

Advanced Micro and Nanofabrication Technologies

Engineering Physics – Ingegneria Fisica - Cod. 055559

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Matteo Cantoni

Dipartimento di Fisica

Politecnico di Milano and Polifab

Ed. 30 - Via G. Colombo 81 – Milano

<https://cantoni.faculty.polimi.it/>

Lecture 5

Physical Vapor Deposition (PVD)

[prof. Matteo Cantoni](#)

matteo.cantoni@polimi.it



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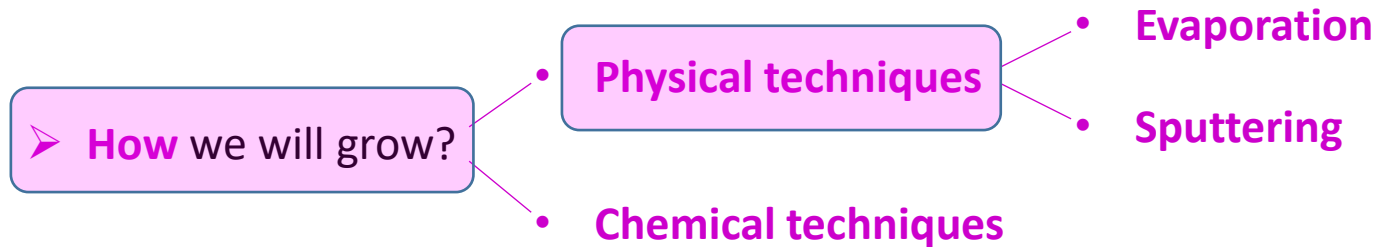


Outline of the course

➤ **Where** we will grow? **Vacuum** ➡ **Vacuum technology: pressure, gas transport, vacuum systems**

➤ **On what** we will grow? **Surfaces** ➡ **Surface properties, nucleation, film growth modes**

➤ **Which kind** of films we will grow? **Epitaxy** ➡ **Crystals, homo/heteroepitaxy, other modes**



➤ **How** we will check the growth? **Characterization**

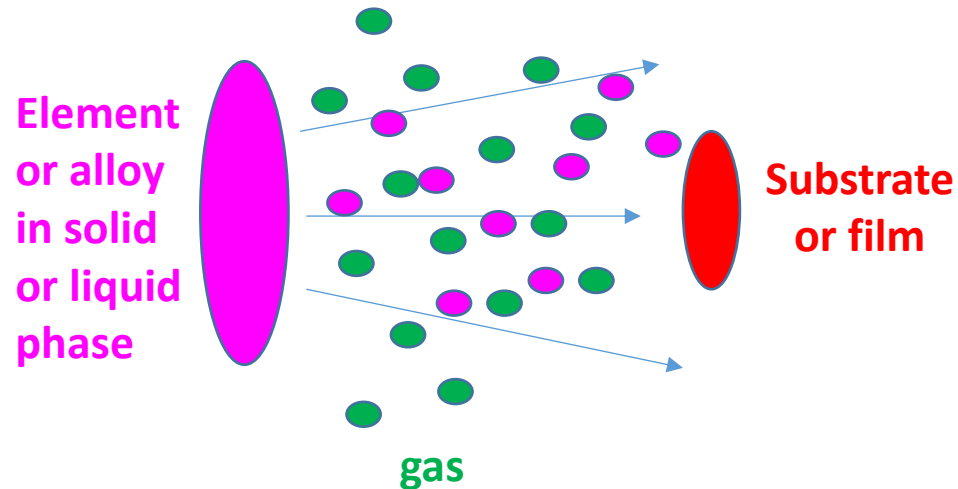
Reference for this lecture: M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3

Scope and methods

Objective of **deposition** techniques:

To controllably **transfer** atoms from a **source** to a **target**

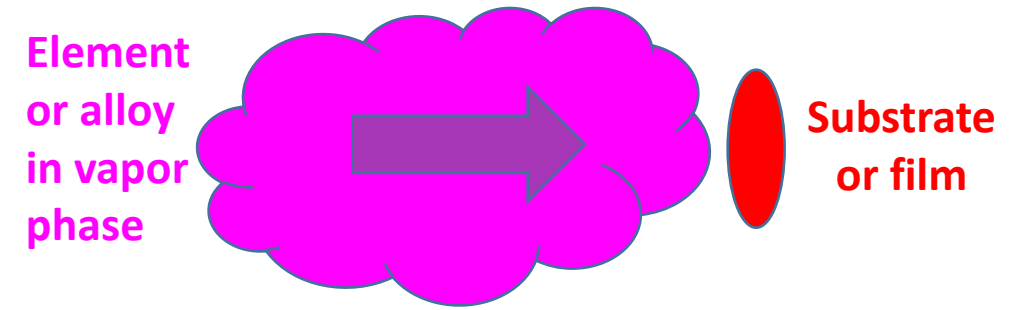
*How the material is transferred from the **source** to the **target**?*



Physically

The **source material** is **physically** transferred from a condensed phase evaporant to the **target substrate**

Physical vapor deposition (PVD)



Chemically

A **volatile** compound of the material to be deposited **chemically** reacts with other gases to produce a **nonvolatile solid** that deposits atomistically on the **target substrate**

Chemical vapor deposition (CVD)

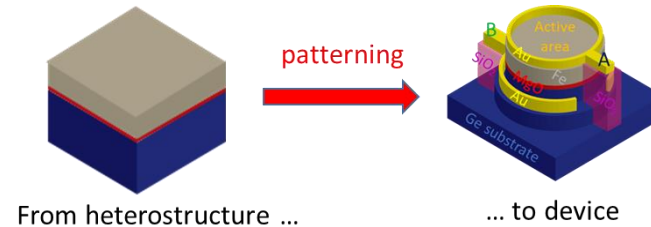
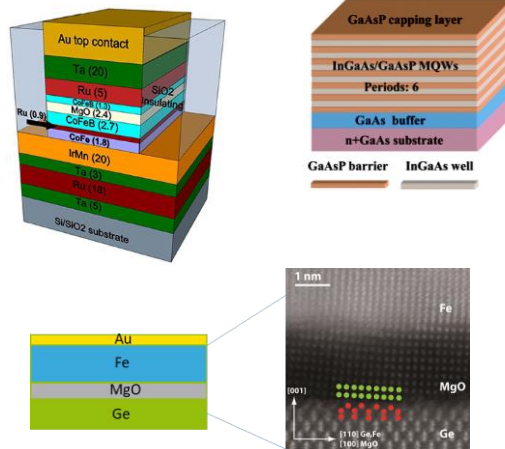
For what is used?

Objective of **deposition** techniques:

To controllably transfer atoms from a source to a target

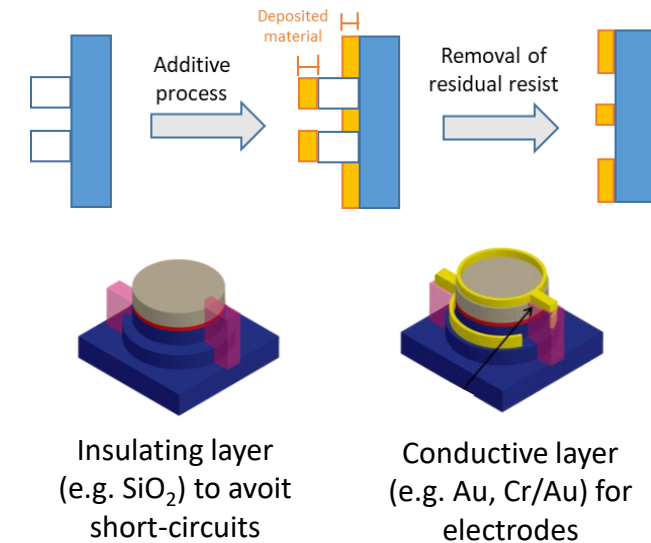
Heterostructure deposition

- High purity
- Controlled thickness
- Uniformity
- Multilayer



Device Fabrication

- Large area and/or thickness
- Purity and thickness control not crucial
 - Single or bi-layer



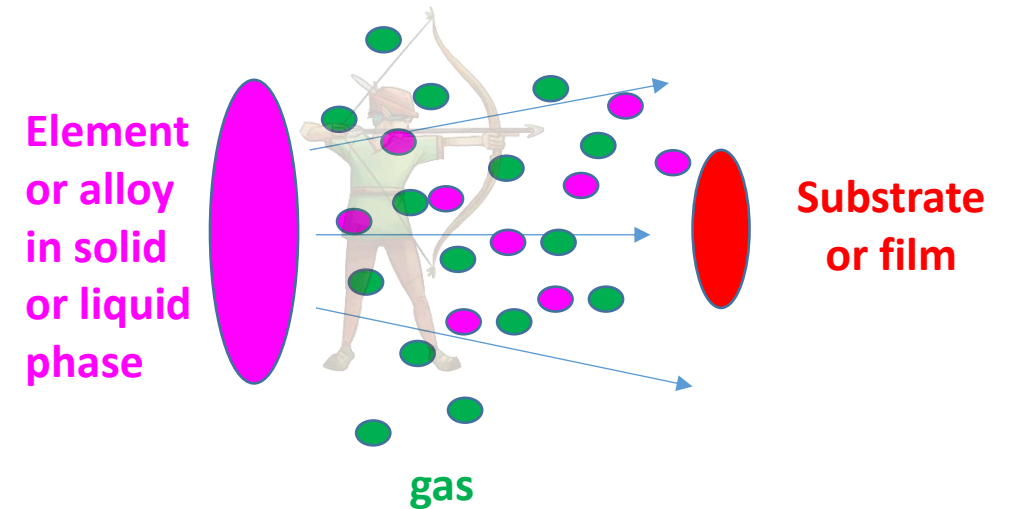
Physical vapor deposition (PVD)

*How the material is transferred from the **source** to the **target**?*

Physically

The **source material** is **physically** transferred from a condensed phase evaporant to the **target substrate**

Physical vapor deposition (PVD)



*Which is the **physical mechanism** for transferring the material from the **source** to the **target**?*

- **evaporation** caused by absorption of **thermal** energy (liquid or solid sources) → *lectures 5*

Which is the mechanism providing thermal energy to source atoms? Electrical, electron beam, pulsed laser,... → lectures 6

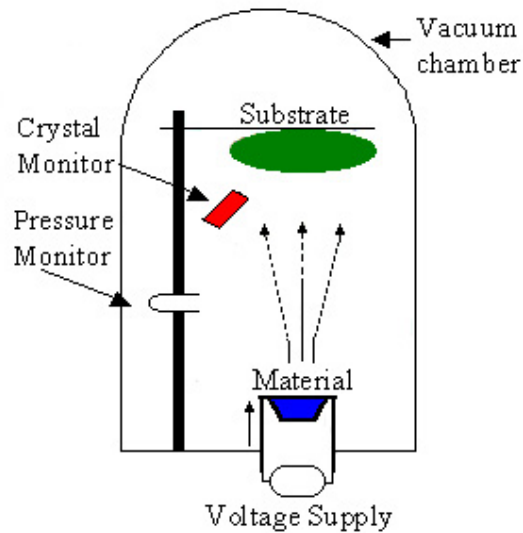
- **sputtering** by **bombarding** solid surfaces with energetic **ions** → *lecture 7*

- In all cases the emitted atoms traverse a **high vacuum region** before to deposit on the target → *lecture 2*

Thermal evaporation

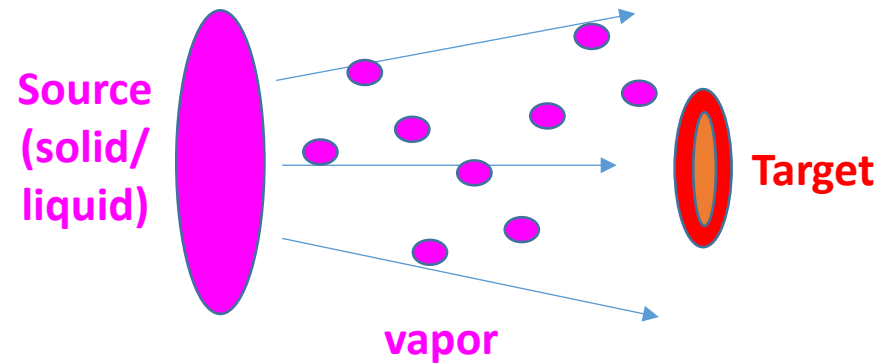
Deposition process by evaporation in vacuum

- The objective is to **controllably transfer** atoms from a **heated source** to a **target** located a distance away, where film growth proceeds **atomistically**.
- **Thermal energy** is imparted to atoms in a **liquid or solid source** which **temperature is raised up to efficiently evaporate or sublime**.



