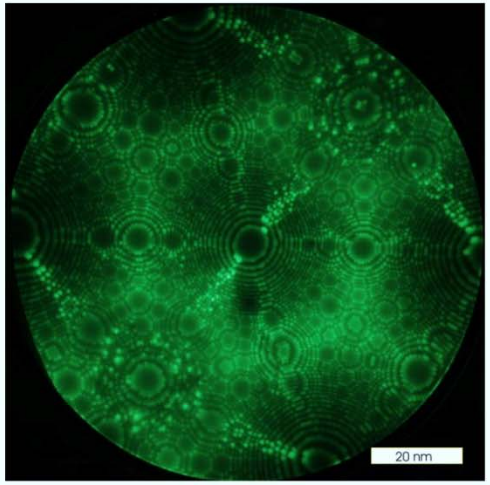
Wiederholung Diffusion

- kT (Arrhenius)
  → Random Walk / Lattice Gas / ‘on site’
- Fick’s laws
- Diffusion affected by cooperativity
- Atomistic Mechanisms
- Elektromigration / Stark Effect

Experimental Techniques

1) Direct observation:



- <u>Field ion microscopy</u> (FIM)

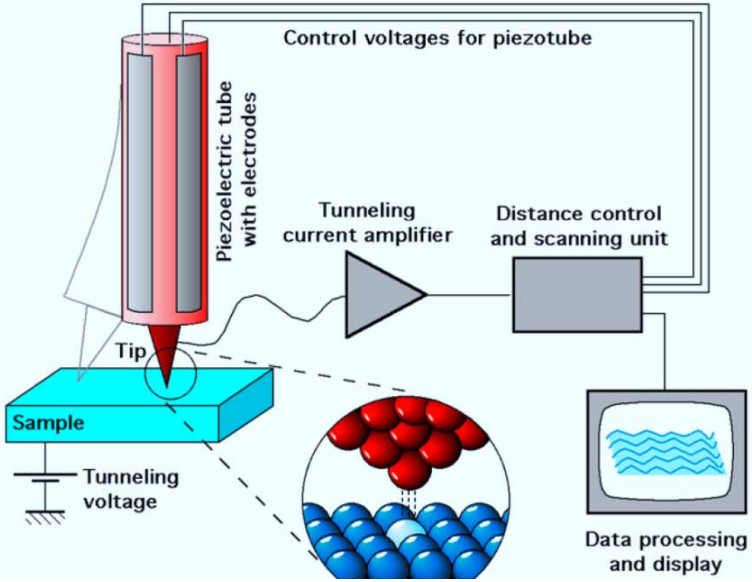
→ "image-anneal-image" technique

- Limited to refractory or noble metal surfaces

- <u>Scanning tunneling microscopy</u> (STM)

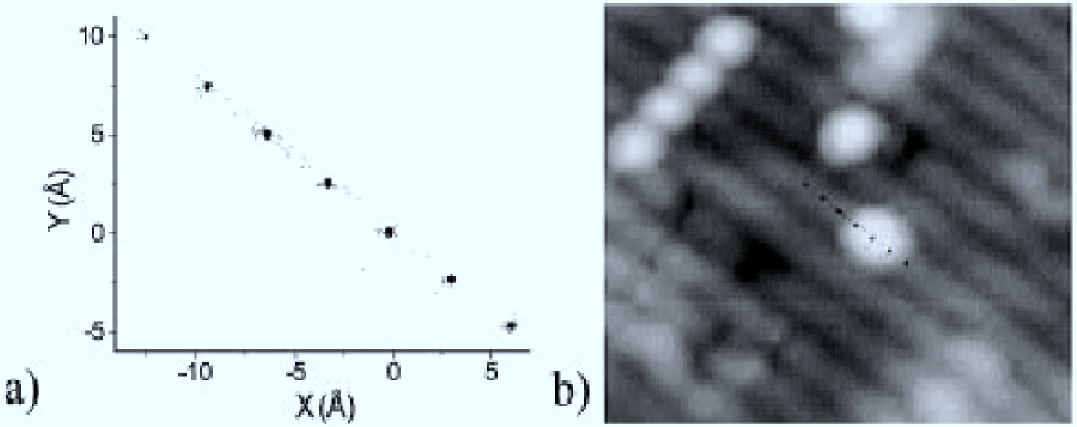
→ "image-while-hot" technique

- STM "movies" can be recorded (at 0.01-1 frames per second)



Experimental Techniques

- Scanning tunneling microscopy (STM) → “atom-tracking” technique
  - STM tip locked onto an adparticle by 2D lateral feedback
  - Example: Si on Si(100) (Swartzentruber, PRL 1996)



  - Electric fields from the STM tip influence surface diffusion!

