Earlier in term you were urged:

when addressing a new problem, topic, technical field…

ask all the *quantitative* questions you can, e.g.

what are the *energies*, *forces*, *length & time scales involved*…

use your familiar equations.

This gives you *context*, *limits* and unimagined *possibilities* …

Richard Rodriquez (American poet, essayist, cultural commentator), in his recent book "*Brown; the last discovery of America*"

"…it is the reader alone who decides a book's universality.

….It is the reader's life that opens a book.

I [as the author] am dead.

Only a reader can testify to the ability of literature to open;…"

This is about hearing something and taking it farther than the source could imagine, about being an *active* reader, an *active* listener, an *active* learner.

You determine the value in the material you are exposed to, by the questions you ask, the experiences and insights you bring.

Only *active learning* will make you the creators and inventors of tomorrow.

PHYSICAL VAPOR DEPOSITION (PVD)

PVD II: Evaporation

- We saw **CVD**
  - Gas phase reactants: $p_g \approx 1$ mTorr to 1 atm.
  - **Good step coverage, $T > 350$ K**
- We saw **sputtering**
  - Noble (+ reactive gas) $p \approx 10$ mTorr; ionized particles
  - High deposition rate, reasonable step coverage
  - Extensively used in electrical, optical, magnetic devices.
- Now see **evaporation:**
  - Source material heated, $p_{eq.vap.} = \sim 10^{-3}$ Torr, $p_g < 10^{-6}$ Torr
  - Generally no chemical reaction (except in "reactive deposition),
  - $\lambda = 10$'s of meters, Knudsen number $N_K >> 1$
  - Poor step coverage, source alloy fractionation: Δp_{vapor}
  - Historical (optical, electrical)

Campbell, Ch. 12 is more extensive than Plummer on evaporation

Standard vacuum chambers

$\Sigma p_i \approx 10^{-6}$ Torr (1.3×10^{-4} N / m^{2})

Mostly H_2O, hydrocarbons, N_2, He

by residual gas analysis (RGA = mass spec.)

Figure removed for copyright reasons.

Figure 2-12 in Ohring, M. *The Materials Science of Thin Films*. 2nd ed. Burlington, MA: Academic Press, 2001. ISBN: 0125249756.

Figure removed for copyright reasons.

Figure 2-8 in Ohring, 2001.

Ultra-high vacuum chambers

$p < 10^{-8}$ Torr demands:

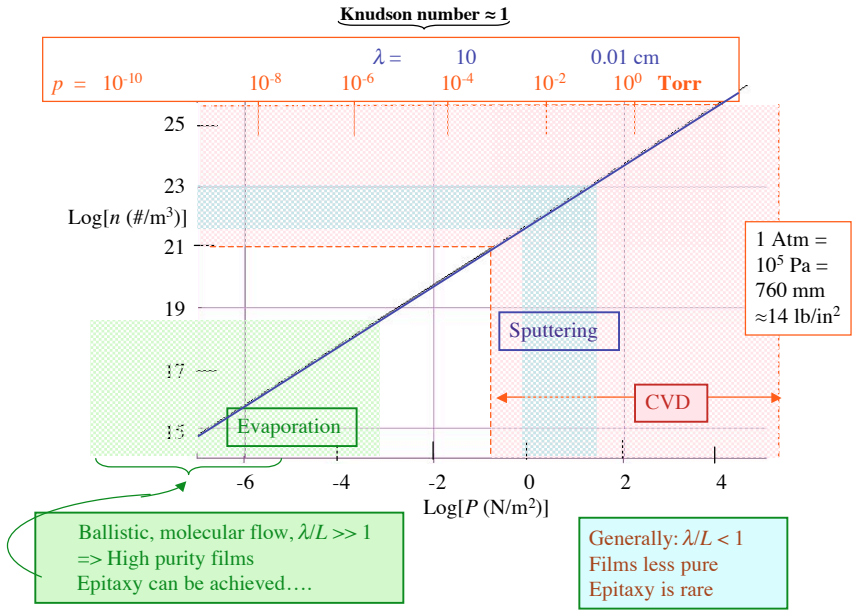
Stainless steel chamber

Bakeable to 150°C

Cryo, ion, turbo pumps

Figure removed for copyright reasons.

Figures 2-10 and 2-11 in Ohring, 2001.