Fundamentals of evaporation

- Evaporation rate from the source \longleftrightarrow vapor pressure
- Deposition geometry \Rightarrow deposition rate on the target
 \searrow film thickness uniformity
- Film purity



Note: Evaporation rate + Deposition geometry \Rightarrow Deposition rate

Evaporation rate (1)

Hertz-Knudsen, 1882:

1. a liquid has a specific ability to evaporate at a given temperature T
2. the **evaporation rate** is *proportional* to the «net pressure» above the liquid, i.e. the difference between
 - **equilibrium pressure (vapor pressure) of the evaporant (P_e)** - at which **vapor and liquid phases are in equilibrium** and coexist
 - **hydrostatic pressure acting on it (P_h)** – from residual gases in the deposition chamber

➡ The **evaporation rate** from **liquid and solid sources** is given by $\phi_e = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MRT)^{1/2}}$

where

- ϕ_e is the evaporation flux (molecules/cm²s) – it is equivalent to the **gas impingement flux** equation $\phi = \frac{N_A P}{(2\pi MRT)^{1/2}}$, see Lecture 2
- α_e is the coefficient of evaporation (0-1) – it defines the fraction of particles that effectively evaporate with respect with those that potentially can do it.

Evaporation rate (2)

The **evaporation rate** from liquid and solid sources is given by $\phi_e = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MRT)^{1/2}}$

The maximum **evaporation rate** is attained when $\alpha_e=1$ and $P_h=0$ (high vacuum or UHV conditions): $\phi_e = \frac{N_A P_e}{(2\pi MRT)^{1/2}}$

$$\Rightarrow \phi_e (\text{molecules/cm}^2\text{s}) = 3.513 \cdot 10^{22} \frac{P_e (\text{torr})}{(MT)^{1/2}}$$

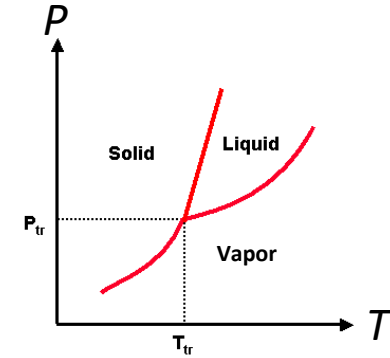
The **mass evaporation rate** instead is $\Gamma_e (\text{g/cm}^2\text{s}) = \phi_e \frac{M}{N_A} = 5.84 \cdot 10^{-2} \left(\frac{M}{T}\right)^{1/2} P_e (\text{torr})$

Note: the evaporation rate **strongly depends on the temperature T** , both through the $T^{-1/2}$ dependence and because T **strongly influences the equilibrium pressure P_e**

Vapor pressure (1)

Clausius-Clapeyron equation for solid-vapor and liquid-vapor equilibria: $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$

- ΔH and ΔV refer to the difference between the **vapor** and the **condensed (solid or liquid)** phases, whereas T is the transition temperature (the two phases are in equilibrium and coexist)
- $\Delta V = V_{\text{vapor}} - V_{\text{condensed}} \approx V_{\text{vapor}}$ because typically $V_{\text{vapor}} \gg V_{\text{condensed}}$
- Considering the vapor as a perfect gas, we have $V_{\text{vapor}} = RT/P$ (for 1 mol)
- In general $\Delta H = \Delta H(T)$, but as a first approximation we assume $\Delta H = \Delta H_e$, the molar heat of evaporation

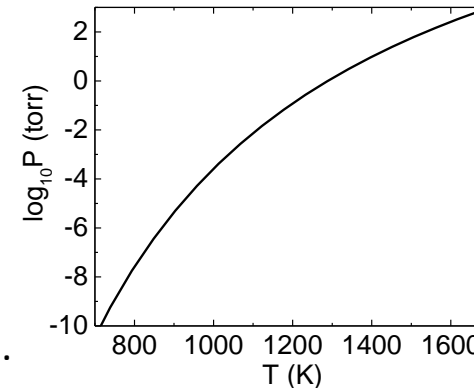


$$\Rightarrow \frac{dP}{dT} = \frac{P\Delta H_e}{RT^2}$$

$$\Rightarrow \frac{dP}{P} = \frac{\Delta H_e}{R} \frac{dT}{T^2} \Rightarrow \ln \frac{P}{P_0} = -\frac{\Delta H_e}{RT} \Rightarrow \ln P = -\frac{\Delta H_e}{RT} + \ln P_0$$

$$P(T) = P_0 \exp\left(-\frac{\Delta H_e}{RT}\right)$$

- P_0 is a constant that can be determined using the boiling point:
 $\Delta H_e = \Delta H_v$ (the latent heat of vaporization), T =boiling temperature, P =1 atm.



$P(T)$ is the **vapor pressure** at temperature T , i.e., the pressure at which **vapor and solid/liquid phases are in equilibrium and coexist**

Note: this equation (**Arrhenius-type law**) holds for small temperature ranges, otherwise the $\Delta H(T)$ dependence must be considered. E.g., for the vapor pressure of liquid a better approximation is

$$\log P \text{ (torr)} = -15.993/T + 12.409 - 0.999 \log T - 3.52 \cdot 10^{-6} T$$

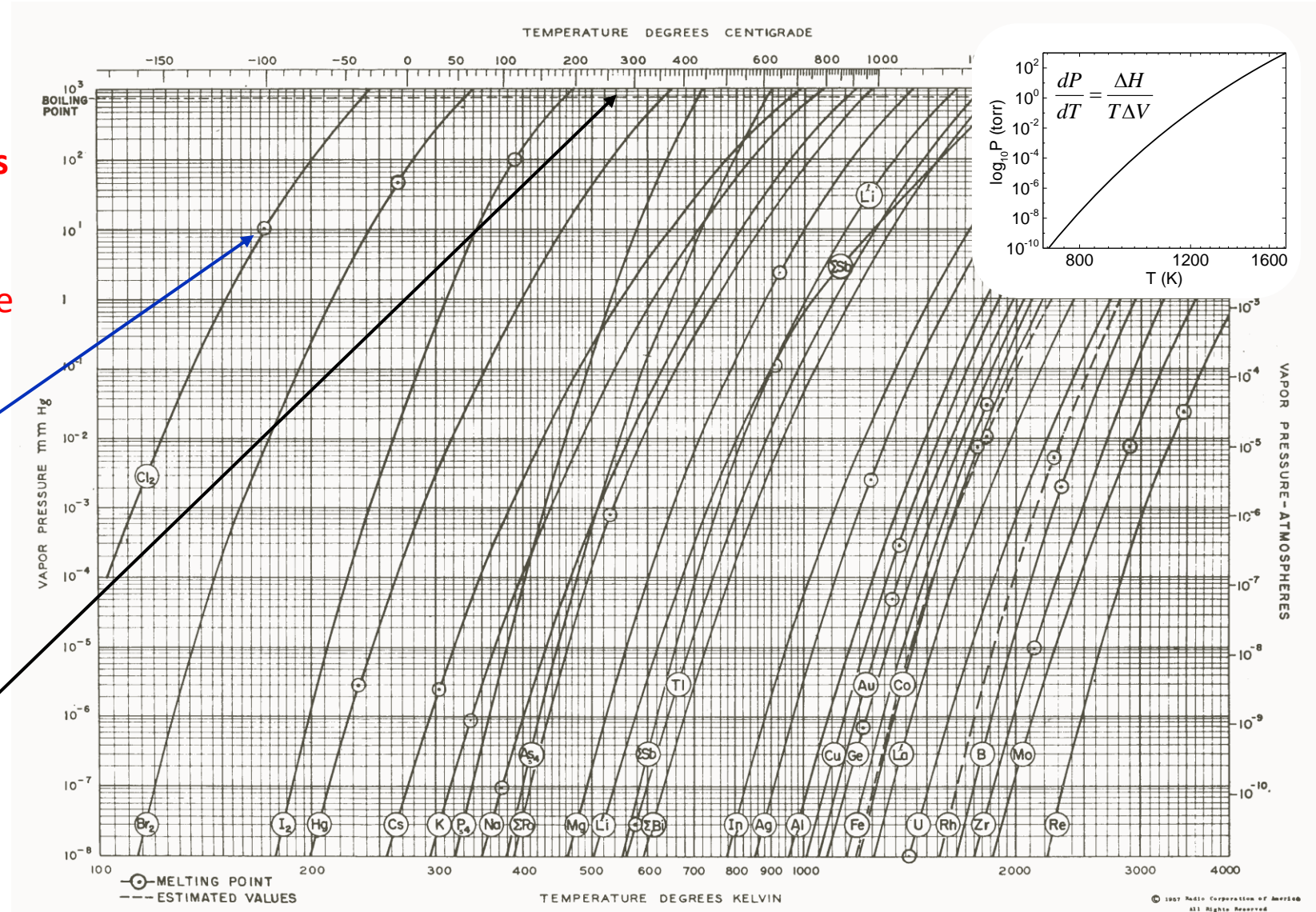
Vapor pressure (2)

➤ **Experimental vapor pressures** (the pressure at which vapor and solid/liquid phases are in equilibrium and coexist) of the more common elements.

➤ Dots represent the melting points:

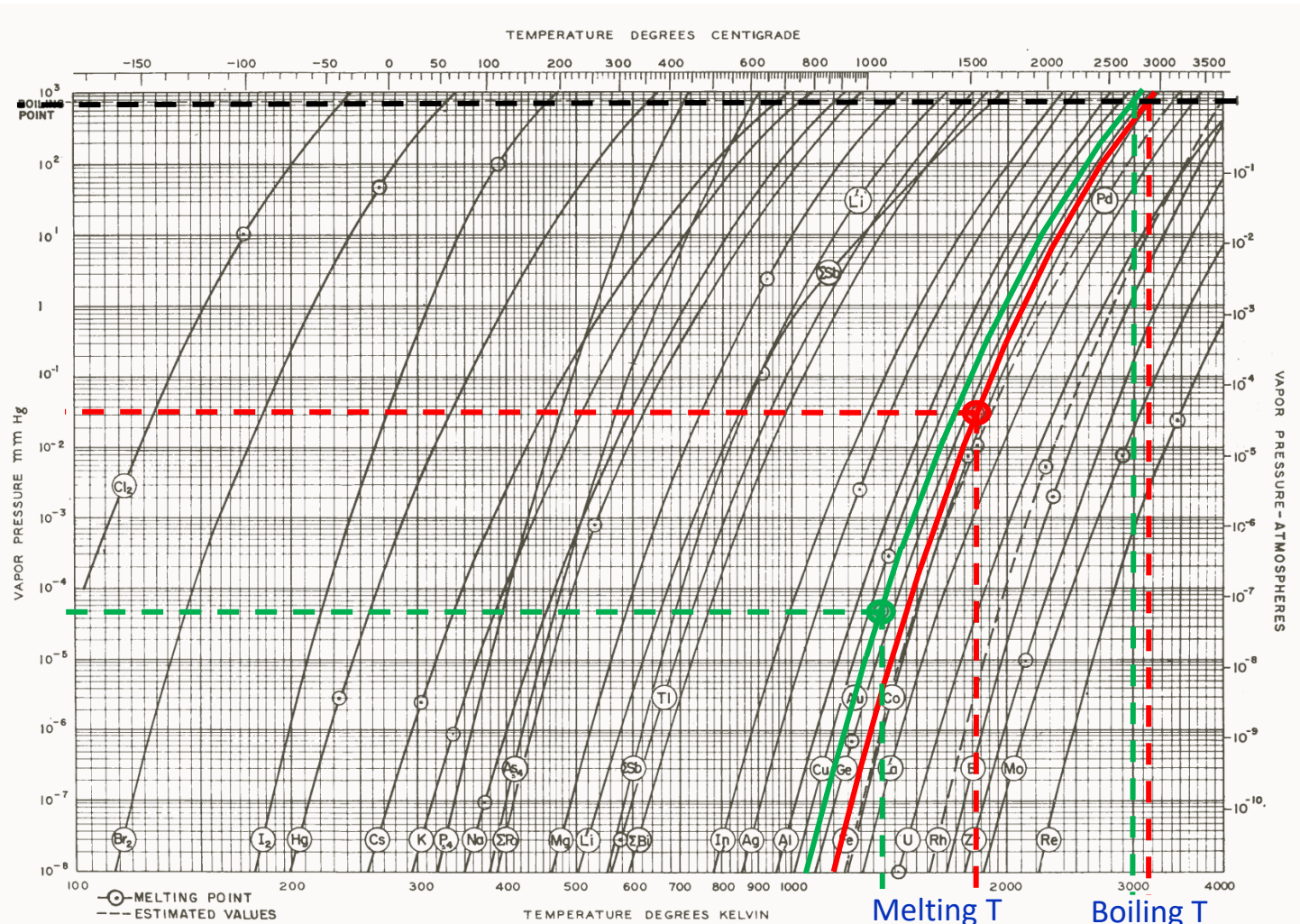
- ✓ Liquid for $T > T_{\text{melting}}$
- ✓ Solid for $T < T_{\text{melting}}$

➤ The intercept with the horizontal dashed line correspond to the boiling points at ambient pressure.



