## *Surface Physics 2010*

# Growth of Thin Films

UNI
BASEL

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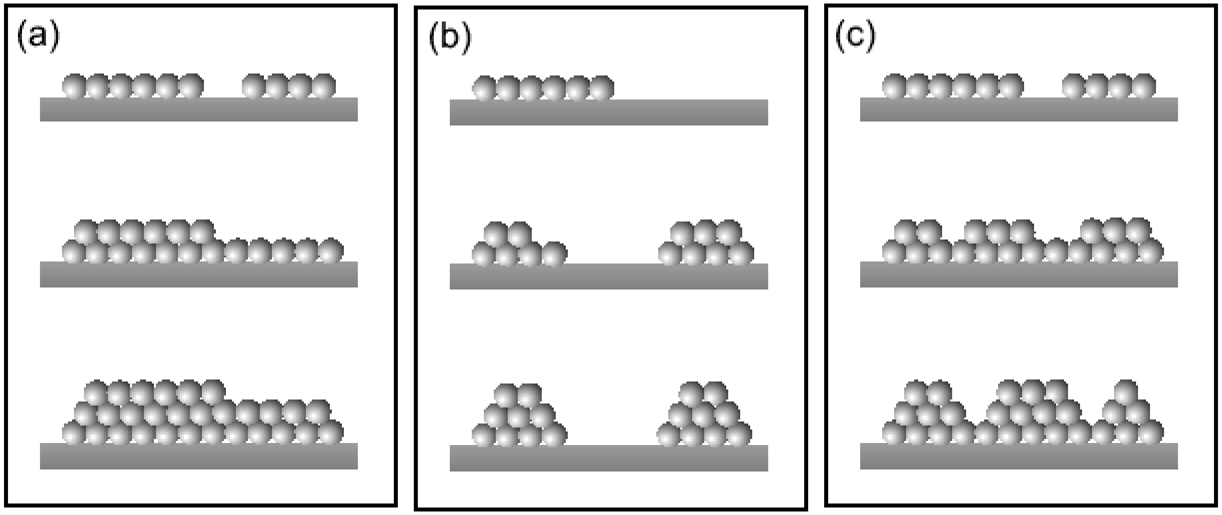
NCCR Nanoscale Science

# Growth Modes

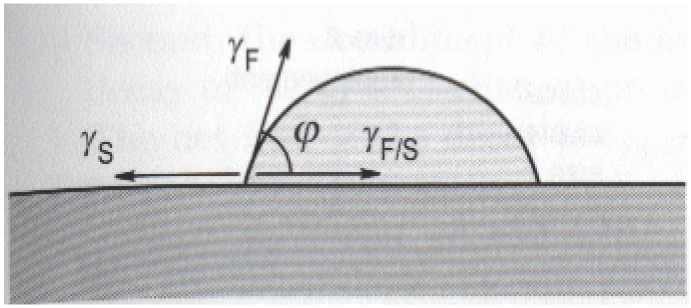


(a) **Layer-by-layer** or **Frank-van der Merve** mode → 2D islands
(b) **Island** or **Vollmer-Weber** mode → 3D islands
(c) **Layer plus island** or **Stranski-Krastanov** mode → 2D layer + 3D islands

# Growth Modes

- **Surface tension** $\gamma$ = work required to build a surface of unit area

  (≡ force per unit length)

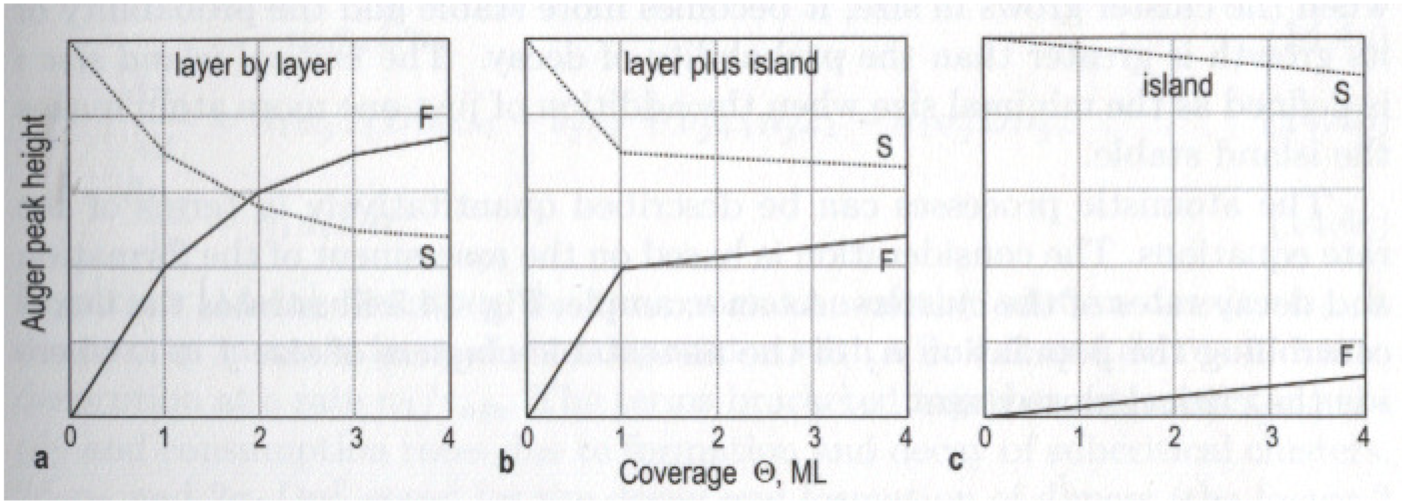


$$\gamma_S = \gamma_{SF} + \gamma_F \cos\varphi$$

- Island growth: $\varphi > 0$ → $\gamma_S < \gamma_{SF} + \gamma_F$
- Layer-by-layer growth: $\varphi = 0$ → $\gamma_S \geq \gamma_{SF} + \gamma_F$

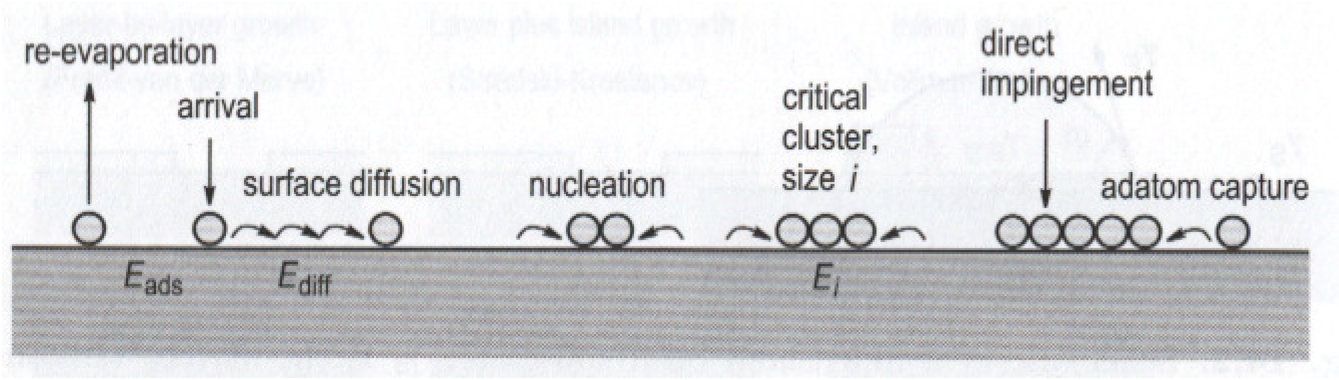
# Growth Modes

- Exp: Monitor Auger signals from film and substrate while depositing...



