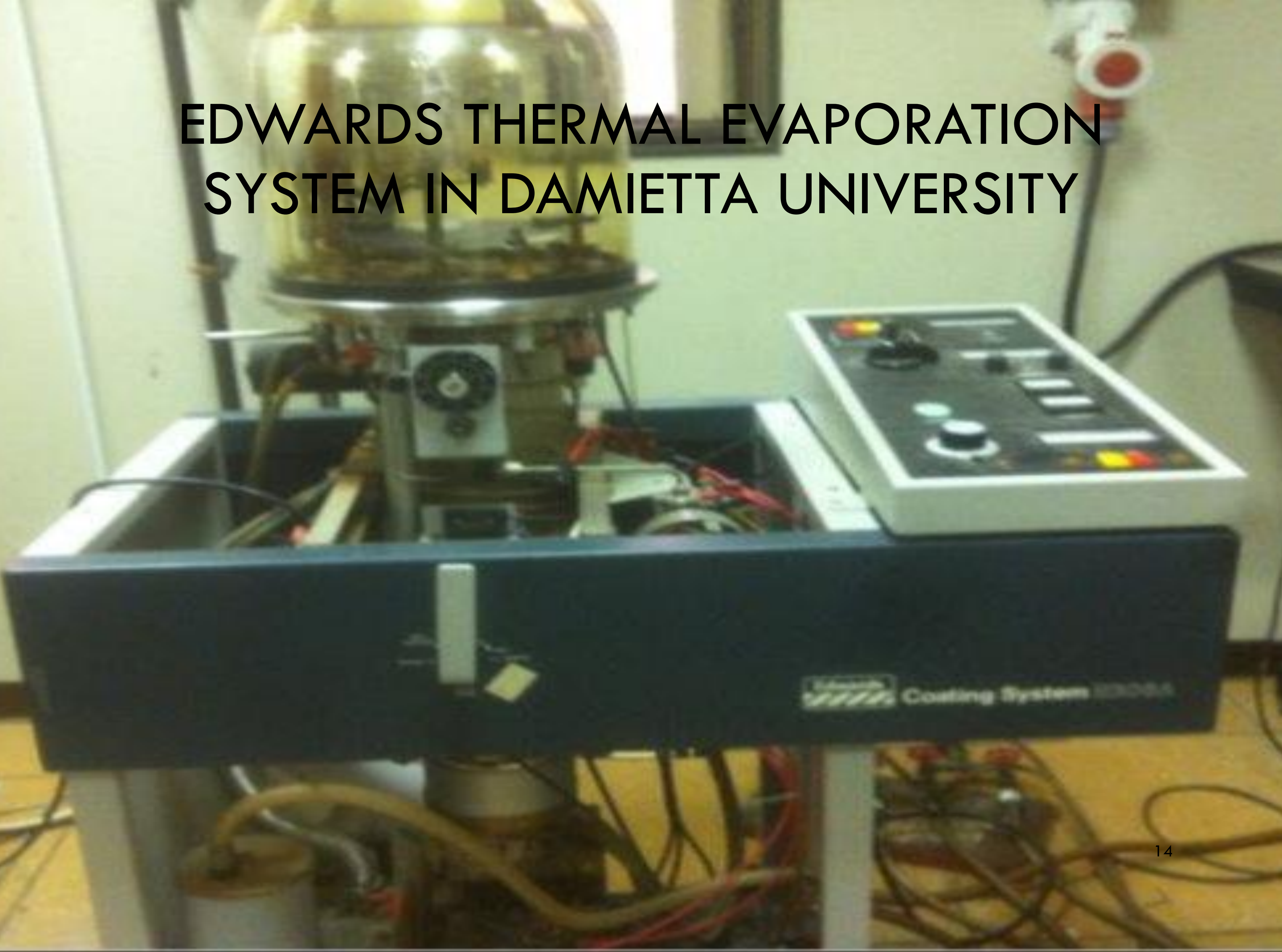
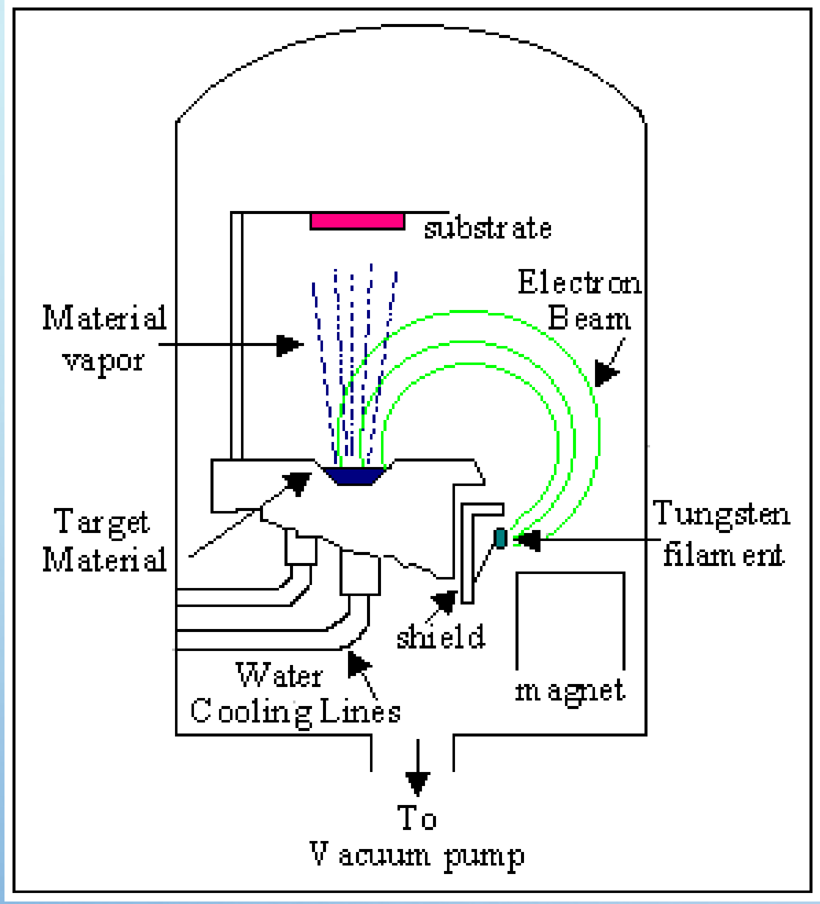