(from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)

Vapor pressure (3)



Ex. **Fe**: $T_{\text{melting}} \approx 1850 \text{ K}$ @ $P \approx 3 \cdot 10^{-2} \text{ torr}$
 $T_{\text{boiling}} \approx 3100 \text{ K}$ @ $P = 1 \text{ atm}$

Ex. **Au**: $T_{\text{melting}} \approx 1350 \text{ K}$ @ $P \approx 5 \cdot 10^{-5} \text{ torr}$
 $T_{\text{boiling}} \approx 3000 \text{ K}$ @ $P = 1 \text{ atm}$

Element	Melting point (K)
Mg	920
Al	930
Si	1684
Cr	2177
Mn	1516
Fe	1808
Co	1765
Ni	1725
Cu	1355
Pd	1825
Ag	1232
Pt	2038
Au	1334

From oxford-vacuum.com

Vapor pressures of the more common elements. Dots represent the melting points. The intercept with the horizontal dashed line correspond to the boiling points, (from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)

Vapor pressure (4)

Which is the criterion for discerning between evaporation from a solid or a liquid?



The *vapor pressure* P_e needed to evaporate with reasonable rates (I_e and ϕ_e are proportional to P_e) effectively emanates from a solid or a liquid source?

«Rule of thumb»: a **melt** will be required if the vapor pressure at the melting point is **lower** than about 10^{-3} torr.

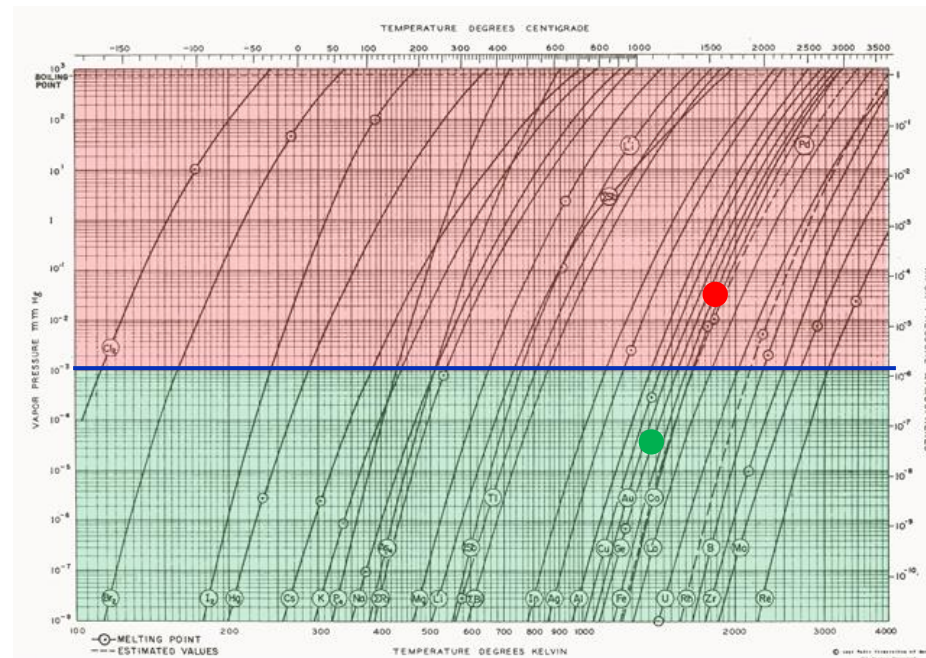
Ex. **Fe**: at the melting point
 $P \approx 3 \cdot 10^{-2}$ torr



no melting



Fe **sublimes** from the **solid phase** (as well as Cr, Ti, Mo, Ni, Si, ...)



Vapor pressures of the more common elements. Dots represent the melting points. The intercept with the horizontal dashed line correspond to the boiling points, (from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)

Ex. **Au**: at the melting point
 $P \approx 5 \cdot 10^{-5}$ torr



melting



Au deposition is attained only when the source is **molten** (as well as Ge, Na, Cs, ..)

Example 1: Fe (1)

- From the [experimental vapor pressures chart](#) we extract the $P_e(T)$ curve.
- The evaporation rates are (with $M=55.84$ g) :

$$\phi_e(\text{atoms/cm}^2\text{s}) = 4.701 \cdot 10^{21} T^{-1/2} P_e(\text{torr})$$

$$\Gamma_e(\text{g/cm}^2\text{s}) = \phi_e \frac{M}{N_A} = 4.364 \cdot 10^{-1} T^{-1/2} P_e(\text{torr})$$

Note that the influence of the **temperature T** is **mainly via $P_e(T)$** and not via the $T^{-1/2}$ dependence

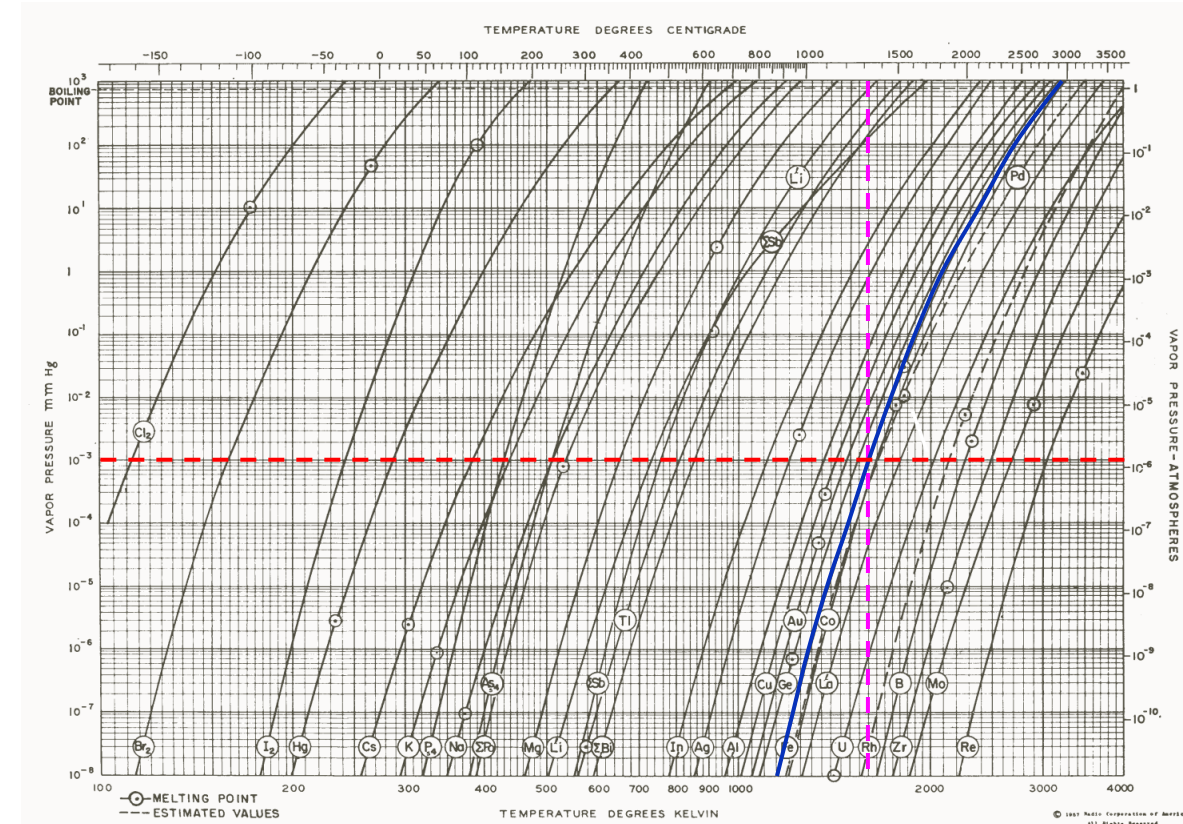
Ex.: which are the evaporation rates corresponding to $P_e=10^{-3}$ torr?

✓ We look on the pressure vapor chart the corresponding temperature (i.e. the temperature at which, at pressure P_e , solid and vapor phases of Fe are in equilibrium) ➡ we find $T \approx 1600$ K

✓ The corresponding evaporation rates are

$$\phi_e = 1.18 \cdot 10^{17} \text{ atoms/cm}^2\text{s}$$

$$\Gamma_e = 1.09 \cdot 10^{-5} \text{ g/cm}^2\text{s}$$



Example 1: Fe (2)

Assuming all evaporated atoms will deposit on a substrate or a film, which is the deposition rate in terms of **monolayer per second**?

1 ML corresponds to about 10^{15} atoms/cm² (see lecture 2)

$$\rightarrow r(\text{ML/s}) = \frac{\phi_e(\text{atoms/cm}^2\text{s})}{10^{15}(\text{atoms/cm}^2\text{ML})} = 3.513 \cdot 10^7 \frac{P_e(\text{torr})}{(MT)^{1/2}}$$

In the same conditions, which is the **time** needed for 1 ML coverage?

$$t_{1\text{ML}}(s) = \frac{1}{r} = 2.85 \cdot 10^{-8} \frac{(MT)^{1/2}}{P_e(\text{torr})}$$

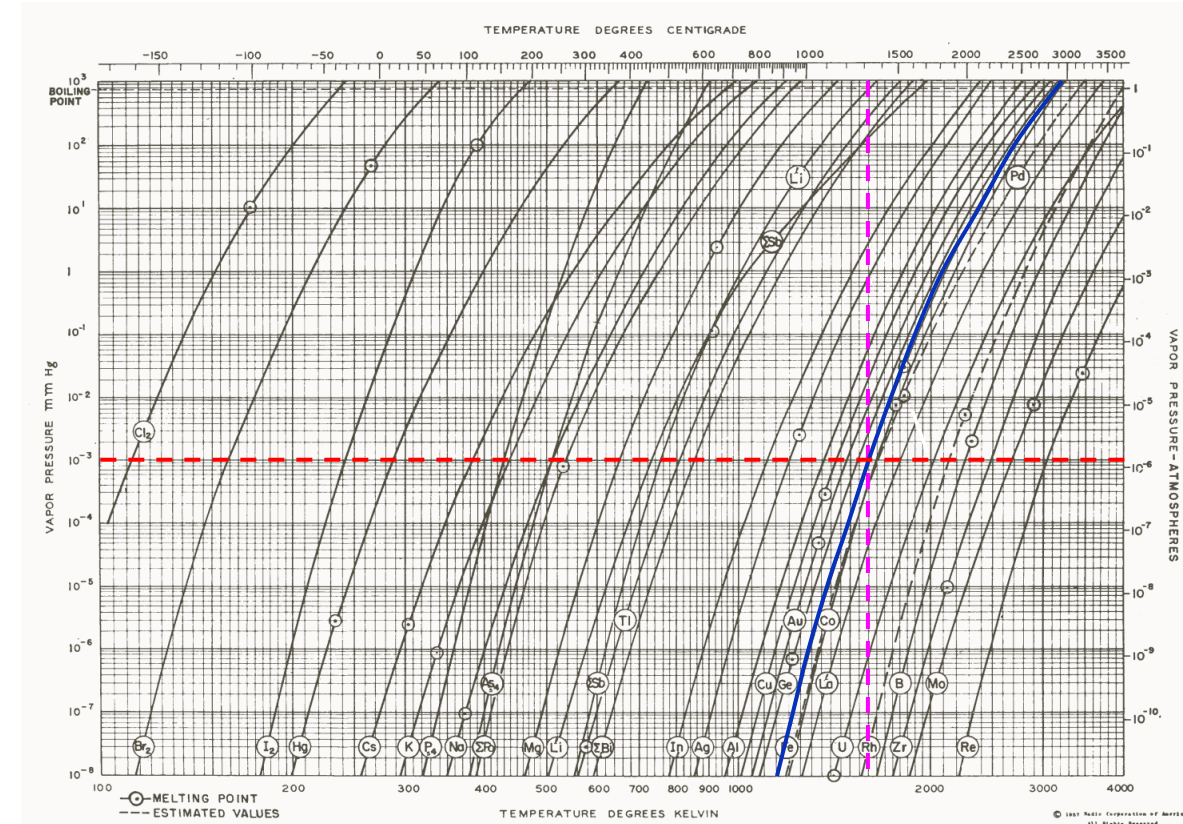
Ex.: which are the deposition rate and time for 1 ML at $P_e=10^{-3}$ torr?

$$T \approx 1600 \text{ K} \rightarrow r \approx 120 \text{ ML/s}$$

$$t_{1\text{ML}} \approx 8.5 \text{ ms}$$

Consider a interlayer spacing of 0.143 nm for bcc Fe $\rightarrow r \approx 17 \text{ nm/s}$

$$t_{1\text{nm}} \approx 60 \text{ ms}$$



Note: if T decreases of 100 K, correspondingly P_e decreases ≈ 10 times \Rightarrow the rate decreases of ≈ 10 times too!

