

There is however another term in the equation (inequality) which affects the way growth occurs (3D vs. 2D)

---

the free enthalpy change in going from vapor to solid

$$\Delta G$$

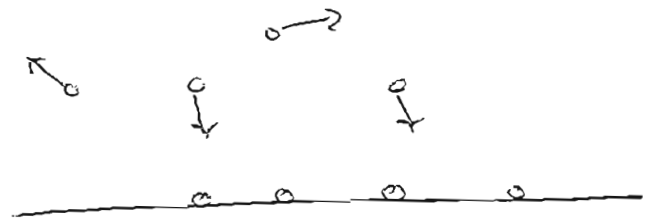
Enthalpy is defined as

$$G = U + PV$$

↑            ↑  
state        internal  
variable    energy

$$\Rightarrow dG = dU + PdV + VdP$$

in going from vapor to ~~the~~ surface adsorbate, there is a change in  $G$



Since gas atoms can be re-emitted from the surface back into the same volume,  $dV = 0$

$$\Rightarrow dG = dU + VdP$$

since the temperature is constant,  $dU = 0$

$$\Rightarrow dG = VdP$$

Therefore the free enthalpy change is

$$\int dG = \int_{P_0}^{P_0} V dP$$

$$PV = NkT$$

$$V = \frac{NkT}{P}$$

$$\Rightarrow \Delta G = \int_P^{P_0} \frac{NkT}{P} dP$$

$$\Delta G = NkT \ln P_0/P$$

per atom,

$$\Delta G_{\text{atom}} = kT \ln P_0/p$$

Since  $p_0$  is the equilibrium vapor pressure defined by the temperature of the surface

and since  $p$  is the incident pressure due to the evaporation source (e.g. effusion cell in MBE) defined by the flux rate

$$R = \frac{P}{\sqrt{2\pi m kT}}$$

Luth, p.100

$$\text{or } R = \frac{P}{2\sqrt{3} m kT}$$

Lecture 3  
Notes

Therefore, ( $P > P_0$ )

$$\Rightarrow \Delta G_{\text{atom}} = kT \ln P_0/p < 0$$

This energy reduction is added to the formation free energy of the surface islands and therefore

$$\begin{aligned} \text{surface formation energy} &= \gamma_F + \gamma_{S/F} + CkT \ln P_0/P \\ \text{for islands} & \\ \text{(per unit area)} & \end{aligned}$$

$C$  is a constant relating the ~~number~~ unit area to the number of atoms in a unit area

So,

$$\text{layer growth: } \gamma_s \geq \gamma_F + \gamma_{S/F} + CkT \ln P_0/P$$

$$\text{island growth: } \gamma_s < \gamma_F + \gamma_{S/F} + CkT \ln P_0/P$$

$$S = P/P_0 = \text{supersaturation}$$

example

$$P_0 = 10^{-11} \text{ Torr}$$

$$P = 10^{-5} \text{ Torr} \Rightarrow S = 10^6$$

$$\ln 10^{-6} = -13.8 \dots$$

$$\text{suppose } kT = .026 \text{ eV}$$

$$\Rightarrow kT \ln P_0/P = -.359 \text{ eV per atom}$$

The implication of supersaturation is important  
It means that layer growth will be enhanced  
for larger values of supersaturation

$C k T \ln P_0/P$  reduces the  
overlayer formation energy

---

---

### The Capillary Model of Nucleation

based purely on surface and interface energies  
and the vapor  $\rightarrow$  solid enthalpy change of a gas  
total free enthalpy for formation of 3D islands is

$$\begin{aligned}\Delta G_{3D} &= j k T \ln(P_0/P) + j^{2/3} X \\ &= -j \Delta \mu + j^{2/3} X\end{aligned}$$

with  $j$  = number of atoms of the island

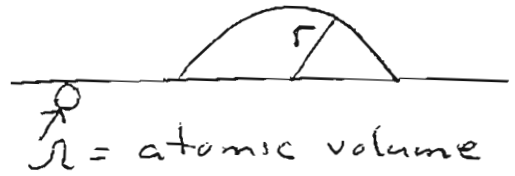
$X$  contains the free energy terms

$$X = \sum_k C_k \gamma_F^{(k)} + C_{S/F} (\gamma_{S/F} - \gamma_S)$$

$j^{2/3}$  represents the number of surface atoms  
for the 3-D island containing  $j$  atoms

for hemispherical nucleus

hemispherical 3D island



can write explicitly

$$\Delta G_{3D} = -\frac{1}{2} \frac{4}{3} \pi r^3 \Omega^{-1} \Delta \mu + 2\pi r^2 \gamma_F + \pi r^2 (\gamma_{S/F} - \gamma_F)$$

comparing to

$$\Delta G_{3D} = -j \Delta \mu + j^{2/3} \left[ \sum_k C_k \gamma_F^k + C_{S/F} (\gamma_{S/F} - \gamma_S) \right]$$