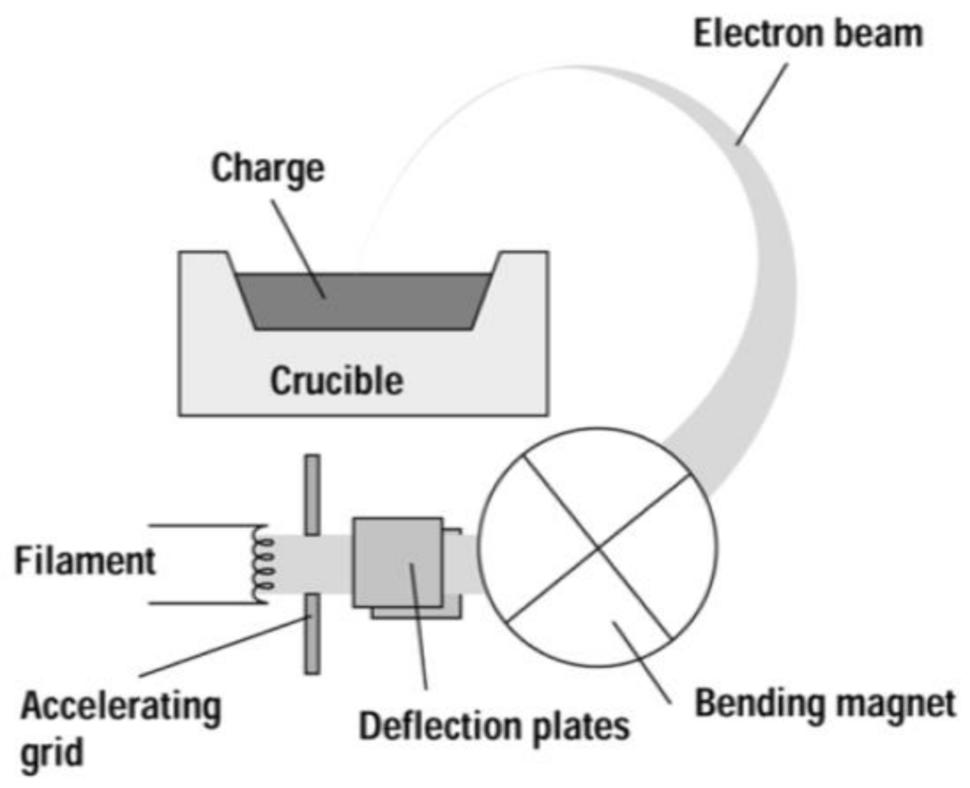
Figure 12.6 Resistive evaporator sources. (A) Simple sources including heating the charge itself and using a coil of refractory metal heater coil and a charge rod. (B) More standard thermal sources including a dimpled boat in a resistive media.