T	P_e	rate	$t_{1\text{ML}}$
1600 K	10^{-3} torr	117 ML/s	8.5 ms
1500 K	10^{-4} torr	12 ML/s	83 ms

Example 2: Ag

Which is the source temperature and state (solid/liquid) needed to obtain an **evaporation rate** of Ag of about $2 \cdot 10^{-5} \text{ g/cm}^2 \text{ s}$?

- The evaporation rates are (with $M=107.87 \text{ g}$) :

$$\phi_e (\text{atoms/cm}^2 \text{ s}) = 4.701 \cdot 10^{21} T^{-1/2} P_e (\text{torr})$$

$$\Gamma_e (\text{g/cm}^2 \text{ s}) = \phi_e \frac{M}{N_A} = 8.421 \cdot 10^{-1} T^{-1/2} P_e (\text{torr})$$
- How to find T and $P_e(T)$ with a single condition on Γ_e ?

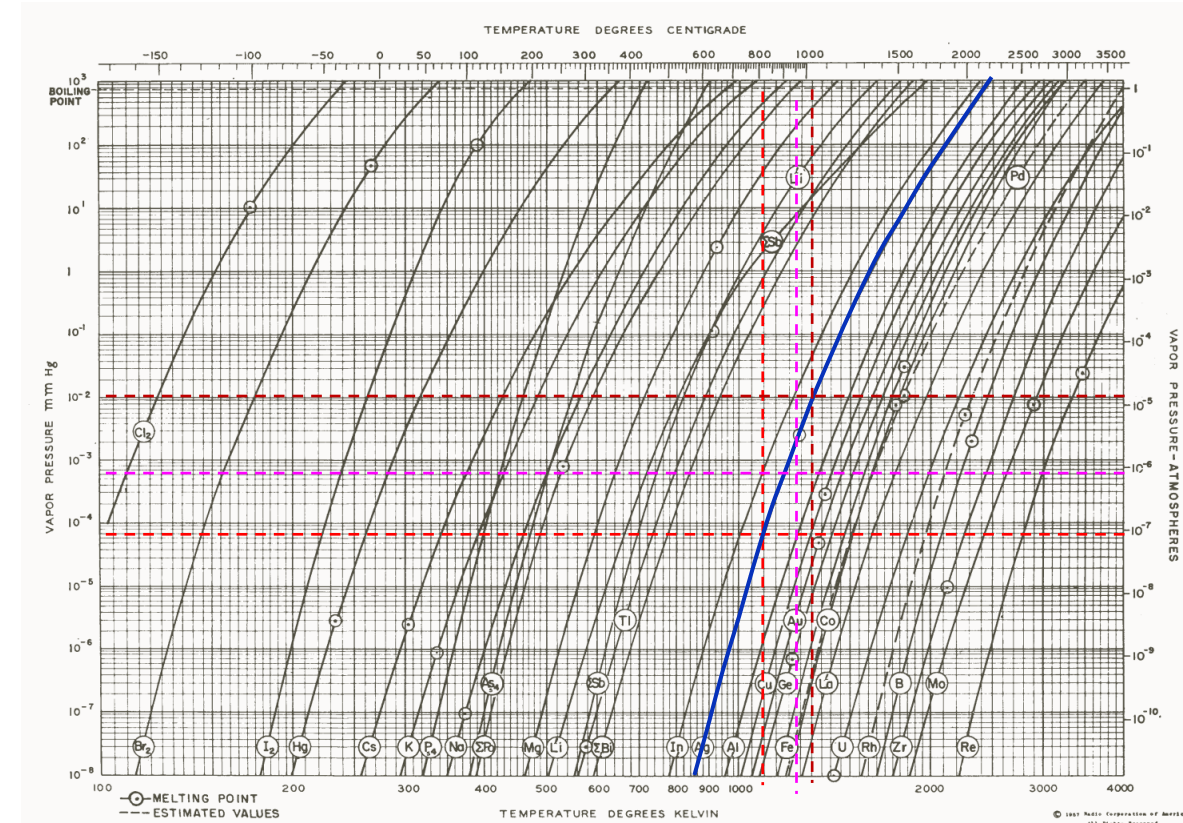
By an iterative process (few steps...)

Remember that the influence of the **temperature T** is **mainly via $P_e(T)$** and not via the $T^{-1/2}$ dependence

- Let's assume $T=1100 \text{ K}$ (for example) $\rightarrow P_e \approx 7 \cdot 10^{-5} \text{ torr}$
 $\rightarrow \Gamma_e \approx 1.8 \cdot 10^{-6} \text{ g/cm}^2 \text{ s}$: *too small*
- Let's increase to $T=1300 \text{ K}$ $\rightarrow P_e \approx 1 \cdot 10^{-2} \text{ torr}$ $\rightarrow \Gamma_e \approx 2.3 \cdot 10^{-4} \text{ g/cm}^2 \text{ s}$: *too large*
- Let's reduce to $T=1200 \text{ K}$ $\rightarrow P_e \approx 9 \cdot 10^{-4} \text{ torr}$ $\rightarrow \Gamma_e \approx 2.2 \cdot 10^{-5} \text{ g/cm}^2 \text{ s}$: *very close, correct within our approximation*



- A source heated at 1200 K will produce the required evaporation rate (within 10% of approximation)
- The source will be in solid state (because $T_{\text{melt}} \approx 1250 \text{ K}$)



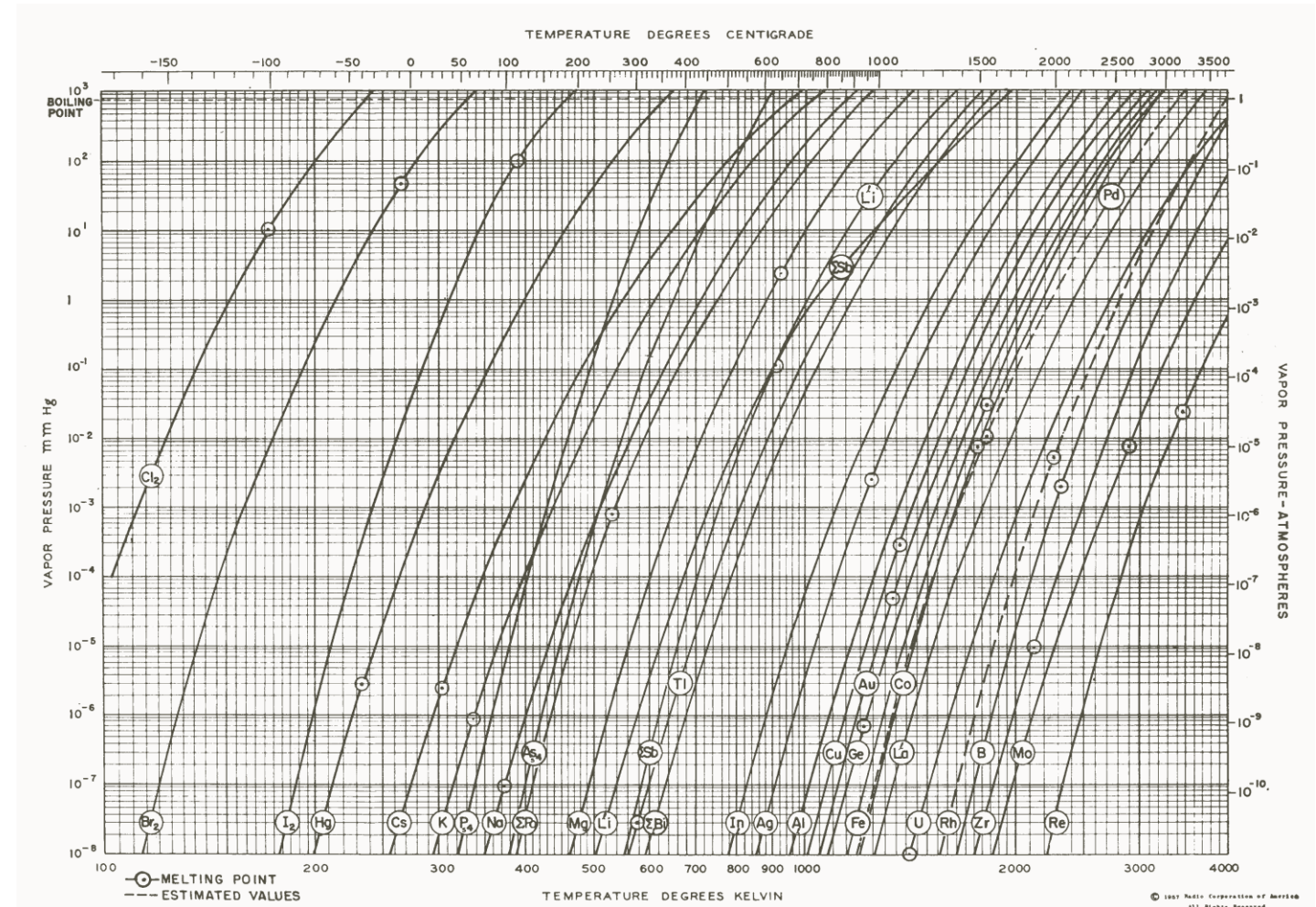
Exercises

Assuming that all evaporated atoms deposit on the substrate, calculate:

- the deposition rate (ML/s) of a Cu rod heated at $T=1200\text{ K}$
- the time needed for the deposition of 1ML of Mg at the evaporation pressure $P_e = 2 \cdot 10^{-5}\text{ torr}$
- the temperature at which a Ge source must be heated to obtain a deposition rate of about 5.5 ML/s
- the temperature at which a Mo source must be heated to deposit a film 3ML thick in about 10s

For each of the cases above, indicate if the source material is, at the evaporation conditions, solid or molten.