# Island Number Density

- Nucleation and growth on surfaces:



- Diffusion coefficient:

$$D = \frac{\nu}{4n_0}\exp\left(-\frac{E_{diff}}{k_B T}\right)$$

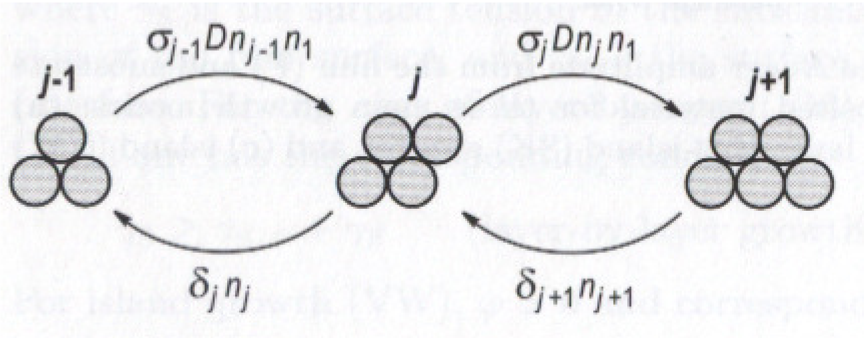
- Residence time:

$$\tau_{ads} = \frac{1}{\nu}\exp\left(\frac{E_{ads}}{k_B T}\right)$$

- **Critical island size** $i$ **:** minimal size when the addition of one atom makes the island stable

# Island Number Density

- Capture and decay processes → cluster size



- Rate equations:

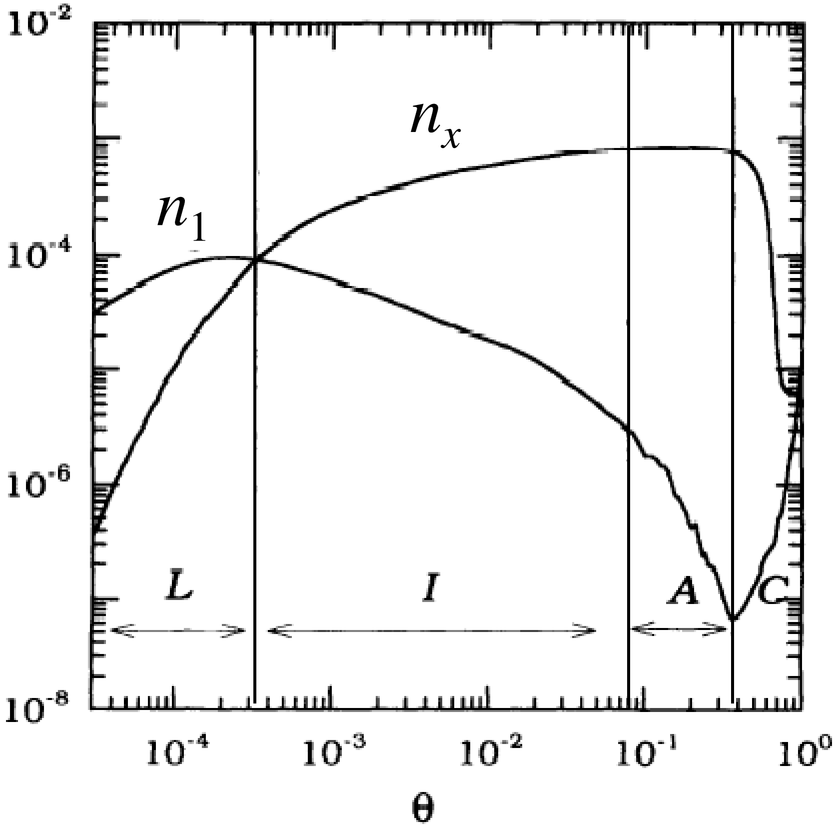
$$\frac{d\overset{\text{adatom density}}{n_1}}{dt}=\underset{\text{deposition rate}}{R}-\frac{n_1}{\tau_{ads}}+\overset{\text{subcritical clusters}}{\boxed{\left(2\delta_2 n_2+\sum_{j=3}^{i}\delta_j n_j-2\sigma_1 Dn_1^2-n_1\sum_{j=2}^{i}\sigma_j Dn_j\right)}}-\underset{\text{stable clusters}}{\boxed{n_1\sigma_x Dn_x}}$$

$$\frac{dn_j}{dt}=n_1\sigma_{j-1}Dn_{j-1}-\delta_j n_j+\delta_{j+1}n_{j+1}-n_1\sigma_j Dn_j \longrightarrow \text{metastable clusters}$$

$$\frac{dn_x}{dt}=n_1\sigma_i Dn_i \longrightarrow \text{stable clusters}$$

# Island Number Density

- Numerical solution for $i = 1$ without re-evaporation (Amar, Family and Lam, PRB 1994):



- Four coverage regimes are found

# Island Number Density

**(1) Low-coverage nucleation regime:** $n_1 >> n_x$

- In such case:

$$n_1 \propto \Theta \qquad n_x \propto \Theta^3$$

When $n_x \sim n_1$ → **(2) Intermediate-coverage regime**

- In such case:

$$n_1 \propto \Theta^{-1/3} \qquad n_x \propto \Theta^{1/3}$$

When mean island separation ~ mean free path of adatoms

→**(3) Aggregation regime** ($\Theta \sim$ 0.1-0.4 ML)

When the island join together

→**(4) Coalescence and percolation regime**

# Island Number Density

- Saturation density (Venables et al., 1984):