EDWARDS THERMAL EVAPORATION SYSTEM IN DAMIETTA UNIVERSITY



Electron beam evaporation



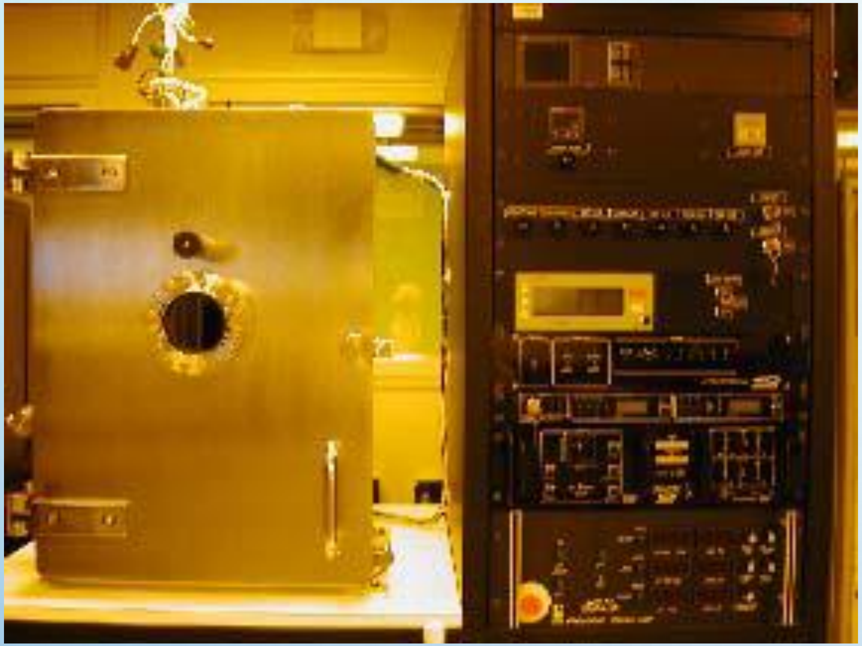


Deflection plates are to raster scan the beam across charge surface.