([Solutions in the last slide](#))



Example 3: BaTiO₃



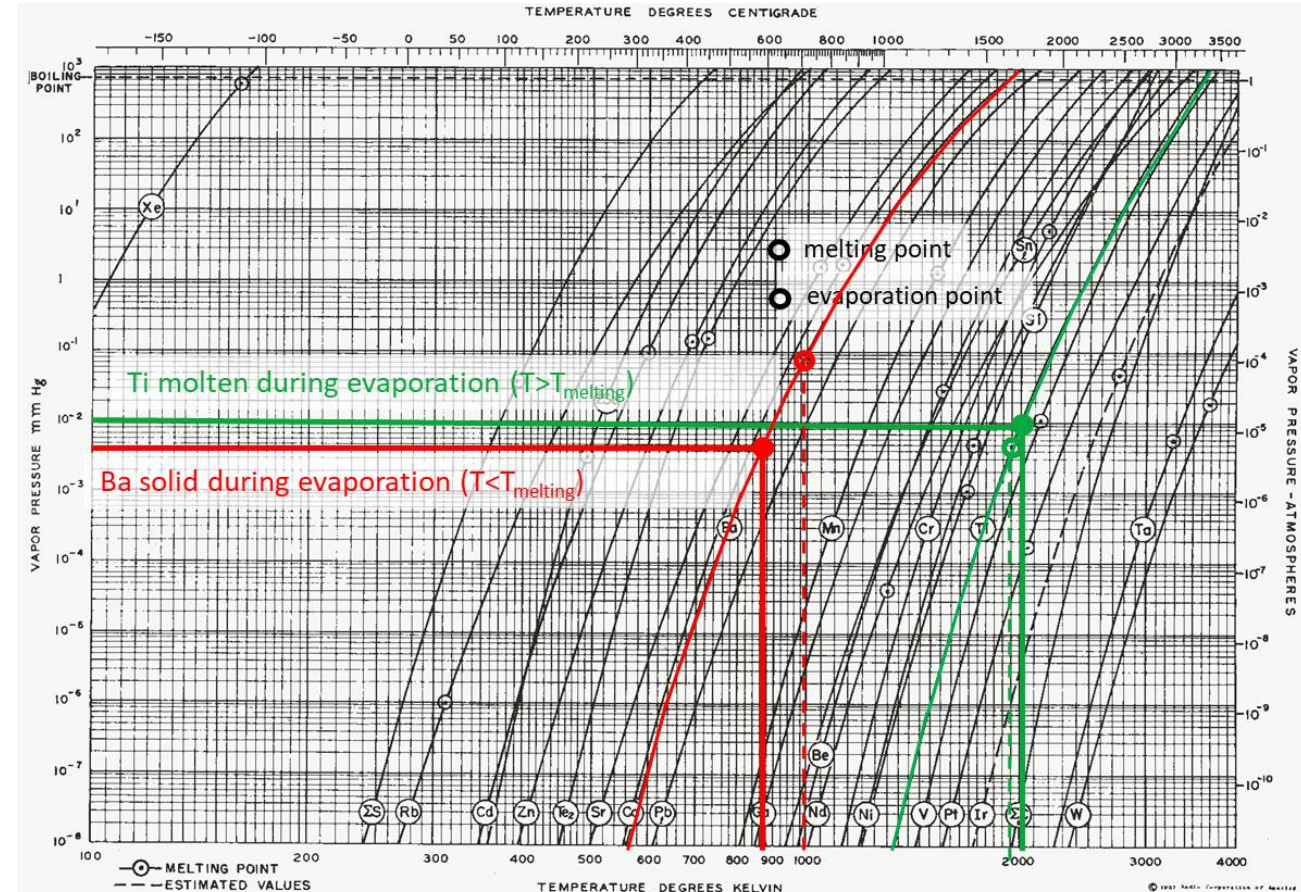
Thermal evaporation

	M (g)	T (K)	P _e (mtorr)	rate (ML/s)	
Ba	48	850	4.5	~700	+ O ₂ gas
Ti	137	2000	10	~700	

To obtain the same rate for Ba and Ti (to guarantee the correct Ba:Ti stoichiometry, i.e. 1:1) we need

- very different temperatures (Ba 850 K – Ti 2000 K)
- different phases (Ba solid – Ti liquid)

BaTiO₃ cannot be deposited from a single multielement source!



(from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)

Multiple separated sources (Ba and Ti solid + O gas) must be used in parallel, with the rates calibrated to obtain the correct stoichiometry of the final film

Evaporation of multielement materials

- **Metals**: they evaporate as atoms or clusters of atoms

- **Compounds**: the vapor composition is usually *different* from that of the liquid/solid source because

- different vapor pressures and/or states (solid/liquid) of components at the same temperature (the evaporation temperature)
 ➡ stoichiometry of the source is typically *not* preserved in the deposited film
- dissociation reactions can happen in the source

Reaction type	Chemical reaction	Examples	Comments
Evaporation without dissociation	$MX(s,l) \rightarrow MX(v)$	SiO, GeO, MgO, CaF ₂	Compound stoichiometry is maintained
Evaporation with dissociation (g + g)			Deposited films are metal-rich
a) Chalcogenides	$MX(s) \rightarrow M(g) + X(g)$	CdS, CdSe, CdTe	Separate sources are usually required
b) Oxides	$MO_2(s) \rightarrow MO(g) + 1/2 O_2(g)$	SiO ₂ , GeO ₂ , TiO ₂	Dioxides (and other complex oxides with larger oxidation number) are better deposited in O₂ partial pressure (reactive evaporation)
Decomposition (s/l + g)	$MX(s) \rightarrow M(s) + X(g)$ $MX(s) \rightarrow M(l) + X(g)$	III-V semiconductors (GaAs, InAs)	Separate sources required

Note: M=metal, X=non-metal

Note#1: when **separate sources** are required, evaporation fluxes must be calibrated (because of different evaporation rates and masses) to obtain the desired stoichiometry ([see Appendix 1](#))

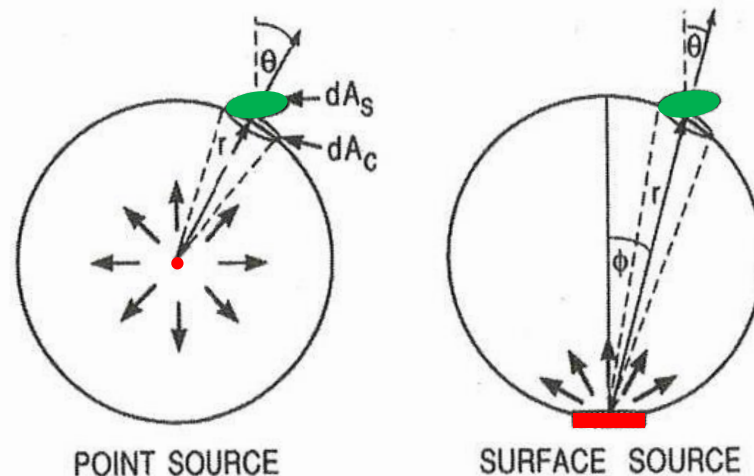
Note#2: during time the **source composition**, and that of the vapor by consequence, evolves (because of the loss of the more volatile component) ⇒ *fluxes must be compensated* in real time, otherwise *a graded film of varying composition will be deposited* (disadvantage of evaporation methods)

Deposition geometry

Typically, the **evaporation rate** from the source is *different* from the **deposition rate** on the substrate/film, because some (or a lot of) evaporated atoms do not arrive at the substrate

Which is the mass per unit area that can be deposited on a substrate/film by a given source?

- Film uniformity depends on the **source – substrate geometry** (orientation, placement, distance, ...)
- The basic geometries are
 - **point source** – evaporant particles originate from an infinitesimally small region of a spherical source
 - **surface source** – evaporant particles originate from an extended area that can be considered a *superposition* of many point sources



Evaporation from a point source and a surface source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

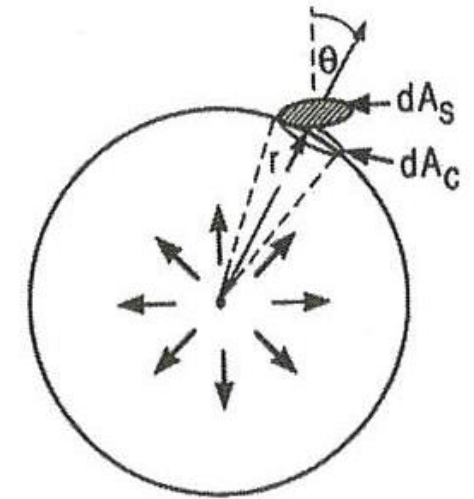
Point source (1)

- **Point source** – evaporant particles originate from an **infinitesimally small region** (dA_e) of a **spherical (point) source** of surface area A_e with a **uniform mass evaporation rate** Γ_e ; the **substrate (S)** is at distance r from the point source

- The **total evaporated mass** M_e is given by $M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt$
- The **mass** dM_s **deposited on the substrate** will fall on the portion of **substrate of area** dA_s , whose projected area on surface of a sphere of radius r is $dA_c = dA_s \cos \theta$, where θ is the angle between the source–deposition area vector and the normal to the substrate surface.
- The following proportionality applies, assuming that the **total evaporated mass** is fully deposited on the sphere of area r :

$$\frac{dM_s}{dA_c} = \frac{M_e}{4\pi r^2}$$

- The deposited mass per unit area finally is $\frac{dM_s}{dA_s} = \frac{dM_s}{dA_c / \cos \theta} = \frac{M_e}{4\pi r^2} \cos \theta$



POINT SOURCE

Evaporation from a point source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

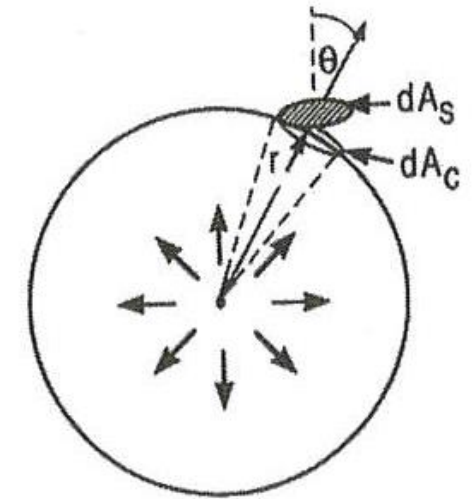
Point source (2)

- **Point source** – evaporant particles originate from an **infinitesimally small region** (dA_e) of a **spherical (point) source** of surface area A_e with a **uniform mass evaporation rate** Γ_e ; the **substrate (S)** is at distance r from the point source

- The deposited mass per unit area is
$$\frac{dM_s}{dA_s} = \frac{dM_s}{dA_c / \cos \theta} = \frac{M_e}{4\pi r^2} \cos \theta$$
- Note that deposited mass varies as
 - i) $1/r^2$ (the source-substrate distance)
 - ii) $\cos \theta$ (the geometric orientation of the substrate)

How to increase the deposition rate?

- i) reduce the source-substrate **distance** (the rate changes as $1/r^2$!) – but it would reduce film uniformity (see slide [25](#))
- ii) place the substrate **perpendicular** to the evaporation beam ($\theta=0$)



POINT SOURCE

Evaporation from a point source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Surface source

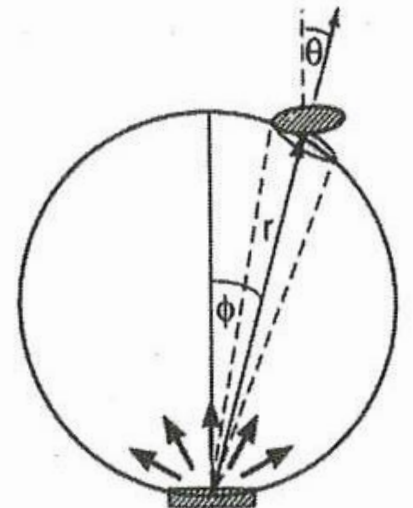
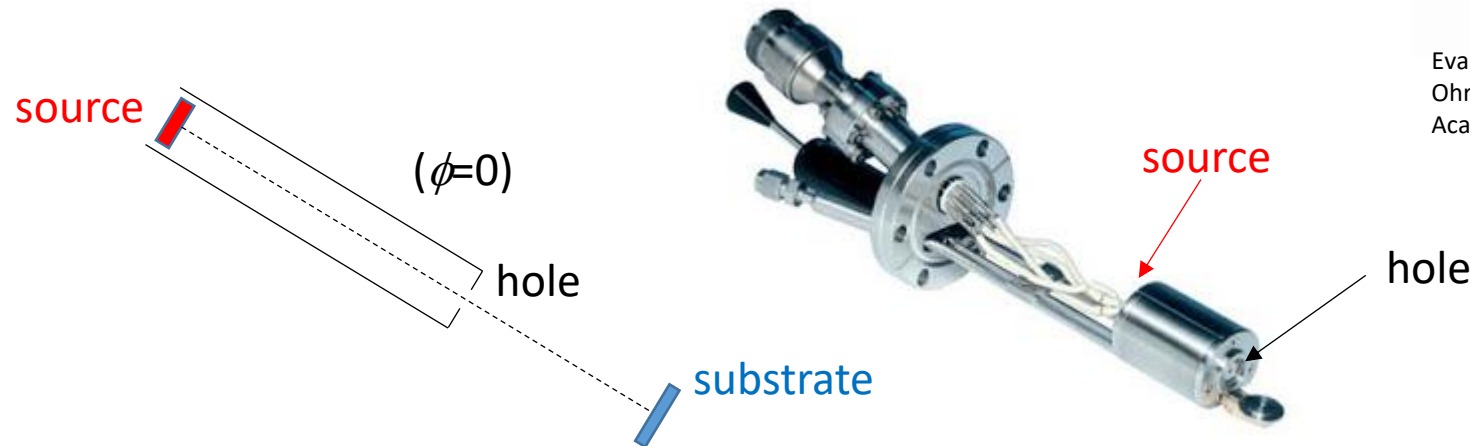
- **Surface source** – it can be considered a superposition of point sources; their contribution to the vapor stream is **stronger** where the **evaporant emission angle ϕ** (the angle between the surface source normal and the straight line connecting the center of the source with the center of substrate) is **near zero**.