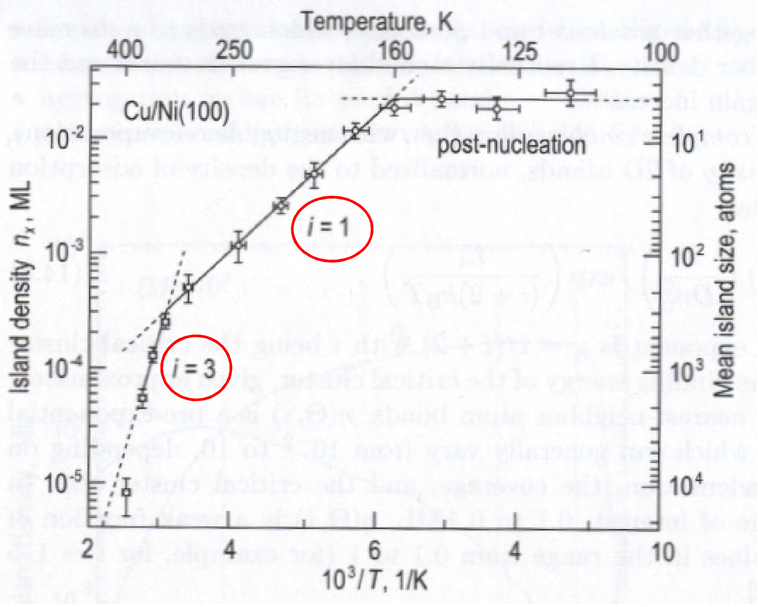
χ

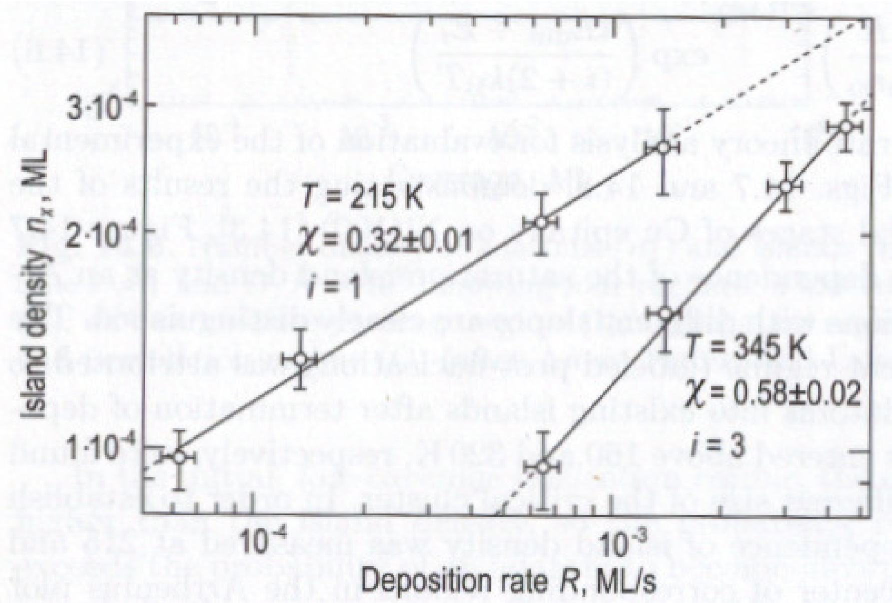
$$\boxed{n_x = n_0 \eta(\Theta, i) \left( \frac{4R}{\nu_0 n_0} \right)^{\frac{i}{i+2}} \exp\left( \frac{iE_{diff} + E_i}{(i+2)k_B T} \right)},$$

binding energy
of critical cluster

$$\eta(\Theta, i) \sim 0.1 - 1$$

- Example: Cu on Ni(100) (Müller et al., PRB 1996)





# Island Shape

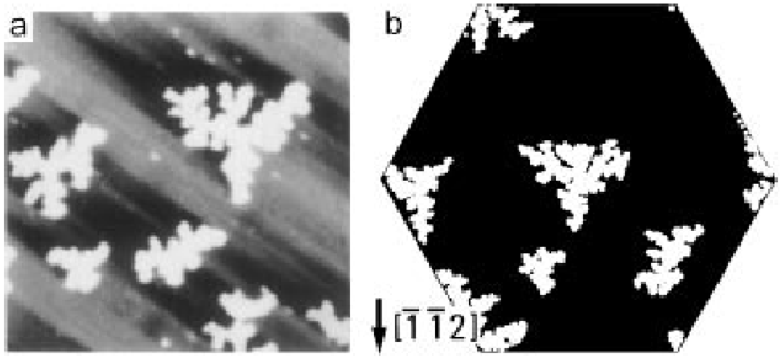
- At low T (slow edge diffusion): **ramified islands**
- **Diffusion-limited-aggregation (DLA) model** (Witten & Sander, PRL 1981):

- Adatoms stick at islands
- Fractal shape
- Branch thickness ~ 1 atom
- No influence of lattice geometry

- In real growth (STM experiments):
  - Fractal shape
  - Branch thickness > 1 atom
  - Influence of lattice geometry

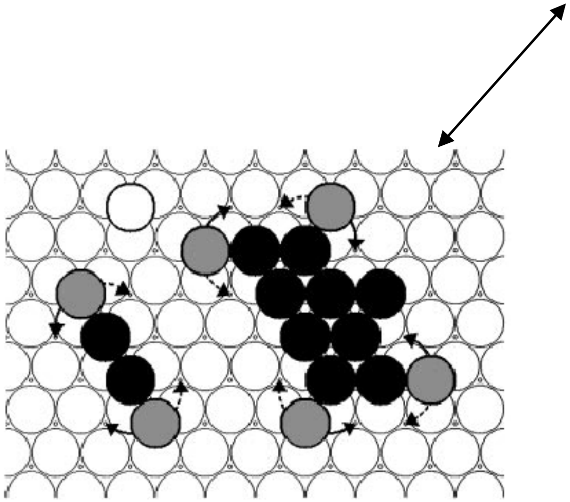
# Island Shape

- Example: Pt/Pt(111) (Hohage et al., PRL 1996)



experiment simulation

- Branch thickness ~ 4 atoms
- Trigonal symmetry

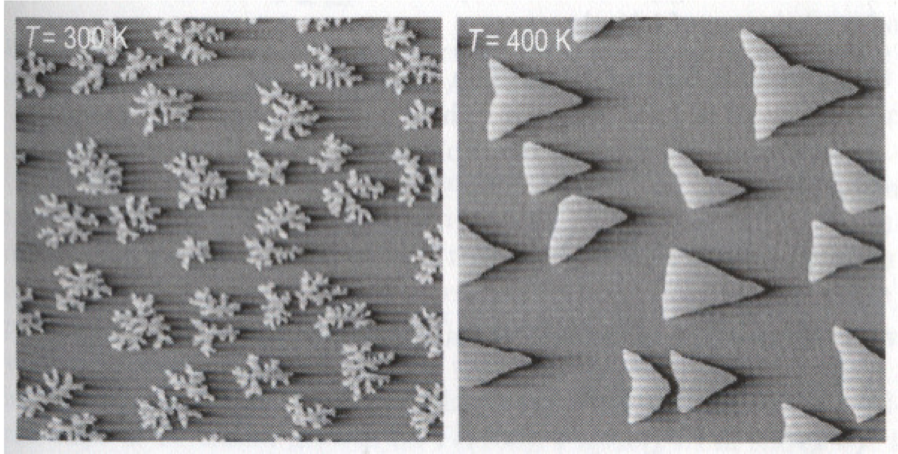


- Higher coordination is preferred

# Island Shape

- At higher T: **compact islands**
- Example: Pt/Pt(111) (Bott et al., PRL 1992)

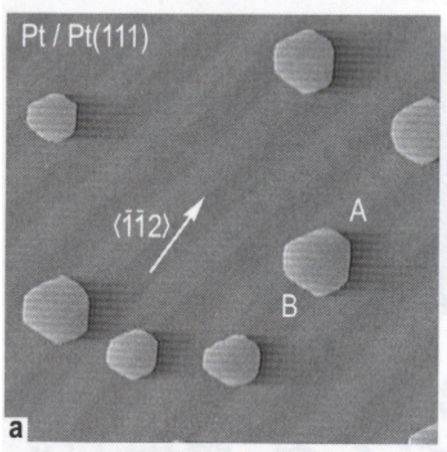
300 K



400 K

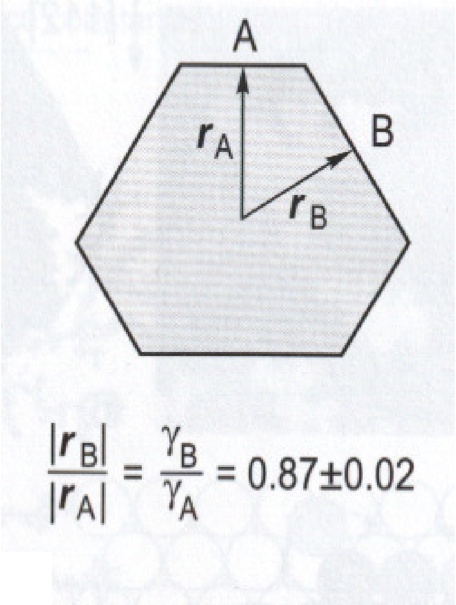
- The equilibrium shape is hexagonal:

(deposition at 425 K + annealing at 700 K)



# Island Shape

- **2D Wulff theorem:** In a 2D crystal at equilibrium, the distances of the borders from the crystal center are proportional to their free energy per unit length