- 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

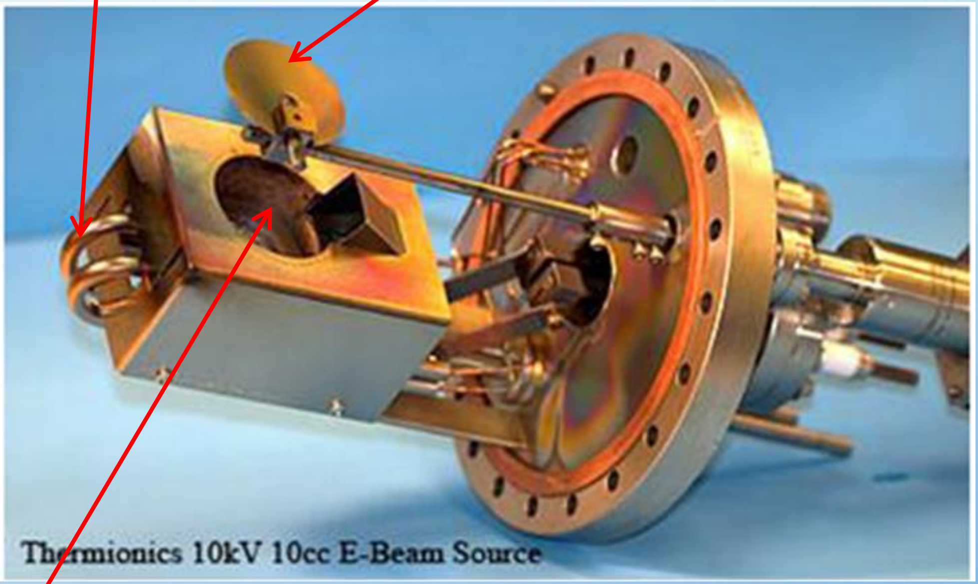


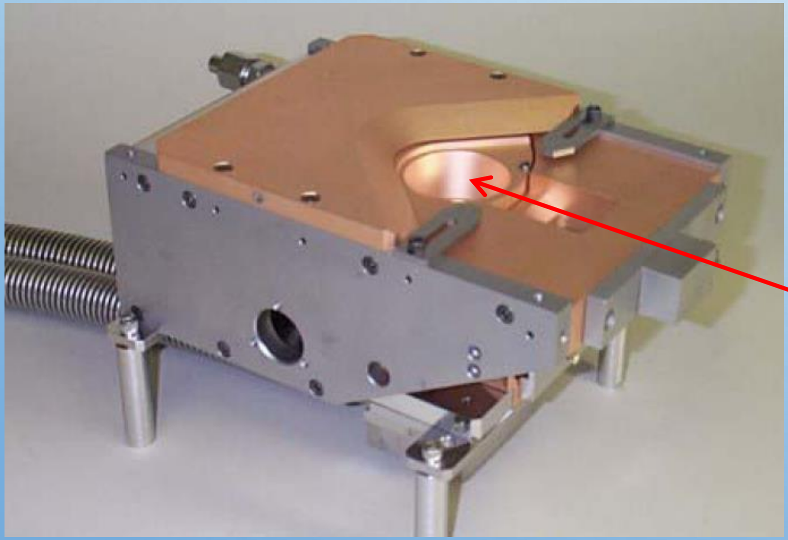
Mechanical shutter:

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, $0.2\text{-}1\,\mathrm{cm}^2 \rightarrow 15\text{-}75\,\mathrm{kW/cm}^2$.

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 °C	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 °C	High

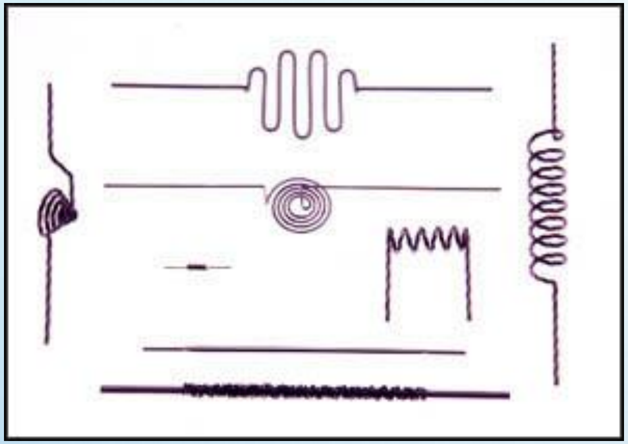
Thermal evaporation:

- 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.

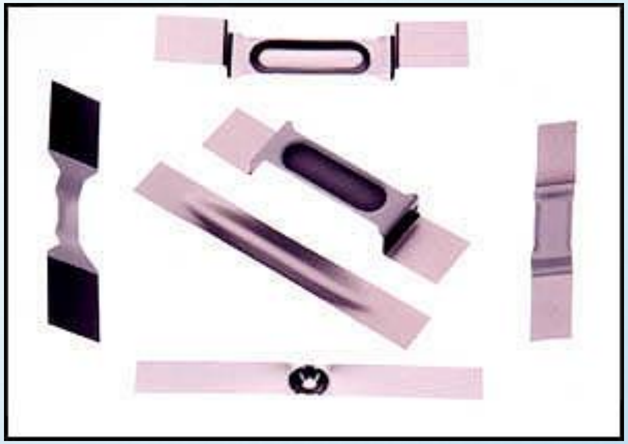
Electron beam evaporation:

- 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



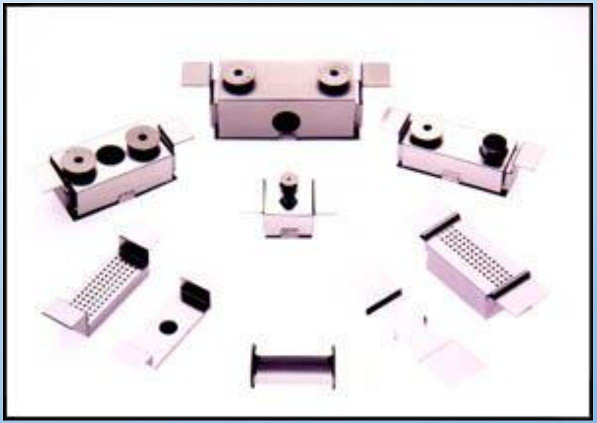
Resistors (put source rod inside coil)