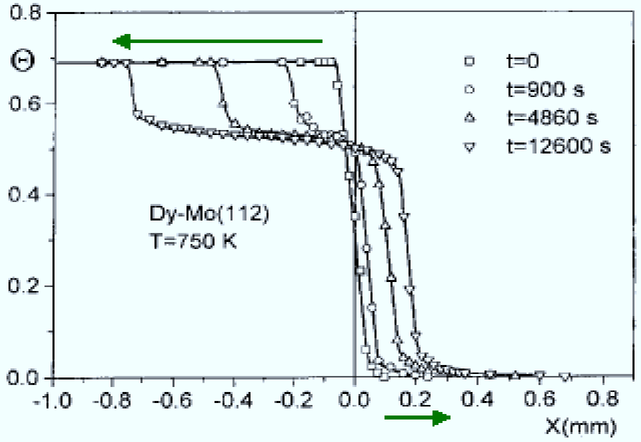
Experimental Techniques

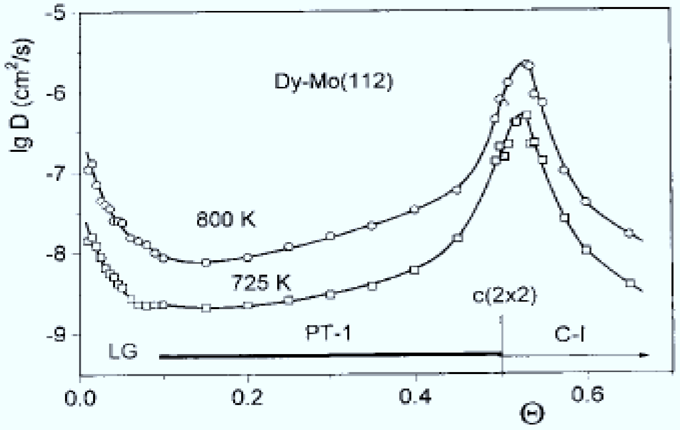
2) Profile evolution method:

- Smearing of a sharp initial concentration profile is monitored

  - Initial profile deposited using a mask
  - AES, SIMS, SEM or local work-function…
  - D(Θ) can be evaluated

- Example: Dy on Mo(112) (Loburets et al., SS 1998)





Experimental Techniques

3) "Capillarity" techniques:

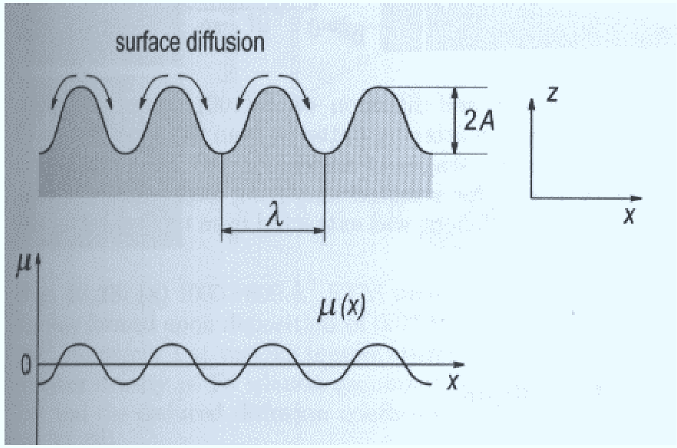
- A surface is perturbed from its lowest energy configuration...

... and allowed to relax via diffusion

- Relaxation rate → Coefficient of diffusion

- For a sinusoidal profile (Mullins, JAP 1999):

$$A(t) = A_0 \exp\left[-\frac{\gamma D n_0 V^2}{k_B T} \left(\frac{2\pi}{\lambda} \right)^4 t \right]$$