$$\pi r^2 = j^{2/3} C_{S/F}$$

$$\Rightarrow C_{S/F} = \pi r^2 j^{-2/3}$$

$$j = \frac{\frac{2}{3} \pi r^3}{\Omega}$$

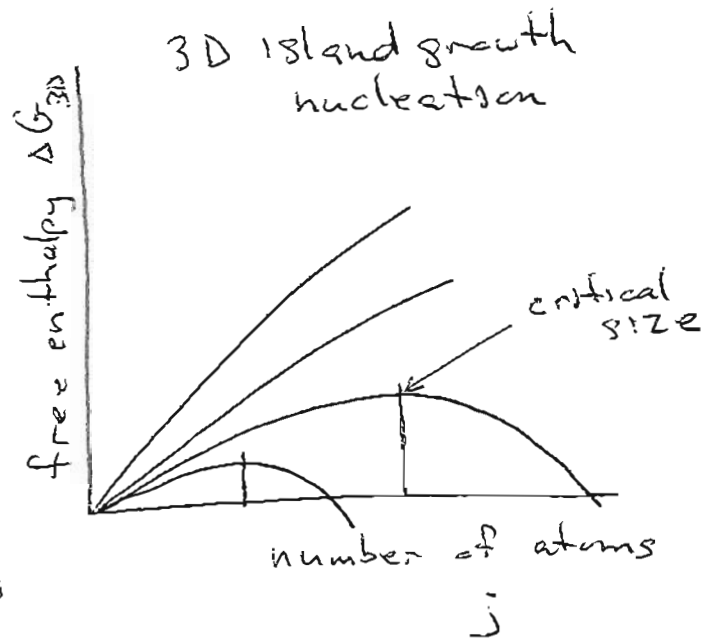
$$\Rightarrow C_{S/F} = \pi r^2 \left( \frac{2\pi r^3}{3\Omega} \right)^{-2/3}$$

$$= \pi \pi^{-2/3} \left( \frac{r^3 \Omega 3}{2 r^3} \right)^{2/3}$$

$$= \pi^{1/3} \left( \frac{3\Omega}{2} \right)^{2/3}$$

At some critical island size  $j_{\text{crit}}$ , the island will become thermodynamically stable.

→ can solve for that size → set derivative = 0



- see Lüth p. 105

---

$$\begin{aligned}\frac{d(\Delta G_{3D})}{dj} &= \frac{d}{dj} (-j\Delta\mu + j^{2/3}X) \\ &= -\Delta\mu + \frac{2}{3}j^{-1/3}X = 0 \\ \Rightarrow j^{-1/3} &= \frac{\Delta\mu}{\frac{2}{3}X}\end{aligned}$$

$$j_{\text{crit}} = \left(\frac{2X}{3\Delta\mu}\right)^3$$

See that  $j_{\text{crit}} \propto X^3$  and  $\left(\frac{1}{\Delta\mu}\right)^3$

qualitatively make sense?

$$X = \sum_k C_k \gamma_F^k + C_{S/F} (\gamma_{S/F} - \gamma_S)$$

✓ If film and interface energies are larger, then those faces of the crystallite are less stable so a bigger island is needed to stabilize it.

✓ If the surface (substrate) free energy is larger, then the bare surface is also less stable so that an island is favorable at smaller size

✓ If the  $\Delta\mu \propto \ln(\text{supersaturation})$  is larger, then incident flux is higher so that critical island size is smaller

$$\Delta\mu = -kT \ln(P_0/P) = kT \ln(P/P_0)$$

Can also use Capillary Model for 2D Nucleation

$$\Delta G_{2D} = -j \Delta \mu + j(\gamma_F + \gamma_{\gamma F} - \gamma_S) \Omega^{2/3} + j^{1/2} \Upsilon$$

$j$  = number of atoms

$\Omega^{2/3}$  = "area" of 1 atom

$j \Omega^{2/3}$  = area of  $j$  atoms

$j^{1/2} \propto$  number of edge atoms

$\Upsilon$  describes the formation energy per edge atom

$$\Upsilon = \sum_l C_l \gamma_E^l$$

$l$  describes different crystallographic edges

$\gamma_E^l$  is the edge free energy of edge  $l$

This can also be written explicitly for a circular 2D island, and the behavior is similar to the 3D case.

There will be a critical 2D island size; ~~below~~ below the critical size, islands will not be stable

A key concept is the saturation ~~of~~ of the surface of the substrate

- related to the nucleation density and nucleation rate  $J_N$

$$J_N = K \exp[-\Delta G^*(i.c.) / kT]$$

eg 3.45,  
Lüth

at lower temperatures,  $T$  is smaller

$\Rightarrow$  larger nucleation rate

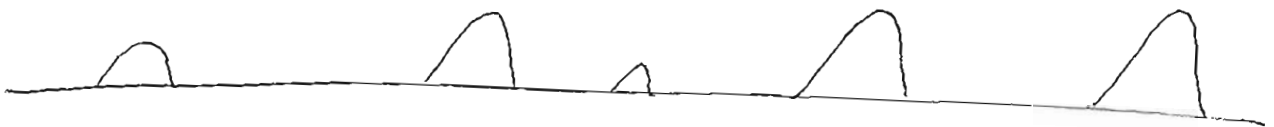
low  $T$

many small clusters



high  $T$

fewer, larger clusters



Note: when critical island sizes approach only a few atoms, the "capillary" model may not be valid

Note: "capillary" model also does not include certain effects due to substrate steps, defects, dislocations, etc.  $\Rightarrow$  limited

# Probing the growth mode

## Experimental Methods

1. use surface sensitive methods which are also chemically sensitive,

i.e.