Atomic flux on surface due to residual gas

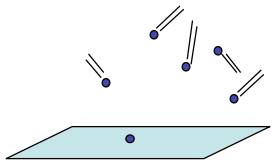
$$J\left(\frac{\text{atoms}}{\text{area}\cdot\text{t}}\right)=\frac{n}{2}\bar{v}_x=\frac{p}{2k_BT}\sqrt{\frac{2k_BT}{\pi m}}=\boxed{\frac{p}{\sqrt{2\pi m k_BT}}=J}$$

Given 10^{-6} Torr of water vapor @ room temp, find flux

$$p=10^{-6}\text{Torr}\times\frac{1\text{atm}}{760\ \text{T}}\times\frac{10^5 P_a}{\text{atm}},\quad k_BT(RT)=0.025\text{eV}=4\times10^{-21}J$$

$$p=1.3\times10^{-4}\frac{N}{m^2}\qquad m_{H_2O}=\frac{18}{N_A}=3\times10^{-26}\text{kg}$$

$$\boxed{J=4.8\times10^{14}\left(\frac{\text{atoms/molecules}}{\text{cm}^2\text{sec}}\right)}$$



What is atomic density in 1 monolayer (ML) of Si?

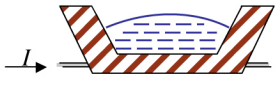
N_{Si} = 5 x 10^{22} cm^{-3} => 1.3 x 10^{15} cm^{-2}.

So at 10^{-6} Torr, 1 ML of residual gas *hits* surface every 3 seconds!

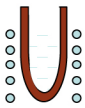
Epitaxy requires slow deposition, high surface mobility,
you must keep pressure low to maintain pure film

So we have a good idea of the chamber…

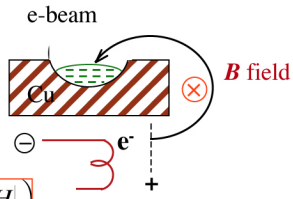
Now add evaporation source



Resistive heater



RF-induction heater

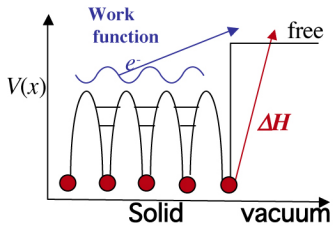


Equilibrium vapor pressure of evaporant:

ΔH = heat of vaporization

$$p_v = p_0 \exp\left(-\frac{|\Delta H|}{k_B T}\right)$$

Strong T dependence, controls deposition rate



Vapor pressure of elements employed in semiconductor materials. Dots correspond to melting points

Rely on tables: $p_{vapor} >> p_{vac}$,

$J \propto p$

Elemental metals easy to evaporate, but…

alloys
compounds

} Differential p_{vapor} so use 2 crucibles or deposit multilayers and inter-diffuse

Figure removed for copyright reasons.

Figure 3-2 in Ohring, 2001.

Oxides, nitrides

May have to deposit in oxygen nitrogen (or other) partial p

Figure removed for copyright reasons.

Table 3-1 in Ohring, 2001.

Figure removed for copyright reasons.

Graph of Vapor Pressures for the Elements. Please see:
http://www.veeco.com/learning/learning_vaporelements.asp

What would you do if you wanted to deposit a Ta or W film?

We expressed flux of residual gas:

$$J = \frac{p}{\sqrt{2\pi m k_B T}}$$

Chamber $p = 10^{-6}$ Torr $\quad J \approx 5 \times 10^{14} \left(\text{molecules} / \text{cm}^2\text{s} \right)$

The source also $\Rightarrow$ flux

$$J = \frac{p_{vap}}{\sqrt{2\pi m_{source} k_B T_{source}}}$$

Aluminum at 1000 K, $p_{vap} = 10^{-7}$ Torr (from figure)

m (species to be evaporated) = 27 amu

$J_{Al} \approx 2 \times 10^{13}$ Al/cm^2-s just above crucible

Note: 3 different temperatures: $T_{source} \approx T_{evaporant} >> T_{substrate} > T_{chamber} = T_{resid\ gas} \approx$ RT.

System NOT in thermal equilibrium

Evaporant toward substrate:	Residual gas $K >> 1$,
ballistic, hot, not in equilibrium	in equilibrium with chamber walls.

only thermal interaction a

conduction **through solid connects (weak contact).**

NO *convection* when $N_K >> 1$.