Heating boat (open top)

Crucibles

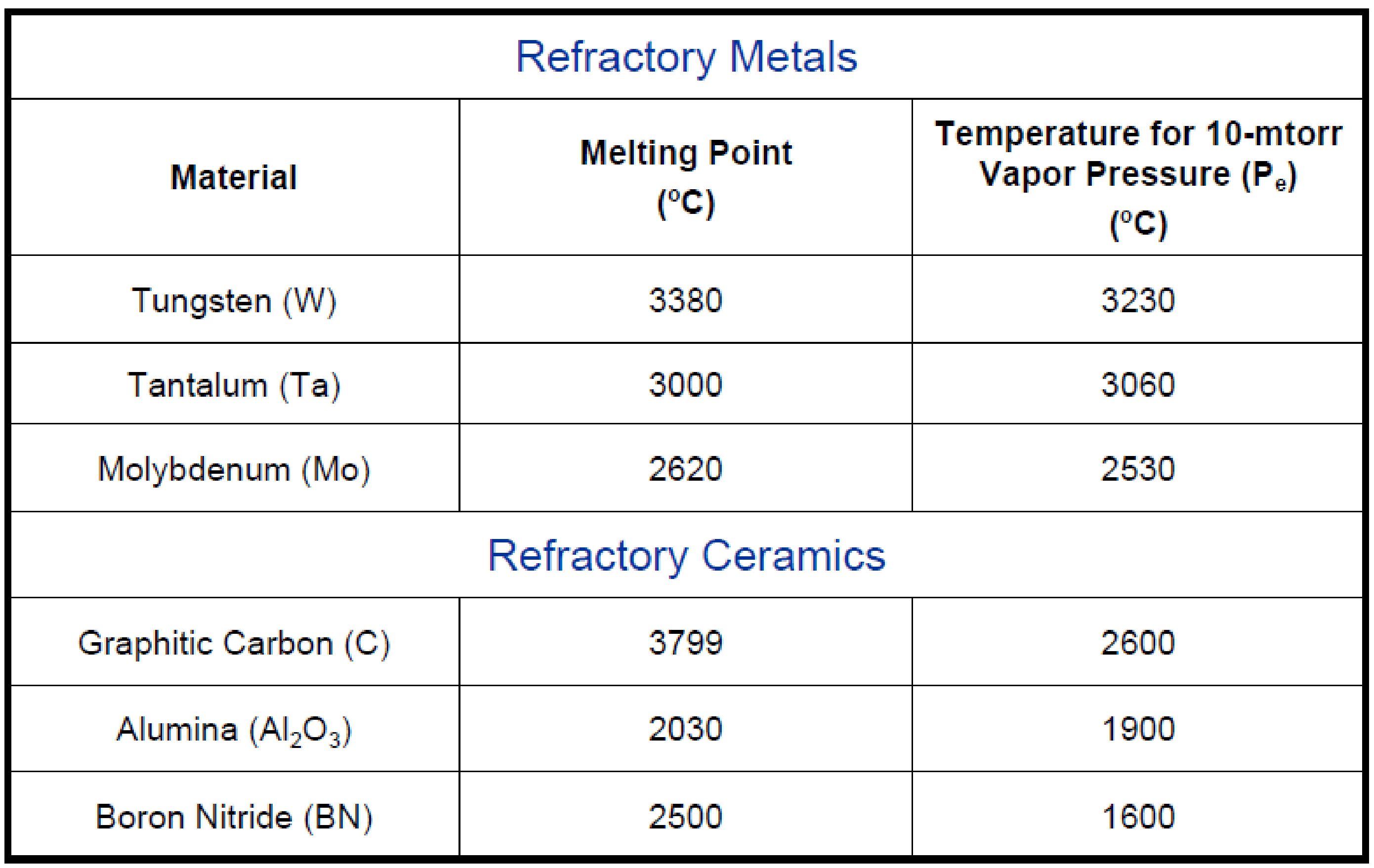
(only choice for e-beam evaporator)



Box with small opening

(Knudsen cell!)