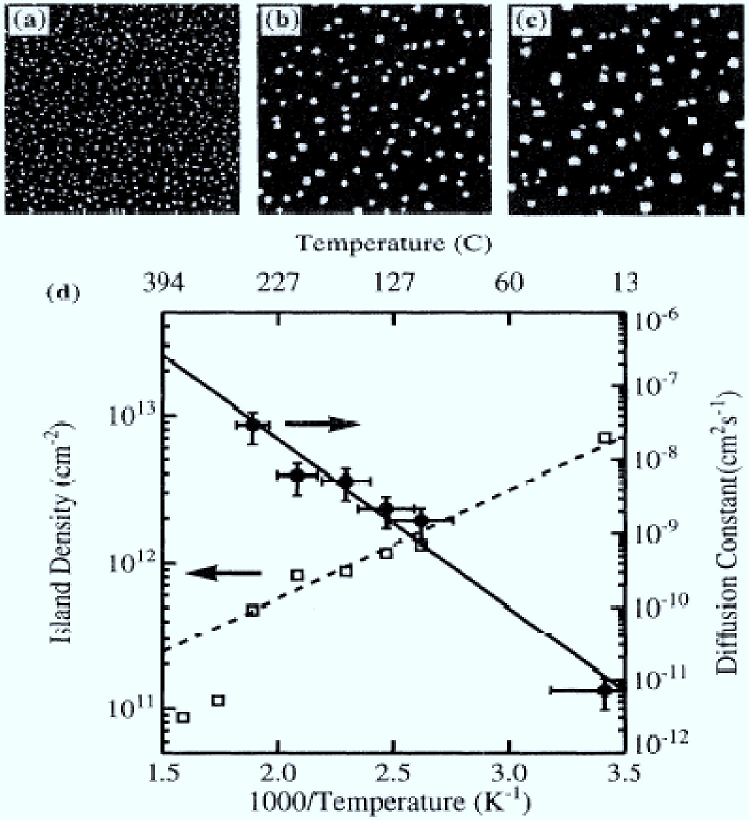


γ = surface tension; V = atomic volume; n_0 = surface density

Experimental Techniques

4) Island growth techniques:

- Number density of islands after submonolayer deposition is monitored
- Example: Fe on Fe(100) (Stroscio et al., PRL 1993)



deposition rate

$$N \propto \left(\frac{R\Theta}{\nu} \right)^{1/3}$$

hopping rate

Further Reading

- K. Oura et al., Surface Science, Springer 2003, chapter 13
- A.G. Naumovets & Yu.S. Vedula, Surf. Sci. Rep. 4 (1985) 365
- R. Gomer, Rep. Prog. Phys. 53 (1990) 917
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Surface Physics 2010