Residual gas flux on substrate: $J \approx 5 \times 10^{14} \left(\text{molecules} / \text{cm}^2\text{s} \right)$

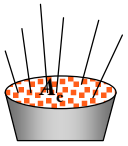
But at 1000 K: $J_{Al} \approx 2 \times 10^{13}$ Al/cm^2-s just above crucible

…. heat Al to $T > 800$ C,

use lower base pressure in chamber,

but that's not all…

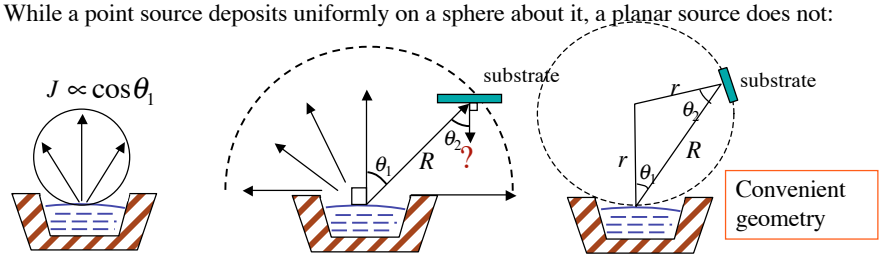
Net flux from crucible ~ $J A_c$ (units: # / t)



Mass flow out of crucible ~ $J A_c m$ (mass / t)

How much evaporant strikes substrate? At 10^{-6} Torr, trajectories are uninterrupted.

While a point source deposits uniformly on a sphere about it, a planar source does not:



Convenient geometry

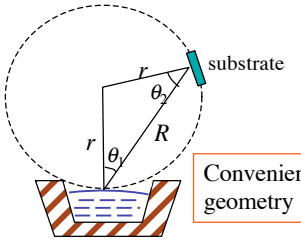
Geometric factor = $\frac{A_c}{2\pi R^2}\cos\theta_1 \overset{?}{\cos}\theta_2$ $\qquad \cos\theta_1 = \cos\theta_2 = \frac{R}{2r}$

Geometric factor = $\frac{A_c}{4\pi r^2}$

Deposition rate = $Jm\frac{A_c}{4\pi r^2}\left(\frac{m}{\text{area}\cdot t}\right)$ or $J\frac{A_c}{4\pi r^2}\left(\frac{\#}{\text{area}\cdot t}\right)$

Film growth rate $= Jm\frac{A_c}{4\pi r^2}\frac{1}{\rho_f}\left(\frac{\text{thick}}{t}\right)$

Planetary substrate holder



Convenient geometry

Figure removed for copyright reasons.

Figure 2-12 in Ohring, 2001.

Film growth rate for evaporation $= Jm\frac{A_c}{4\pi r^2}\frac{1}{\rho_f}\left(\frac{\text{thick}}{t}\right)$

$$v = \frac{p_{\text{vap}}}{\sqrt{2\pi m_{\text{source}} k_B T_{\text{source}}}}\frac{m}{\rho_m}\frac{A_c}{4\pi r^2} = \frac{p_{\text{vap}}}{\rho_m}\frac{A_c}{4\pi r^2}\sqrt{\frac{m_{\text{source}}}{2\pi k_B T_{\text{source}}}}$$

Cf. CVD $v_f = \dfrac{C_g/N}{\frac{1}{n_g}+\frac{1}{k}}$

Oxide growth: $v_{\text{ox}} = \dfrac{H\,p_g/N}{\frac{1}{h}+\frac{t_{\text{ox}}}{D}+\frac{1}{k_s}}$

In PVD growth, strike balance

$R = \dfrac{\text{deposition rate}}{\text{Surface diffusion rate}}$

$R > 1$ stochastic growth, rough

$R < 1$ layer by layer, smooth (can heat substrate)

Exercise

Deposit Al (2.7 g/cm^3) at $r = 40$ cm from 5 cm diam. crucible heated to 950 K (cf $T_{\text{melt}} \approx 950$ K) $p_{\text{Al vap}} \approx 10^{-8}$ Torr,

$p_{H_2O} = 10^{-7}$ Torr (this is not good vac.)