- The deposited mass per unit area is:
$$\frac{dM_S}{dA_S} = \frac{M_e \cos \theta \cos \phi}{\pi r^2}$$

(Note that in the $\phi=90^\circ$ direction there is no emission)

- **Knudsen cell source** – it makes use of an **isothermal enclosure** with a **small hole** through which the evaporant atoms or molecules will **diffuse**

$\phi=0 \rightarrow$ maximum deposition rate (dM_S/dA_S)



SURFACE SOURCE

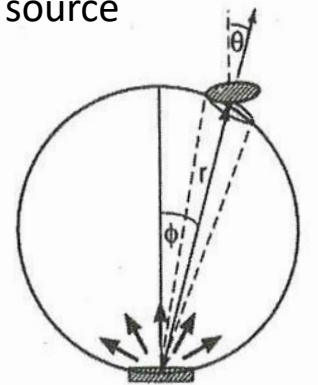
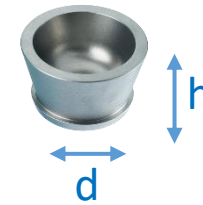
Evaporation from a surface source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Flux directionality

- Practically, the angular distribution of the **evaporant flux** depends on many parameters (as the evaporation crucible geometry)

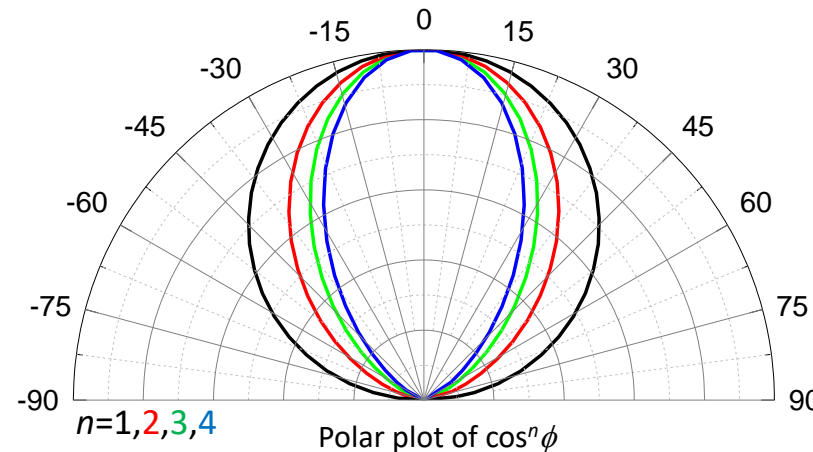
→ $\cos^n \phi$ dependence (instead of $\cos \phi$) has been experimentally found to be more appropriated

- The **mass deposited per unit area** is now
$$\frac{dM_S}{dA_S} = \frac{M_e(n+1) \cos^n \phi \cos \theta}{2\pi r^2}$$
- n determines the **shape** of the vapor cloud and the **angular distribution** (versus ϕ) of the evaporant flux from the source
- n scales as the ratio between the depth and the surface area of the molten source material \Rightarrow *narrower crucibles (smaller d/h ratio) have larger n (they are used to confine the evaporated material to a narrow angular spread)*



Note: because of the **increased directionality** of the source, the **receiving surface area** scales down as $\frac{2\pi r^2}{n+1}$

Note: for $n=1$ the area is πr^2 as in slide [23](#)

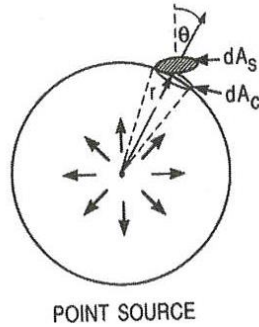


Evaporation from a surface source or Kundsén cell (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Thickness uniformity (1)

Thickness uniformity is required for some applications (microelectronics, optical interference filters, ...), down to $\pm 1\%$.

Which is the film uniformity that can be obtained by a given source?



Consider the evaporation from a **point source** to a **plane substrate** as in the figure

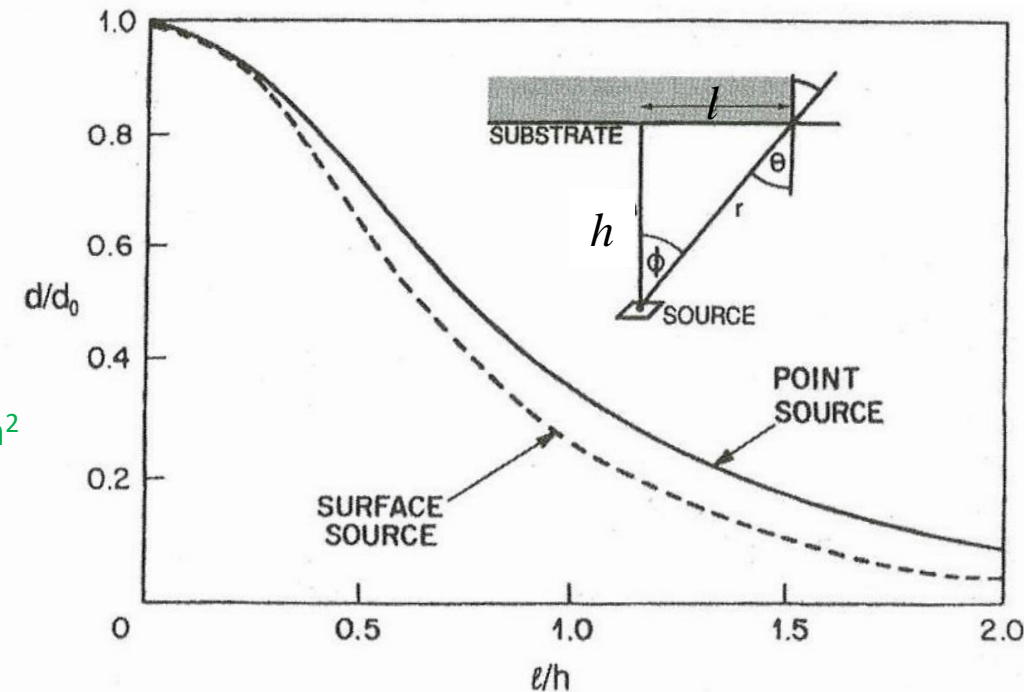
\Rightarrow the **film thickness** is given by $d = \frac{1}{\rho} \frac{dM_s}{dA_s}$ where ρ is the density of the deposited material

- For **point source**: $d = \frac{dM_s}{\rho dA_s} = \frac{M_e \cos \theta}{4\pi \rho r^2} = \frac{M_e}{4\pi \rho r^2} \frac{h}{r} = \frac{M_e h}{4\pi \rho (h^2 + l^2)^{3/2}}$

The thickest deposit occurs at $l=0$ (in the substrate center) $\Rightarrow d_0 = \frac{M_e}{4\pi \rho h^2} \propto 1/h^2$

The **film uniformity** is given by $\frac{d}{d_0} = \frac{h^3}{(h^2 + l^2)^{3/2}} = \frac{1}{(1 + (l/h)^2)^{3/2}} = f(l/h), \text{ or } f(\theta)$

(In the limit $h \gg l$ we have $d/d_0 \approx 1$, i.e. the film is uniform)

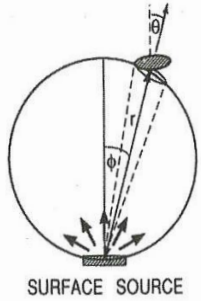


Film thickness uniformity for point and surface sources (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Thickness uniformity (2)

Thickness uniformity is required for some applications (microelectronics, optical interference filters, ...), down to $\pm 1\%$.

Which is the film uniformity that can be obtained by a given source?



Consider the evaporation from a **surface source** to a **plane substrate** (with surface parallel to the surface source $\Rightarrow \phi = \theta$)

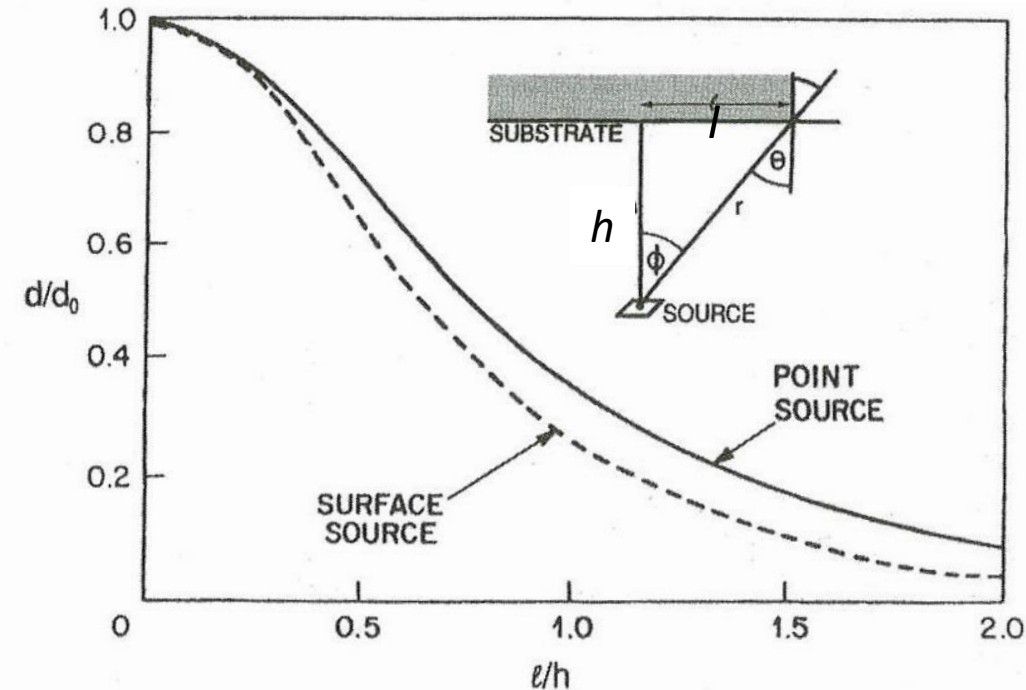
\Rightarrow the **film thickness** is given by $d = \frac{1}{\rho} \frac{dM_s}{dA_s}$ where ρ is the density of the deposited material

- For **surface source**: $d = \frac{dM_s}{\rho dA_s} = \frac{M_e \cos \phi \cos \theta}{\pi \rho r^2} = \frac{M_e}{\pi \rho r^2} \frac{h}{r} \frac{h}{r} = \frac{M_e h^2}{\pi \rho (h^2 + l^2)^2}$

The thickest deposit occurs at $l=0 \Rightarrow d_0 = \frac{M_e}{\pi \rho h^2} \propto 1/h^2$

The **film uniformity** is given by $\frac{d}{d_0} = \frac{h^4}{(h^2 + l^2)^2} = \frac{1}{(1 + (l/h)^2)^2} = f(l/h), \text{ or } f(\theta, \phi)$

(In the limit $h \gg l$ we have $d/d_0 \approx 1$)

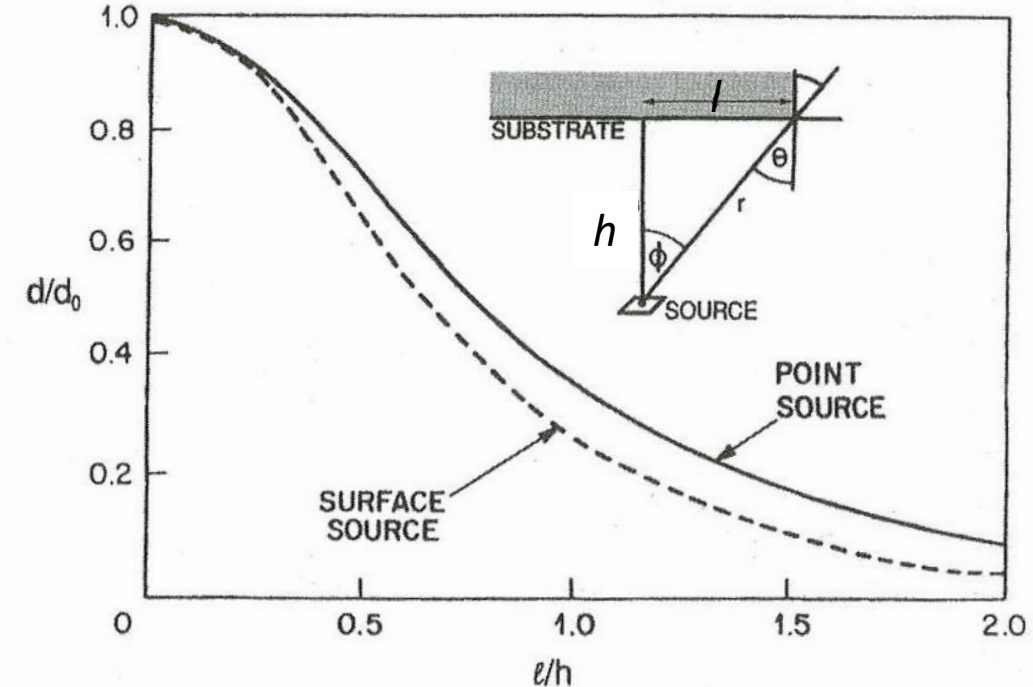


Film thickness uniformity for point and surface sources (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Thickness uniformity (3)

Which is the film uniformity that can be obtained by a given source?