1. Auger electron spectroscopy

2. X-ray photoelectron spectroscopy

Measure substrate and film signals vs. the amount of deposition

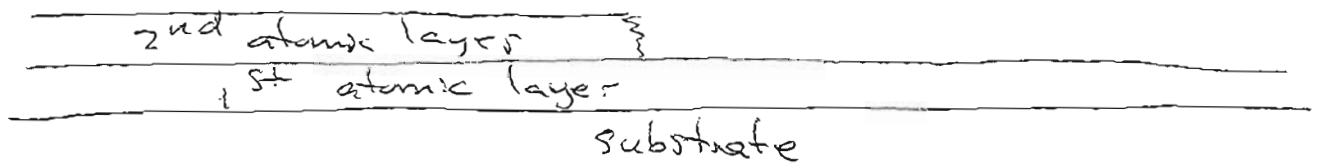
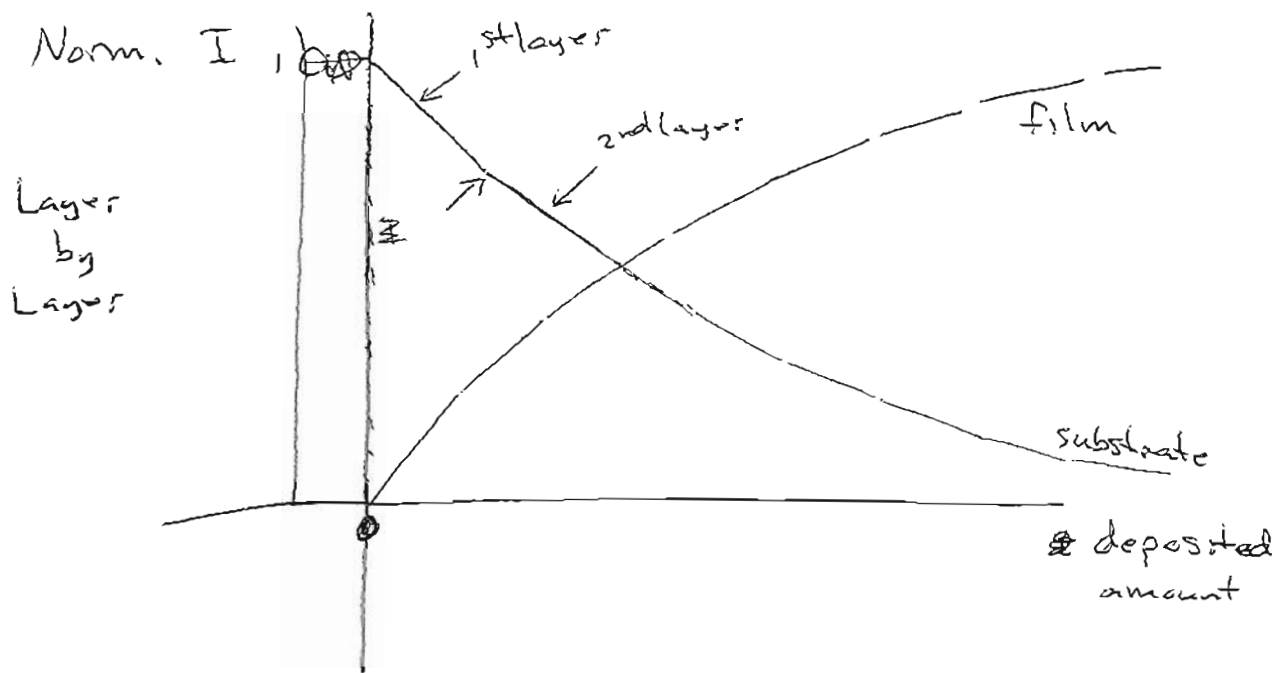
For uniform coverage vs. deposited amount, expect simple absorption behavior, as in nuclear absorption

$$I^F/I_\infty^F = 1 - \exp(-\theta'd/\lambda) \quad 3.47 \text{ Lieth}$$

$$I^S/I_0^S = \exp(-\theta'd/\lambda) \quad 3.48 \text{ Lieth}$$

If the growth behavior is layer-by-layer, expect good agreement with the simple absorption behavior

Note: the intensity should fall off linearly with the completion of a single layer



Deviations from the ideal absorption behavior can indicate other types of growth modes