$A_c = \pi\left(\frac{5}{2}\right)^2$

Compare arrival rate of Al and H_2O at substrate…and calculate film growth rate

$$J_{H_2O} = \frac{\left(10^{-7}/760\right)\times 10^5}{\sqrt{2\pi\times(0.025\text{eV}\times e)\times(18/N_A)}} = 1.5\times 10^{19}\ \frac{\text{molecules}}{\text{m}^2\text{s}}$$

$$J_{\text{Al}} = \frac{\left(10^{-8}\times 10^5/760\right)}{\sqrt{2\pi\times(950k_B)\times(27/N_A)}}\left(\frac{A_c}{4\pi r^2}\right) = 6.7\times 10^{14}\ \frac{\text{atoms}}{\text{m}^2\text{s}}$$

$$v = J\frac{m_{\text{source}}}{\rho_m}\frac{A_c}{4\pi r^2} \approx 4.35\times 10^{-13}\ m/s$$ slow!

Check my math:
Avogadro's number,
N_A = 6.02 x 10^{23} (atoms/mole)
but in MKS
N_A = 6.02 x 10^{26} (atoms/kg-mole)

Leave shutter closed so initial Al deposition can getter O_2 and H_2O.

Hard to achieve higher deposition rate; use better vac., or sputter deposition.

$$J_{Al} = \frac{\left(5\times10^{-7}\times10^{5}/760\right)}{\sqrt{2\pi\times\left(1010k_B\right)\times\left(27/N_A\right)}}\left(\frac{A_c}{4\pi r^2}\right) = 1.0\times10^{19}\ \frac{\text{atoms}}{\text{m}^2\text{s}}$$

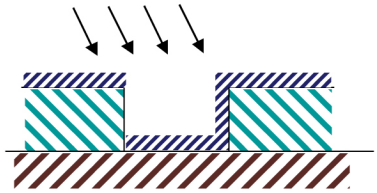
$$v = J\frac{m_{source}}{\rho_m}\frac{A_c}{4\pi r^2} \approx 1.66\times10^{-9}\ \ m/s$$

17 Å/s

Evaporation Characteristics of Materials

Figure removed for copyright reasons.
Table 3-3 in Ohring, 2001.

Step coverage is poor in evaporation (ballistic) - Shadow effects



Heat substrate to increase surface diffusion.

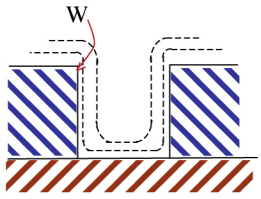
$$D^S = D_0^S \exp\left(-\frac{E_a^{Surf}}{kT}\right) \qquad E_a^S << E_a^{bulk}$$

By contrast, metal CVD and sputtering => better step coverage

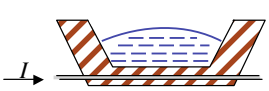
e.g. $WF_6 + 3H_2 \rightleftarrows W + 6HF$

$\Delta G \approx 70\,^{kJ}/_{mole}$ (0.73eV)

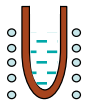
Can do below 400°C



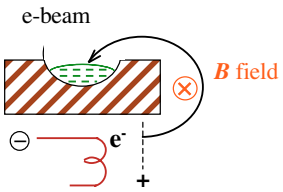
We mentioned these methods of heating charge:



Resistive heater



RF-induction heater

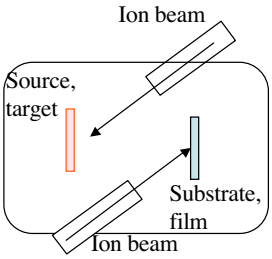


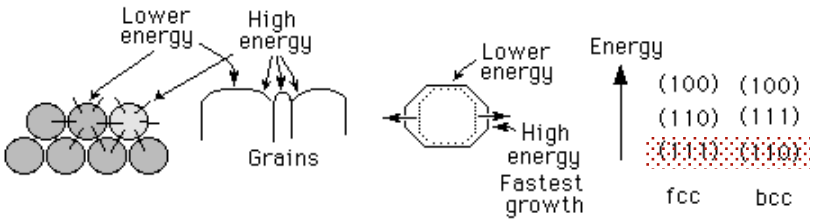
Can you suggest other methods?

- Laser: Pulsed Laser Deposition (PLD), laser ablation
- Ion beam deposition (IB)D:

  keep substrate chamber at low *P*, bring in ion beam through differentially pumped path.