- For Pt(111): B/A ~ 0.87

# Island Size Distribution

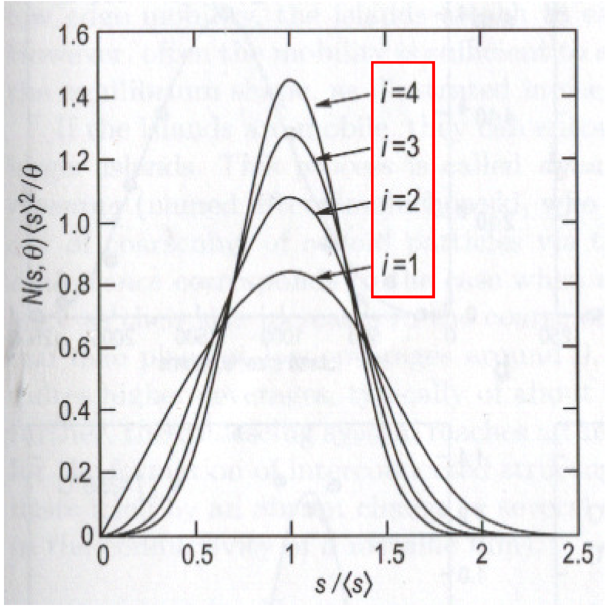
- **Island size distribution** depends on:
  - Critical island size
  - Coverage
  - Substrate structure
  - “Coarsening” (at high Θ)

- From **scaling theory** (Amar et al., PRB 1994):

$$N_s = \frac{\Theta}{\langle s \rangle^2} f_i\left(\frac{s}{\langle s \rangle}\right)$$

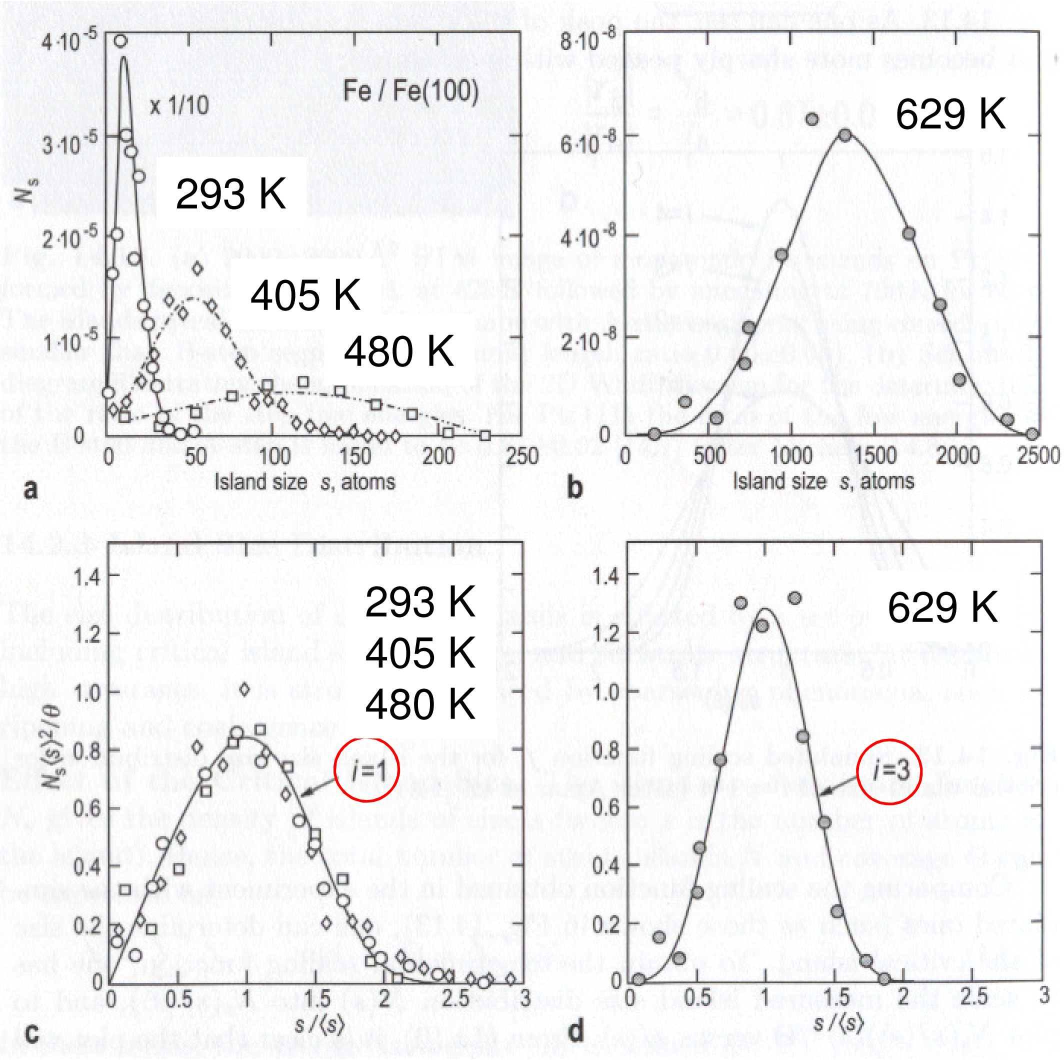
- Comparing with experimental results

→ critical island size



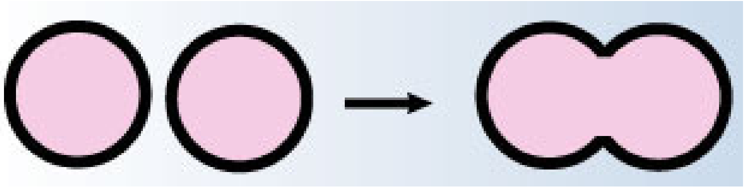
# Island Size Distribution

- Example: Fe on Fe(100) (Stroscio et al., PRL1993, Amar et al., PRB 1994)



# Coarsening Phenomena

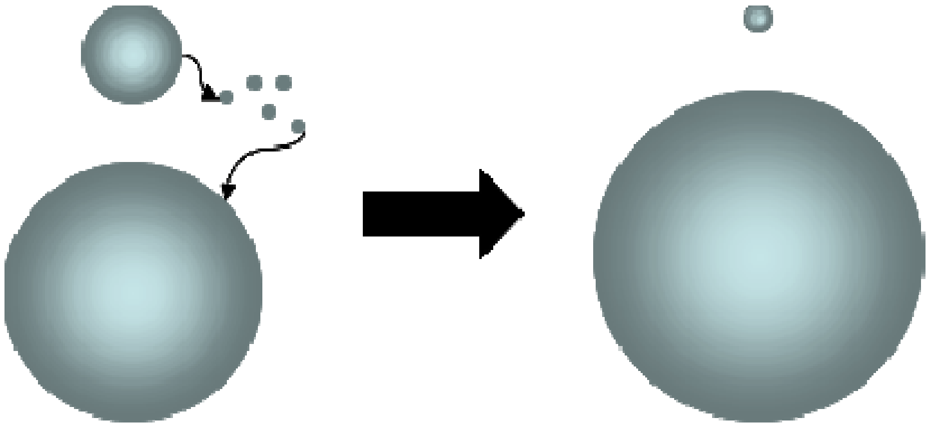
**1) Coalescence**:



- At 0.1 ML coverage: **dynamic coalescence** (**Smoluchowski ripening**)
- At 0.4-0.5 ML: **static coalescence**
- Higher coverages → **percolation** growth (→ change of physical properties!)