Source	Point	Surface
Thickness d	$\frac{M_e h}{4\pi\rho(h^2 + l^2)^{3/2}}$	$\frac{M_e h^2}{\pi\rho(h^2 + l^2)^2}$
Maximum thickness d_0 ($l=0$)	$\frac{M_e}{4\pi\rho h^2}$	$\frac{M_e}{\pi\rho h^2}$
Thickness uniformity d/d_0	$\frac{1}{\left(1 + \left(\frac{l}{h}\right)^2\right)^{3/2}}$	$\frac{1}{\left(1 + \left(\frac{l}{h}\right)^2\right)^2}$



Film thickness uniformity for point and surface sources (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Notes:

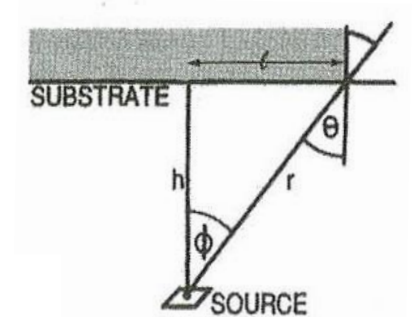
- for a given l/h value, the point source is more uniform (larger d/d_0) than the surface one
- the deposition rate in identical conditions (e.g. $\phi = \theta = 0$) is larger for the surface source ($dM_S/dA_S = M_e/\pi r^2$) than for the point one ($dM_S/dA_S = M_e/4\pi r^2$)

Example 1

We want to coat a circular substrate with 2 inches diameter, with a thickness tolerance of $\pm 5\%$, employing one evaporation surface source.

Which must be the distance between the source and the substrate?

- The film uniformity is given by $\frac{d}{d_0} = \frac{1}{(1 + (l/h)^2)^2} = \frac{h^4}{(h^2 + l^2)^2}$
- The tolerance can be expressed as $t = \frac{d_0 - d}{d_0} = 1 - \frac{1}{(1 + (l/h)^2)^2} = 1 - \frac{h^4}{(h^2 + l^2)^2}$
- the source-substrate distance h giving the tolerance t at distance l from the substrate center is given by
$$h = l \left(\frac{1}{(1-t)^{1/2}} - 1 \right)^{-1/2}$$
- The more critical point is the substrate boundary ($l = D/2 = 1 \text{ inch} = 2.54 \text{ cm}$) $\Rightarrow h \approx 16 \text{ cm}$ ($h/l \approx 6.2$)



Geometry of evaporation onto a parallel substrate (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Example 2

We want to coat a 150 cm wide strip, with a thickness tolerance of $\pm 10\%$, employing two evaporation sources separated by the distance $2D$.

Which must be the distance between the sources ($2D$) and with the substrate (h_v)?

$$d = \frac{M_e h_v^2}{\pi \rho (h_v^2 + (r + D)^2)^2} + \frac{M_e h_v^2}{\pi \rho (h_v^2 + (r - D)^2)^2} \quad (\text{superposition of sources})$$

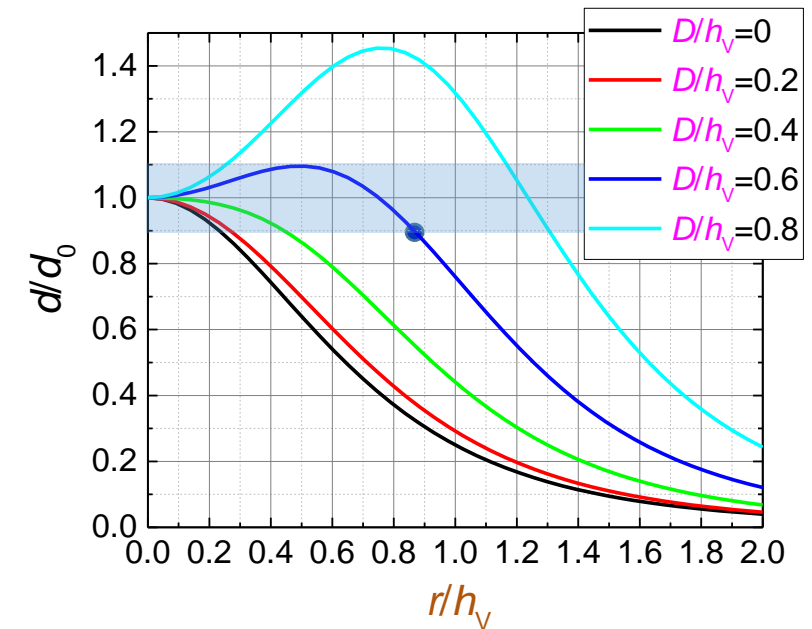
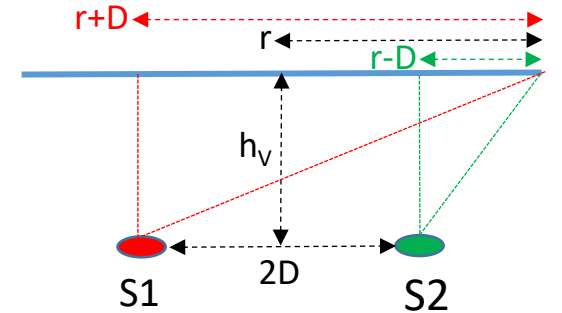
$$d_0 = d(r = 0) = \frac{M_e h_v^2}{\pi \rho (h_v^2 + D^2)^2} + \frac{M_e h_v^2}{\pi \rho (h_v^2 + D^2)^2} = 2 \frac{M_e h_v^2}{\pi \rho (h_v^2 + D^2)^2}$$

$$\Rightarrow \frac{d}{d_0} = \frac{\left(1 + \left(\frac{D}{h_v}\right)^2\right)^2}{2 \left(1 + \left(\frac{r}{h_v} + \frac{D}{h_v}\right)^2\right)^2} + \frac{\left(1 + \left(\frac{D}{h_v}\right)^2\right)^2}{2 \left(1 + \left(\frac{r}{h_v} - \frac{D}{h_v}\right)^2\right)^2} = f\left(\frac{D}{h_v}, \frac{r}{h_v}\right)$$

We want d/d_0 between 0.9 and 1.1 for any $r \leq R \Rightarrow$ one solution is $D/h_v = 0.6$ with $r/h_v = 0.87$.

Considering the limit case $r = R = 150\text{cm}/2 = 75\text{cm}$, we obtain $h_v = 86.2\text{ cm}$ and $2D = 103.4\text{ cm}$.

Note that this is the solution that minimize h_v (maximize D/h_v), that should be preferred in order to reduce the evaporator dimension.



Example 3

- We want to deposit an optical coating where a $\pm 1\%$ film thickness is required (e.g. for interference filters).
- In order to even out source distribution anomalies and minimize preferential film growth, a *rotating* substrate is employed.
- Since the sample is a multilayer, different sources will be needed, each one *off from the substrate axis* in order to accomodate all of them.



Which must be the distance between the source and the substrate planes (h_v), assuming the axis offset $R=20\text{cm}$ and the substrate diameter $2r=25\text{cm}$?

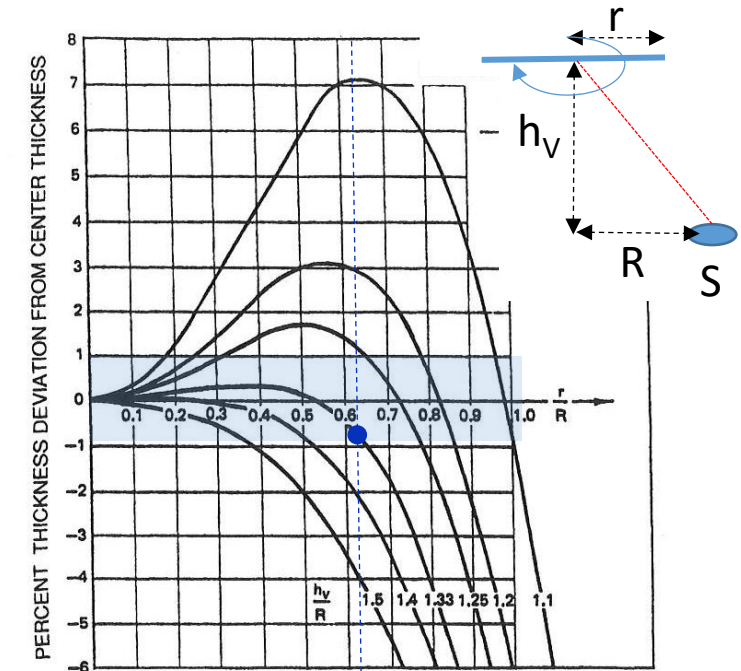
We need to average the mass distribution on the substrate over one period.

➡ In figure is reported the percent deviation of the tickness from the center value ($t=(d_o-d)/d_o$) as a function of the substrate radius (r/R) for different source-substrate planes distances (h_v/R)

In our case $r/R=(25\text{cm}/2)/20\text{cm}=0.625$.

We want t between -1% and 1% for $r/R=0.625 \Rightarrow h_v/R=1.33$ is the only solution (t is -0.6% for $r/R=0.625$ and stays in the range $-0.6\div 0.5\%$ for all r values between 0 and 12.5cm)

Since $R=20\text{ cm}$, we obtain $h_v=26.6\text{ cm}$.

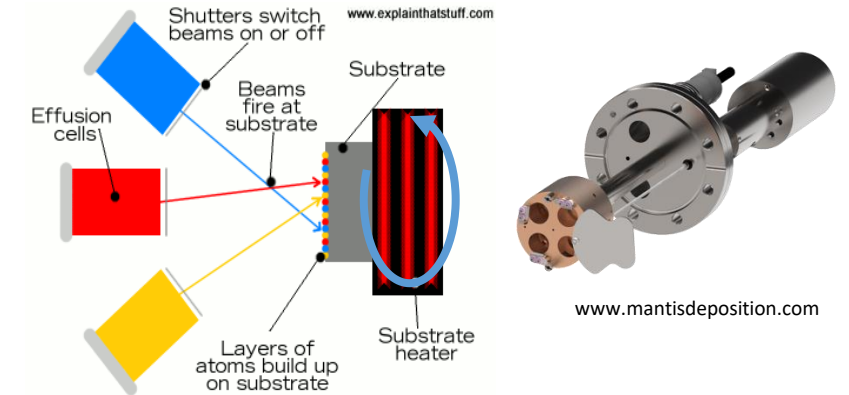


Calculated film thickness variation across the radius of a rotating substrate (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

More examples

What if we use different sources?