Typical boat/crucible material



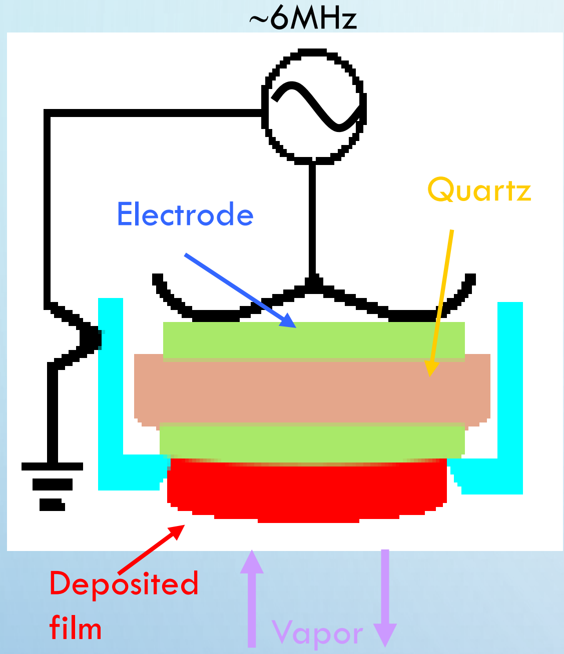
Refractory Metals		
Material	**Melting Point (°C)**	**Temperature for 10-mtorr Vapor Pressure (P_e) (°C)**
Tungsten (W)	3380	3230
Tantalum (Ta)	3000	3060
Molybdenum (Mo)	2620	2530
Refractory Ceramics		
Graphitic Carbon (C)	3799	2600
Alumina (Al_2O_3)	2030	1900
Boron Nitride (BN)	2500	1600

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.

http://en.wikipedia.org/wiki/Quartz_crystal_microbalance

SPUTTERING

- SPUTTERING OCCURS WHEN THE ION IMPACT ESTABLISHES A TRAIN OF COLLISION EVENTS IN THE TARGET LEADING TO THE EJECTION OF A MATRIX ATOM.

TYPES OF SPUTTERING:

- DC SPUTTERING
- RF SPUTTERING
- REACTIVE SPUTTERING
- MAGNETRON SPUTTERING
- BIAS SPUTTERING

SOL-GEL METHOD

- ”FORMATION OF AN OXIDE NETWORK THROUGH POLYCONDENSATION REACTIONS OF A MOLECULAR PRECURSOR IN A LIQUID.”
- A SOL (SOLUTION) IS A STABLE DISPERSION OF COLLOIDAL PARTICLES OR POLYMERS IN A SOLVENT. THE PARTICLES MAY BE AMORPHOUS OR CRYSTALLINE. AN AEROSOL IS PARTICLES IN A GAS PHASE, WHILE A SOL IS PARTICLES IN A LIQUID,
- A GEL CONSISTS OF A THREE DIMENSIONAL CONTINUOUS NETWORK, WHICH ENCLOSES A LIQUID PHASE, IN A COLLOIDAL GEL, THE NETWORK IS BUILT FROM AGGLOMERATION OF COLLOIDAL PARTICLES. IN A POLYMER GEL THE PARTICLES HAVE A POLYMERIC SUB-STRUCTURE MADE BY AGGREGATES OF SUB-COLLOIDAL PARTICLES. GENERALLY, THE SOL PARTICLES MAY INTERACT BY VAN DER WAALS FORCES OR HYDROGEN BONDS. A GEL MAY ALSO BE FORMED FROM LINKING POLYMER CHAINS. IN MOST GEL SYSTEMS USED FOR MATERIALS SYNTHESIS, THE INTERACTIONS ARE OF A COVALENT NATURE AND THE GEL PROCESS IS IRREVERSIBLE. THE GELATION PROCESS MAY BE REVERSIBLE IF OTHER INTERACTIONS ARE INVOLVED.
- •THE IDEA BEHIND SOL-GEL SYNTHESIS IS TO “DISSOLVE” THE COMPOUND IN A LIQUID IN ORDER TO BRING IT BACK AS A SOLID IN A CONTROLLED MANNER.
- •MULTI COMPONENT COMPOUNDS MAY BE PREPARED WITH A CONTROLLED STOICHIOMETRY BY MIXING SOLS OF DIFFERENT COMPOUNDS.
- •THE SOL-GEL METHOD PREVENTS THE PROBLEMS WITH CO-PRECIPITATION, WHICH MAY BE INHOMOGENEOUS, BE A GELATION REACTION.
- •ENABLES MIXING AT AN ATOMIC LEVEL.
  •RESULTS IN SMALL PARTICLES, WHICH ARE EASILY SINTERABLE