# Coarsening Phenomena

**2) (Ostwald) Ripening**:



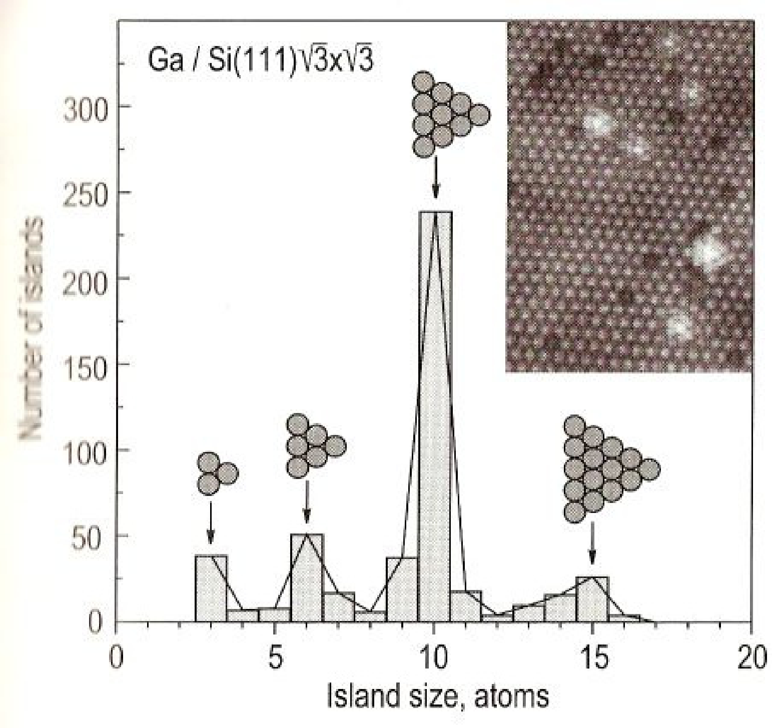
- Chemical potential of a circular island:

$$\mu(r) \propto \frac{\gamma}{r}$$

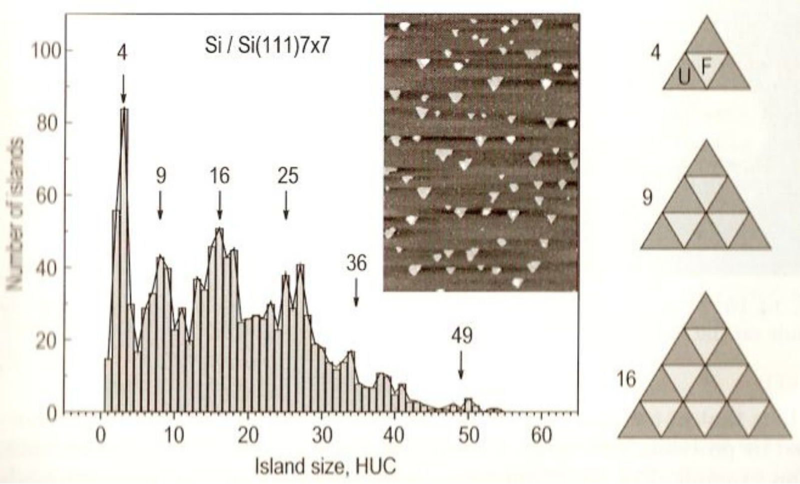
Reducing free energy → net flow from smaller to larger islands!

# Magic Islands

- Ga on Si(111)√3x√3 (Lai & Wang, PRL 1998):



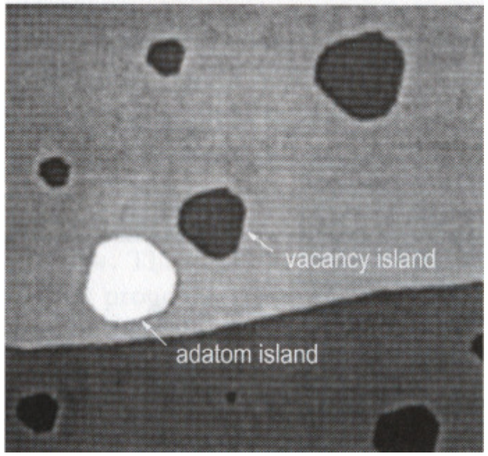
- Si on Si(111)7x7 (Voigtländer et al., PRL 1998):



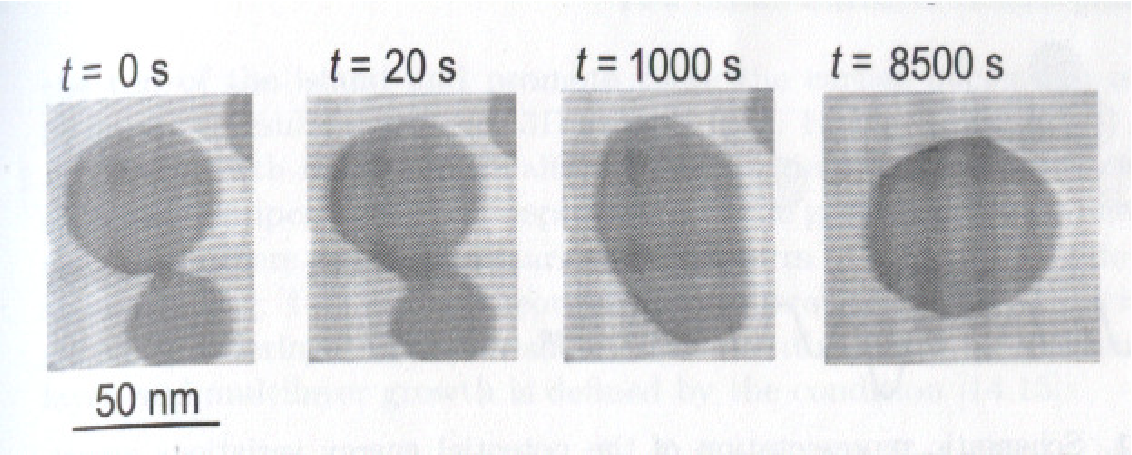
Formation of a new row → high energy cost!

# Vacancy Islands

- Ion bombardment → formation of **vacancy islands**

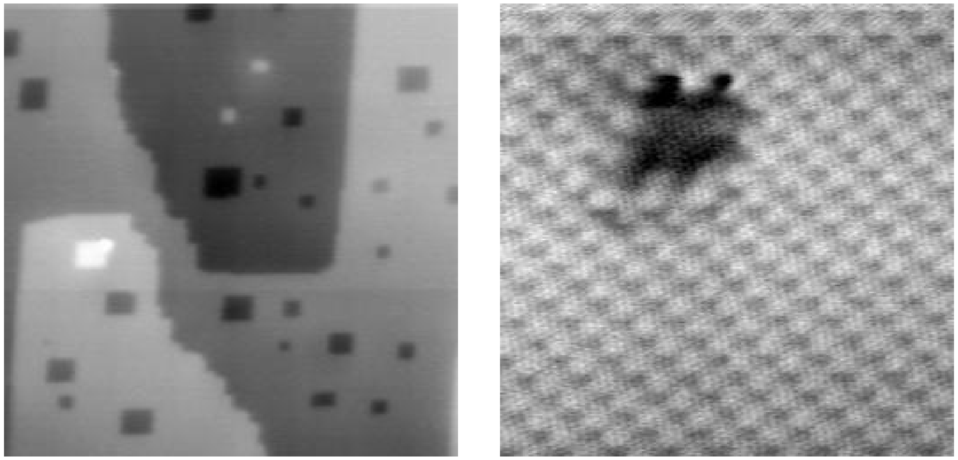


- Analogies with adatom islands



# Vacancy Islands

- Electron bombardment on insulating surfaces (Bennewitz et al., SS 2001):



KBr(100)