- E.g., if the sample is a **multilayer**, different sources will be needed, each one *off from the substrate axis* in order to accomodate all of them → uniformity is *reduced* with respect to the single Knudsen cell with $\phi=0$.
- In order to even out source distribution anomalies and minimize preferential film growth (→ to improve uniformity), a **rotating** substrate is employed.



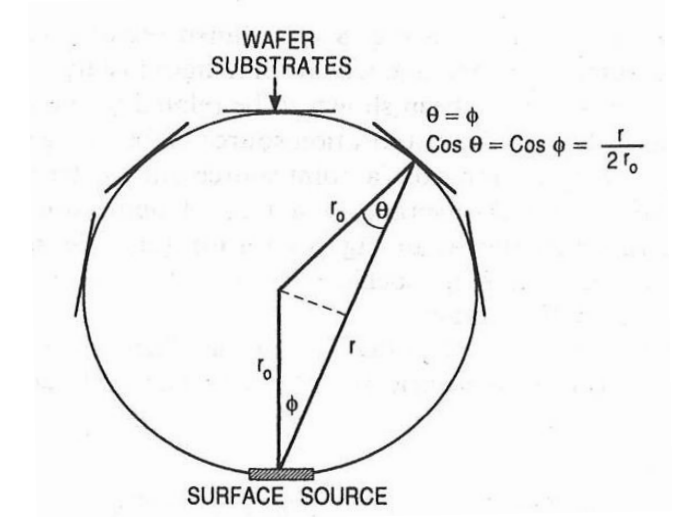
What if we deposit on different substrates?

- E.g., for increasing the production rate of devices in industry, or to do not waste precious materials (Au, Pt, ...), deposition can be done on **different substrates** at the same time.
- To achieve maximum thickness uniformity on all substrates, both the surface sources and the substrates must be placed **tangent** to the surface of a sphere

$$\Rightarrow \theta = \phi \Rightarrow \cos \theta = \cos \phi = (r/2)/r_0 \Rightarrow \frac{dM_S}{dA_S} = \frac{M_e \cos \phi \cos \theta}{\pi r^2} = \frac{M_e}{\pi r^2} \frac{r}{2r_0} \frac{r}{2r_0} = \frac{M_e}{4\pi r_0^2}$$

Note:

- the deposit thickness is **independent** on angle
- this works with **surface sources** ($n=1$), but *fails with more directional ones* ($n>1$) because of the **$\cos^n \phi$ dependence**



(from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

Thickness uniformity or deposition rate?

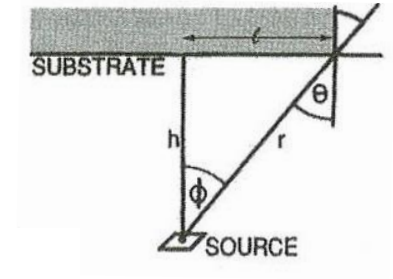
- **Surface source:**

- The deposited mass per unit area is: $\frac{dM_S}{dA_S} = \frac{M_e \cos \theta \cos \phi}{\pi r^2}$

- The film uniformity is: $\frac{d}{d_0} = \frac{h^4}{(h^2 + l^2)^2} = \frac{h^4}{r^4}$



- **Deposition rate** increases by *decreasing* the substrate-source distance (r, h)
- **Film uniformity** increases by *increasing* the substrate-source distance (so to achieve $h \sim r$)



Which is the «best» substrate-source distance?

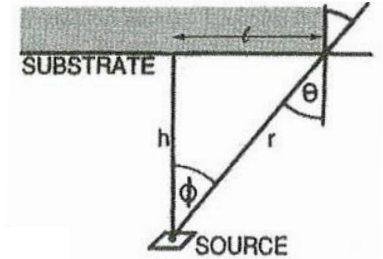
It depends on applications

Examples

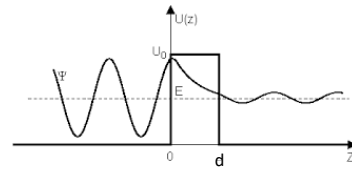
- **Surface source:**

- The deposited mass per unit area is: $\frac{dM_S}{dA_S} = \frac{M_e \cos \theta \cos \phi}{\pi r^2}$

- The film uniformity is: $\frac{d}{d_0} = \frac{h^4}{(h^2 + l^2)^2} = \frac{h^4}{r^4}$



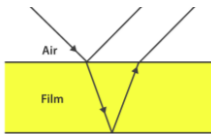
Ex. **Tunneling junction**: $T \propto e^{-2\alpha d}$, where d is the barrier thickness



- *Very good uniformity* because the transmission T strongly depends on d
- A low deposition rate can be accepted because a thin barrier layer ($\sim \text{nm}$) is needed

→ *large* substrate-source distance is preferred

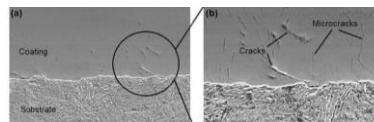
Ex. **Spectral filter**: $d = (2m + 1) \frac{\lambda}{4n}$ (interference from a thin film with thickness d and refractive index n)



- *Good uniformity* because $\Delta\lambda \propto \Delta d$
- Thickness \sim hundreds of nm

→ *medium* substrate-source distance

Ex. **Protective coating**: insulating and/or high density and/or good thermal conductivity ...



- *Large thickness*
- Uniformity non relevant

→ *small* substrate-source distance

Film purity

The **chemical purity** of evaporated films depends on:

- i. **impurities** (which ones and how many they are?) initially present in the **source** or in the **reacting gas**
 - The purity level of a material or gas is indicated in percentage, e.g. 99.99% means that impurities are no more than 0.01% (one part on 10^4)
- ii. source contamination from the **heater**
 - It can be avoided separating the heater from the deposition region (e.g. e-beam evaporation)
- iii. **residual gases** in the vacuum system
 - Background pressure must be as low as possible (HV, UHV) to reduce their partial pressure

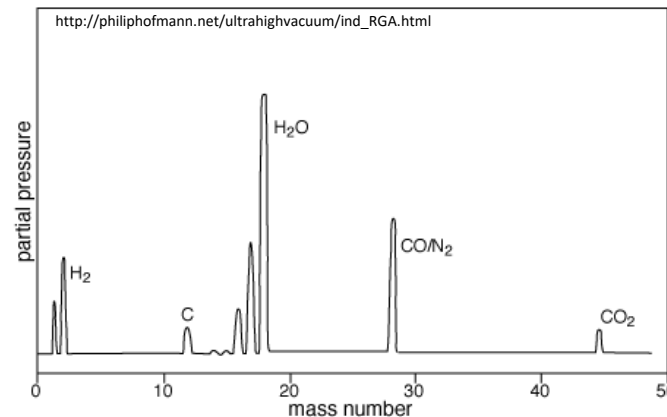


Al

Sputtering Targets

8" x 0.125

99.99%



Film purity: residual gases (1)

- During deposition the atoms of both the **evaporant** and **residual gases** impinge on the substrate at the same time

- The residual gas flux(molecules/cm²s) is (see lecture 2):

$$\phi_g(\text{particles/cm}^2\text{s}) = 3.513 \cdot 10^{22} \frac{P(\text{torr})}{(M_g T)^{1/2}}$$

where M_g is the molecular mass of residual gases, and P is the residual gas vapor pressure (torr).

- The evaporant vapor flux (molecules/cm²s) is:

$$\phi_{ev}(\text{particles/cm}^2\text{s}) = \frac{\rho N_A}{M_{ev}} \dot{d}$$

where ρ is the film density (g/cm³), M_{ev} is the molecular mass of evaporant ($\rightarrow \rho/M_{ev}$ =mole number per cm³, $\rho N_A / M_{ev}$ = molecules/ cm³), \dot{d} is the film deposition rate (cm/s).

- The ratio between the residual gas and evaporant vapor fluxes (or impingement rates) results:

$$r = \frac{\phi_g}{\phi_{ev}} = \frac{3.513 \cdot 10^{22} P (M_g T)^{-1/2}}{\frac{\rho N_A \dot{d}}{M_{ev}}} = \frac{5.82 \cdot 10^{-2} P M_a}{(M_g T)^{1/2} \rho \dot{d}}$$

Film purity : residual gases (2)

- The relative concentration of contaminants, i.e. the ratio between **residual** gas and **evaporant** vapor fluxes (or the corresponding impingement rates) is:

$$r = \frac{\phi_g}{\phi_{ev}} = \frac{3.513 \cdot 10^{22} P (M_g T)^{-1/2}}{\frac{\rho N_A \dot{d}}{M_{ev}}} = \frac{5.82 \cdot 10^{-2} P M_a}{(M_g T)^{1/2} \rho \dot{d}} \propto \frac{P}{\dot{d}}$$

r	Deposition rates (nm/s)			
P_{O_2} (torr)	0.1	1	10	100
10^{-9} (UHV)	10^{-3}	10^{-4}	10^{-5}	10^{-6}
10^{-7} (HV)	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-5} (HV)	10	1	0.1	0.01
10^{-3} (MV)	10^3	10^2	10	1

Es.: maximum oxygen (O_2) relative concentration (r) in Tin films deposited at room temperature

- In order to have a small impurity concentration (r), you need

- (i) **high** deposition rates \dot{d}
- (ii) **low** residual pressure P

This is easily achieved with **thermal evaporation**, while with **sputtering** was not until a decade ago (it was not considered a «clean» technique as thermal evaporation is).

- At 10^{-3} torr the oxygen incorporation is high \Rightarrow this can be exploited (intentionally introducing oxygen in the chamber) in **reactive evaporation processes** where reactions with the evaporant metal in the deposited oxide film are promoted.

Appendix 1: evaporation of multielement materials

*How to evaporate metal alloy films (e.g. Fe-Ni, Ni-Cr, Al-Cu) from a solution **preserving** the stoichiometry?*

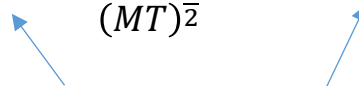
- Atoms in **metallic alloys** are *less tightly bound* than in oxides \Rightarrow they tend to evaporate *separately* (as in III-V semiconductors) \Rightarrow they enter the vapor phase as *single atoms* (as if they were pure metals)
- We assume that the interaction energy between A and B atoms in an the AB solution (the source alloy) is the same of AA and BB pairs in pure materials.
- The Raoult law holds:
$$\begin{cases} P_A = X_A P_{A0} \\ P_B = X_B P_{B0} \end{cases}$$

(P_A is the **vapor pressure** of A in solution, P_{A0} is the vapor pressure of pure A, X_A is the **mole fraction** of A in the solution; the same for B; $X_A + X_B = 1$)

- In real situations, the mole fraction X must be replaced by the **activity** a that is the *effective* concentration of the material in the solution during the evaporation, taking into account the *different* evaporation rates from the solution (AB) with respect to pure materials (AA, BB). E.g., if A atoms are physically bound more tightly to each other than in the solution, their tendency to evaporate from the solution is facilitated.
- The *activity* can be related to the concentration by the activity coefficient γ : $a = \gamma X \Rightarrow \begin{cases} P_A = \gamma_A X_A P_{A0} \\ P_B = \gamma_B X_B P_{B0} \end{cases}$
- Because the evaporation flux ϕ_e from the source alloy of each material is proportional to P_e / \sqrt{M} (see slide 8), at a fixed T , finally we can evaluate the ratio of the fluxes of A and B atoms in the vapor stream emanating from the AB source:
$$\frac{\phi_A}{\phi_B} = \frac{\gamma_A X_A P_{A0}}{\gamma_B X_B P_{B0}} \left(\frac{M_B}{M_A} \right)^{1/2}$$

However, during time the **source composition**, and that of the vapor by consequence, evolves (because of the loss of the more volatile component)
 \Rightarrow *if the fluxes are not compensated, a graded film of varying composition is deposited (disadvantage of evaporation methods!)*

Solutions to exercises

$$r\left(\frac{ML}{s}\right) = 3.513 \cdot 10^7 \frac{P_e(\text{torr})}{(MT)^{\frac{1}{2}}} \quad t_{1ML}(s) = \frac{1}{r}$$


material	M	Pe (torr)	T (K)	rate (ML/s)	t _{ML} (s)	Solid/Molten
Cu	63.55	6E-06	1200	0.76	1.31E+00	S
Mg	24.31	2E-05	580	5.92	1.69E-01	S
Ge	72.64	5E-05	1400	5.51	1.82E-01	M
Mo	95.96	4E-06	2200	0.31	3.27E+00	S