  Can also use ion beam on film to add energy (ion beam assisted deposition, IBAD)

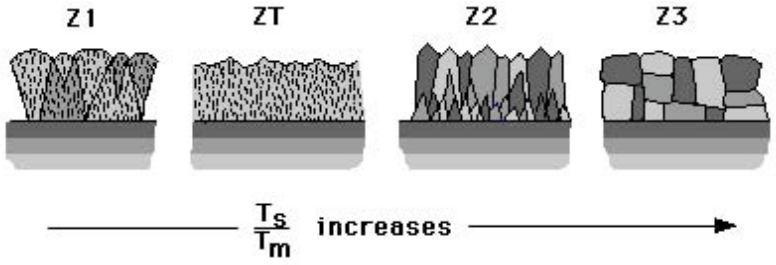




Surface energy in a growing film depends on the number of bonds the adsorbed atom forms with the substrate (or number unsatisfied).

This depends on the crystallography of the surface face and on the type of site occupied (face, edge, corner, crevice). Macroscopically, a curved surface has higher surface energy (more dangling bonds) than a flat surface.

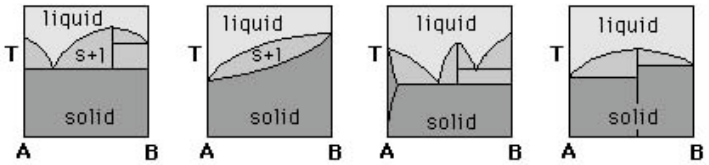
Microstructure types observed in sputtered films
with increasing substrate temperature
normalized to melting temperature of deposited species.



Quenched growth **Thermally activated growth**

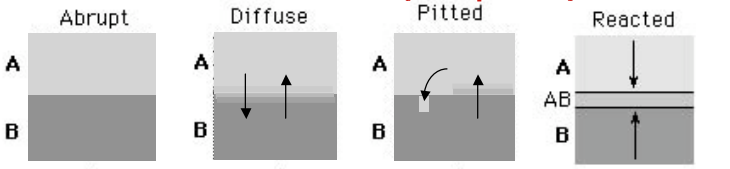
$\lambda_{surf} < a$ $\lambda_{surf} < a$ $T_s/T_m > 0.3$ $T_s/T_m > 0.5$

Four characteristic *equilibrium*, binary phase diagrams.



low mutual solubility | Complete solubility | B diffuses in A, A does not in B | AB compound, A, B not soluble in AB

Interfaces between dissimilar materials (non-equilibrium)

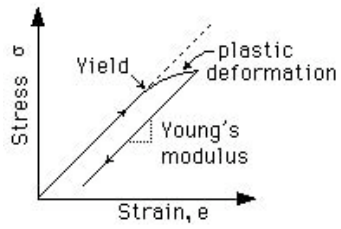


Co/Cu, Co/Au | Ni/Cu, Ni/Cr | Al/Si | self passivating

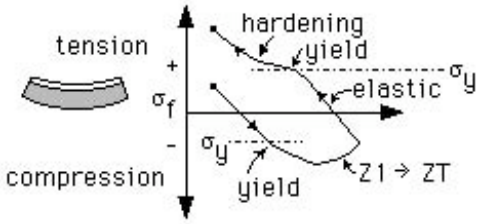
Examples

Si-Ti **Si-Ge.** **B diffuses into A, A swells. A forced by swelling into B as a second phase.** **GaAs compound forms at interface**

Schematic stress strain curve showing plastic deformation beyond the yield point.



Upon thermal cycling, a film deposited under conditions that leave it in tensile stress may evolve through compression then even greater tension .



Summary: Evaporation

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  - Gas phase reactants: $p_g \approx 1$ mTorr to 1 atm.
  - **Good step coverage, $T >$ 350 K**
- We saw **sputtering**
  - Noble gas ions & e^- (+ reactive gas) $p \approx 10$ mTorr
  - High rate, reasonable step coverage
  - Extensively used in electrical, optical, magnetic devices.
- Now see **evaporation:**
  - Source material heated, $p_{eq.vap.} = \sim 10^{-3}$ Torr, $p_g < 10^{-6}$ Torr
  - Generally no chemical reaction (except in "reactive" deposition),
  - λ = 10's of meters, Knudsen number $N_K >> 1$
  - Poor step coverage; alloy fractionation: Δp_{vapor}
  - Historical (optical, electrical)