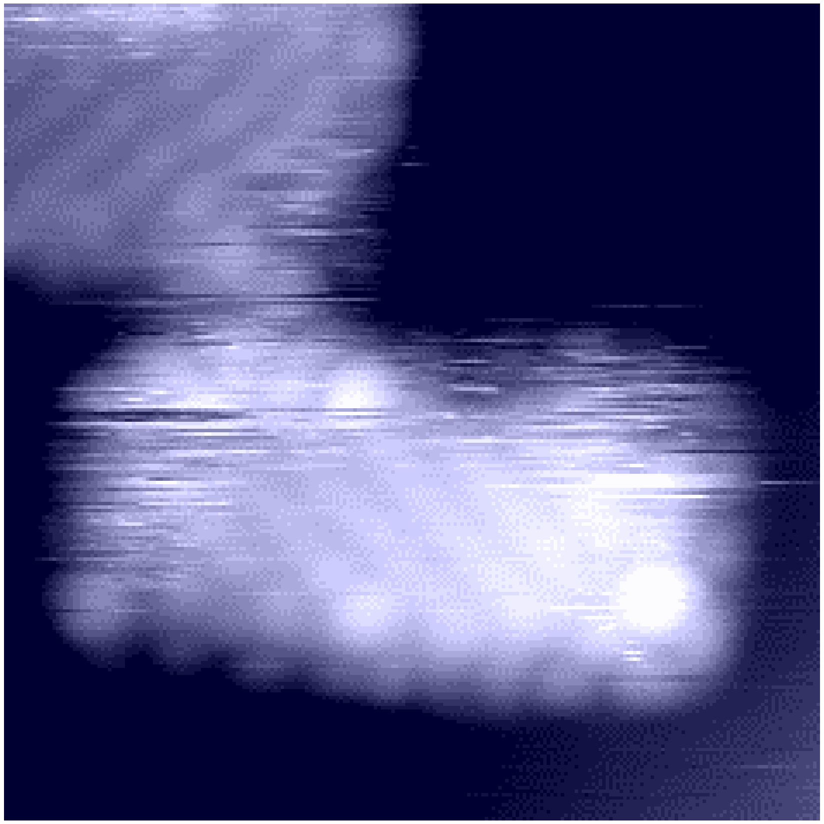
- Irradiation with 1 keV electrons at 130 ºC

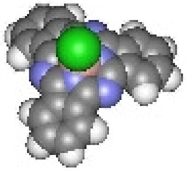
- Rectangular pits with area of 1x1 $nm^2$ up to 30x30 $nm^2$

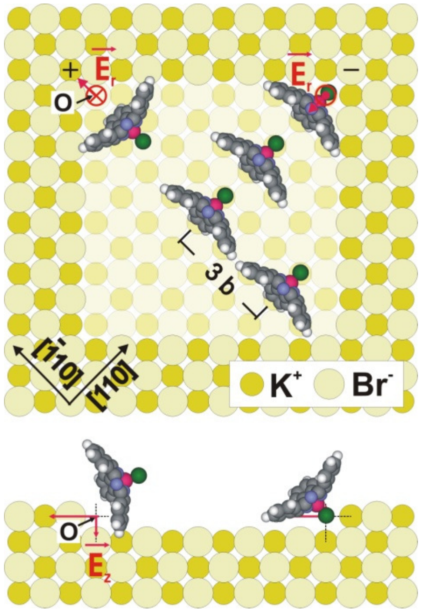
- 1 ML deep (0.33 nm)

# Vacancy Islands

- Vacancy islands can be used as <u>molecular traps</u> (Nony et al., NL 2004)

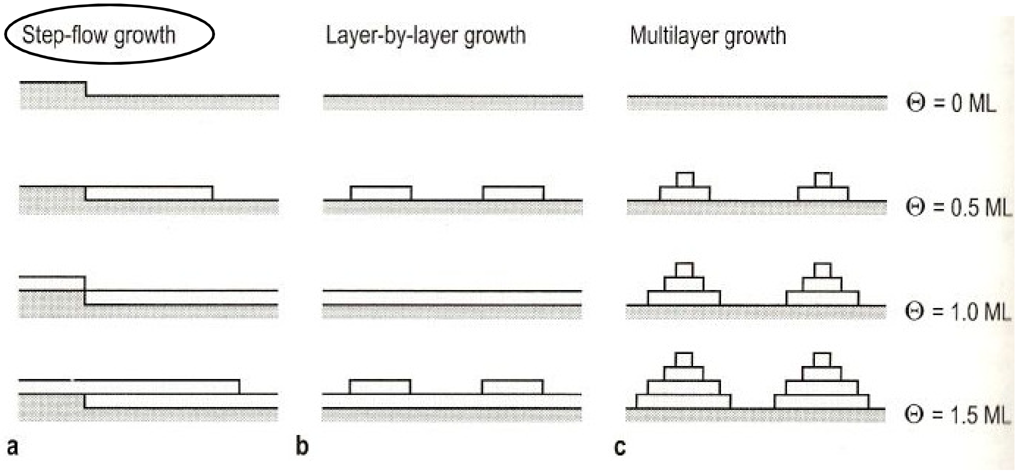




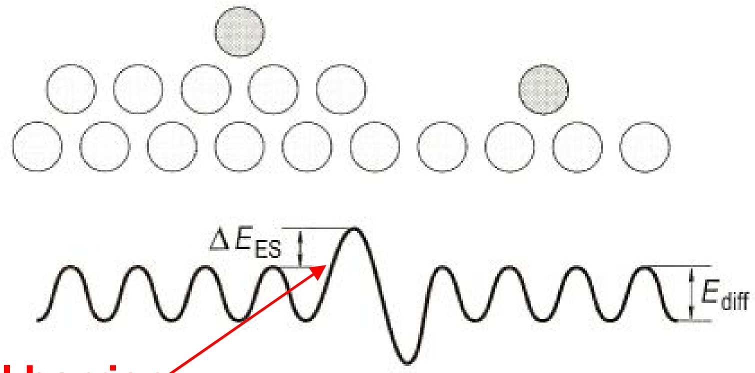


# Kinetic Effects in Homoepitaxy

- Thermodynamics → Layer-by-layer growth but…
- Kinetic processes → Other growth modes are possible!



- **Interlayer** mass transport:

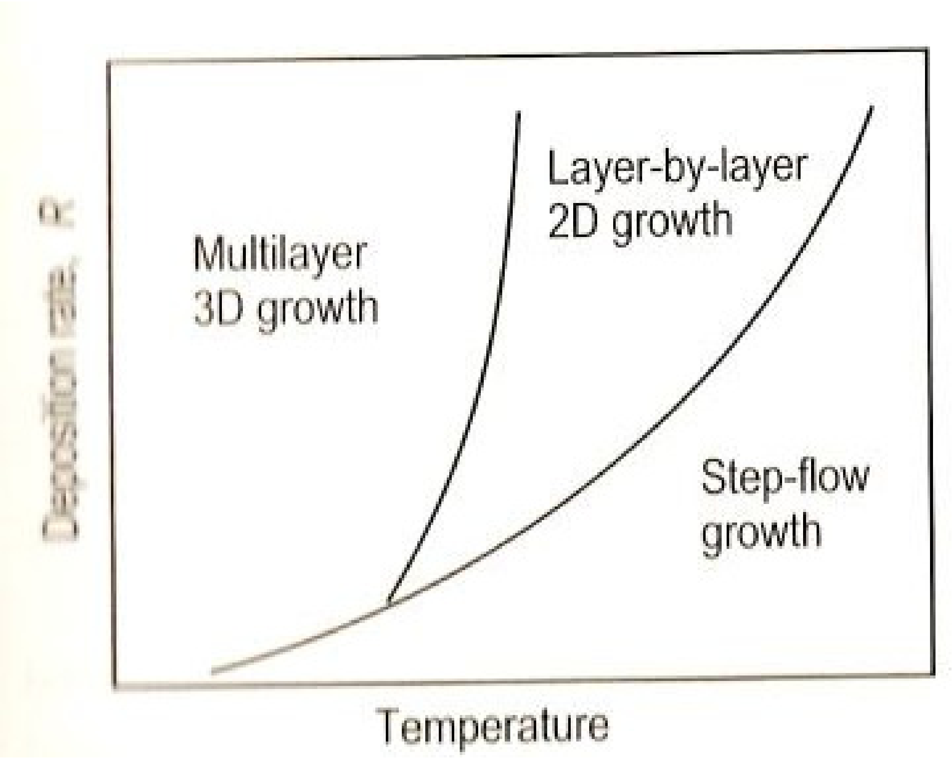


**Ehrlich-Schwöbel barrier**

# Kinetic Effects in Homoepitaxy

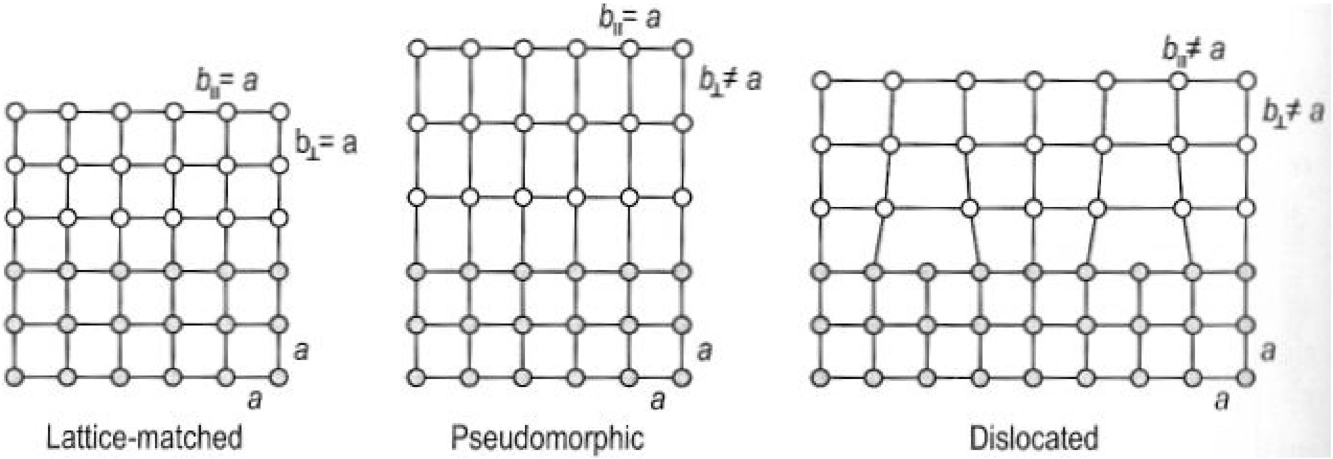
- Deposition rate and Temperature are important!

- Growth mode diagram (Rosenfeld et al., 1997):



# Strain Effects in Heteroepitaxy

- Heteroepitaxy growth modes:

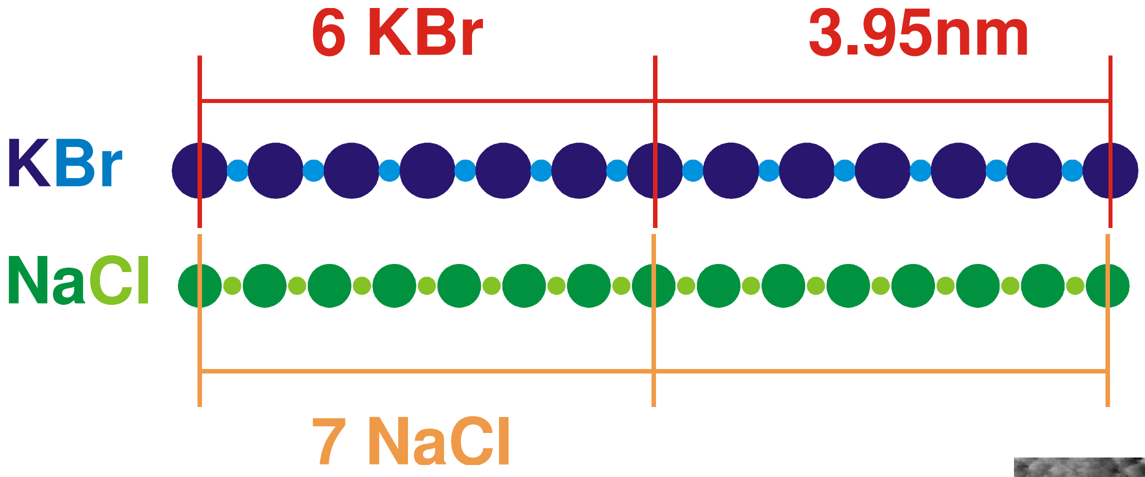


- Lattice **misfit** → elastic strain and dislocations

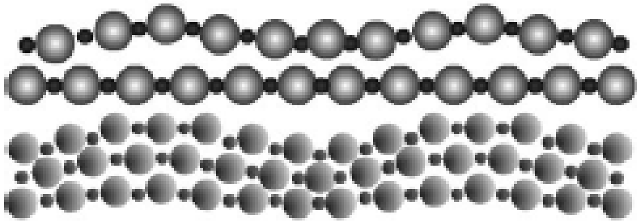
- Pseudomorphic growth below critical misfit and film thickness

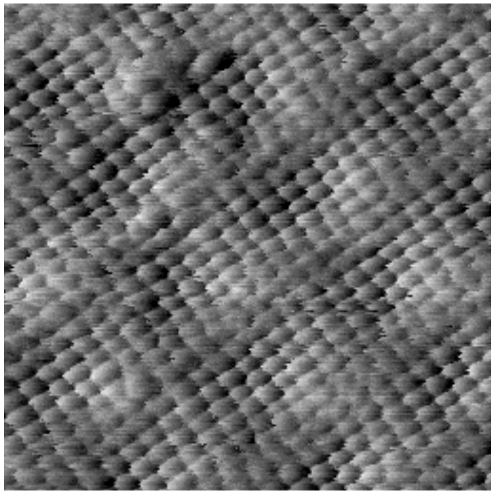
# Strain Effects in Heteroepitaxy

- Heteropitaxy on insulating surfaces (Maier et al., PRB 2007):

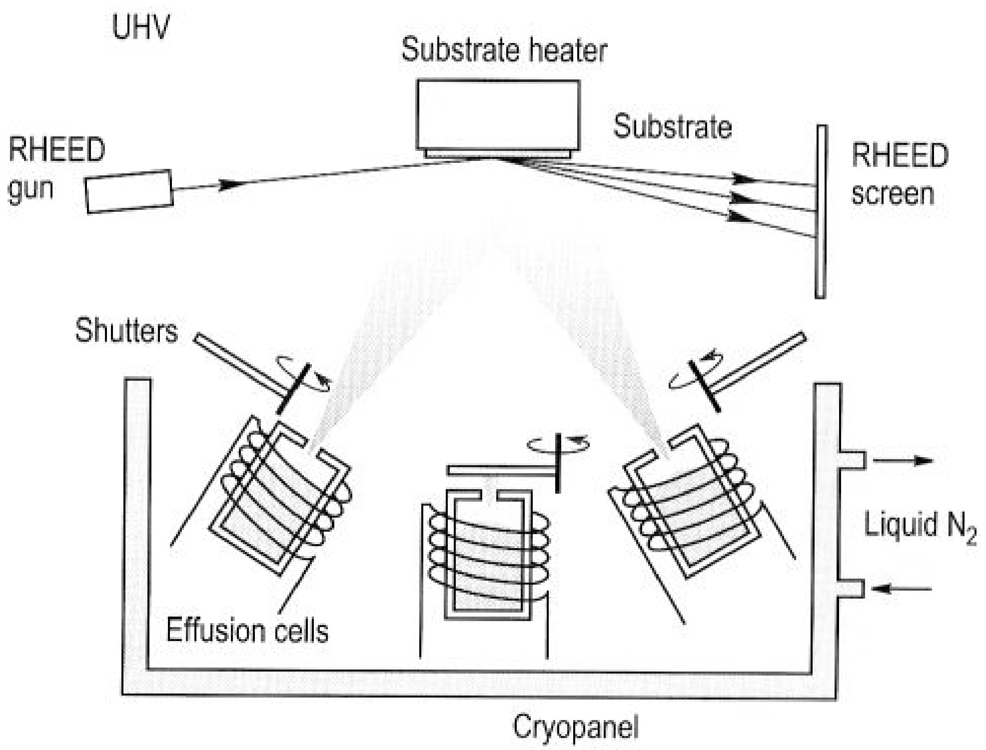


- A “Moiré pattern” appears (also in the substrate?)





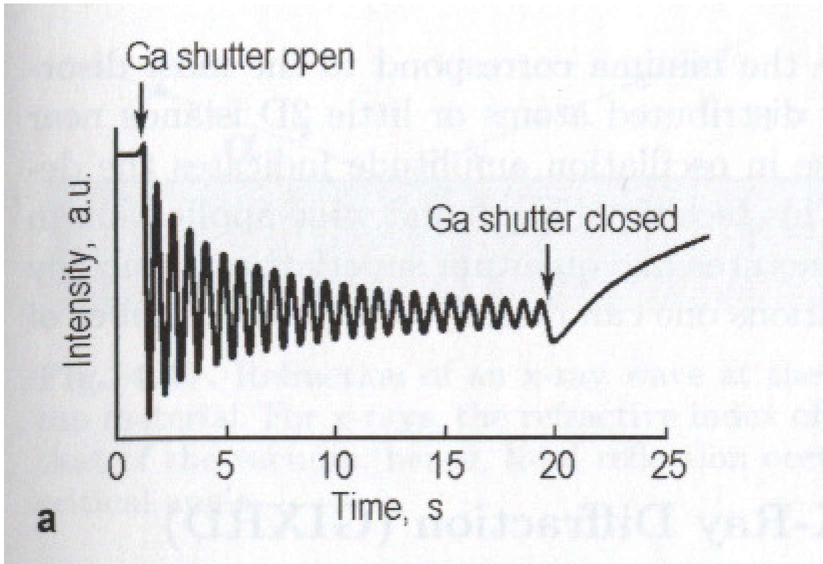
# Molecular Beam Epitaxy

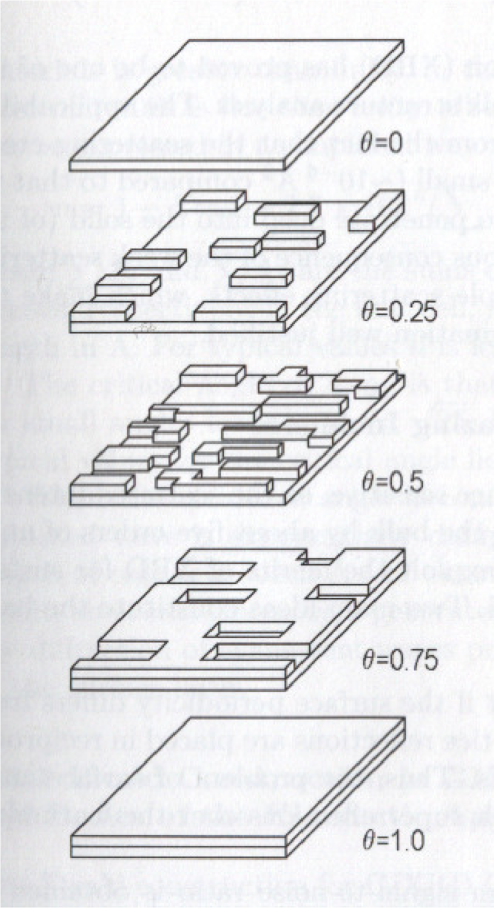


- Used both in research and in semiconductor device fabrications

# Molecular Beam Epitaxy

- The growth process can be monitored by RHEED:





# Solid Phase Epitaxy

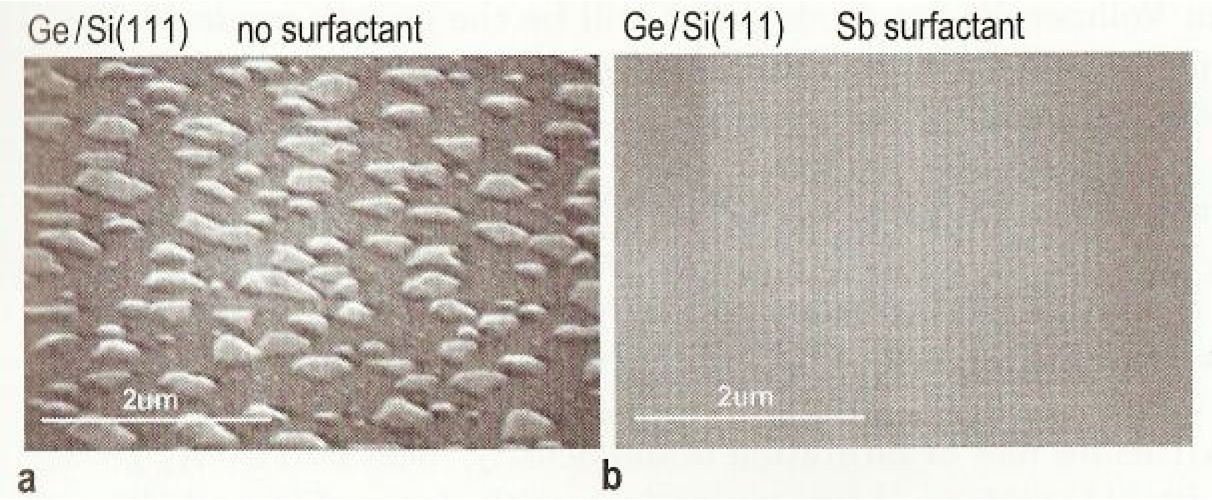
- Amorphous film deposited at low T and then crystallized upon heating at high T
- Lower crystallinity than MBE
- Used in semiconductor industry

# Chemical Beam Epitaxy

- Growth by surface chemical reactions
- High temperature required
- High grow rate and cristallinity

# Surfactant-Mediated Growth

- Impurity **(surfactant)** → different growth mode!
- Surfactant can be either segregated or trapped
- Example: Ge on Si(111) (Zahl et al., APA 1999)
  - Bare surface → Stranski-Krastanov mode
  - With surfactant (Sb) → Layer-by-layer mode



# Further Reading

- K. Oura et al., Surface Science, Springer 2003, chapter 14
- J.A. Venables et al., Rep. Prog. Phys. 47 (1984) 399
- H. Brune, Surf. Sci. Rep. 31 (1998) 121