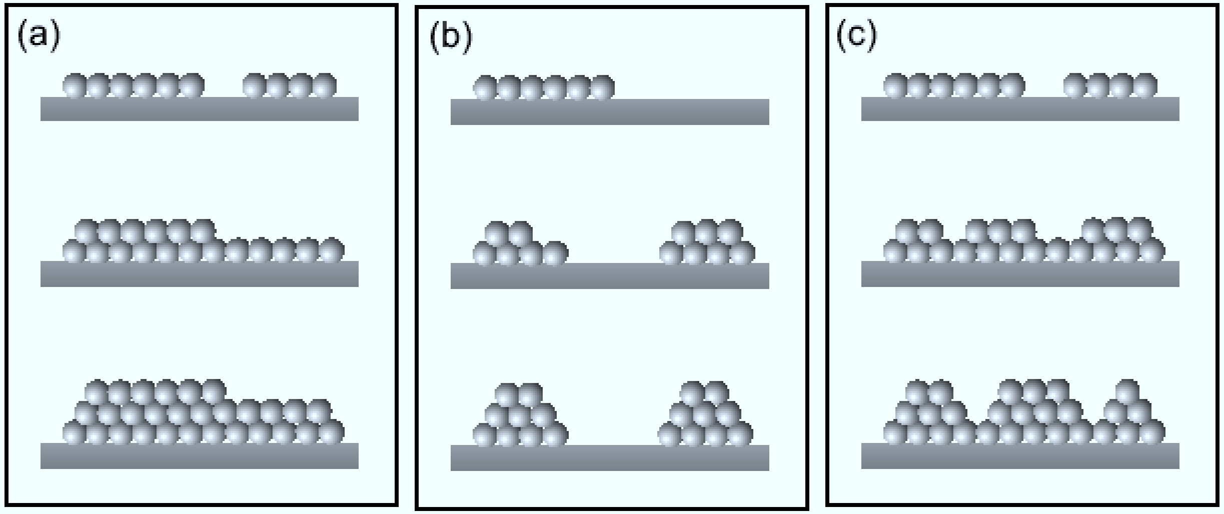
Growth of Thin Films

UNI
BASEL

Lecturer: Dr. Enrico Gnecco

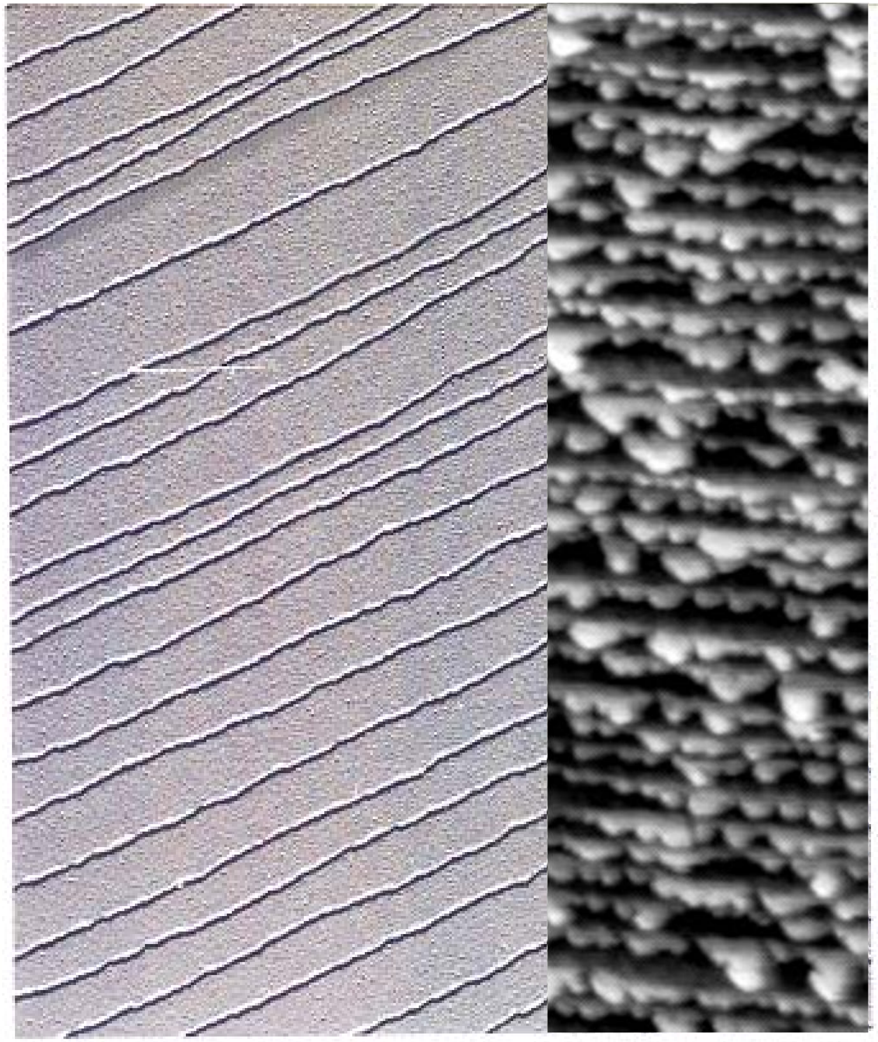
NCCR Nanoscale Science

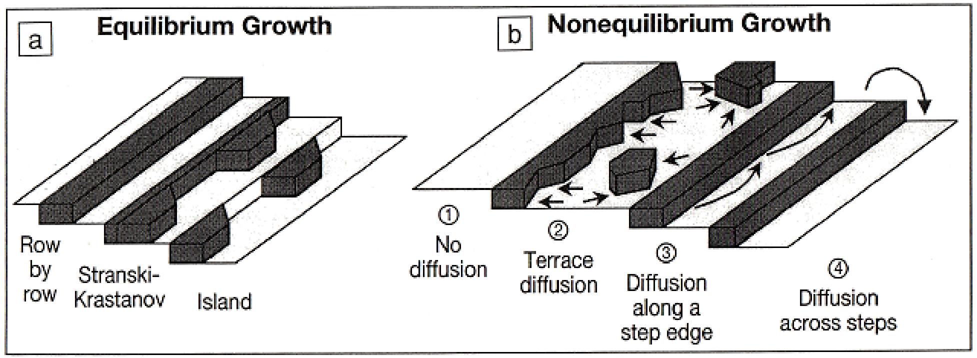
Growth Modes

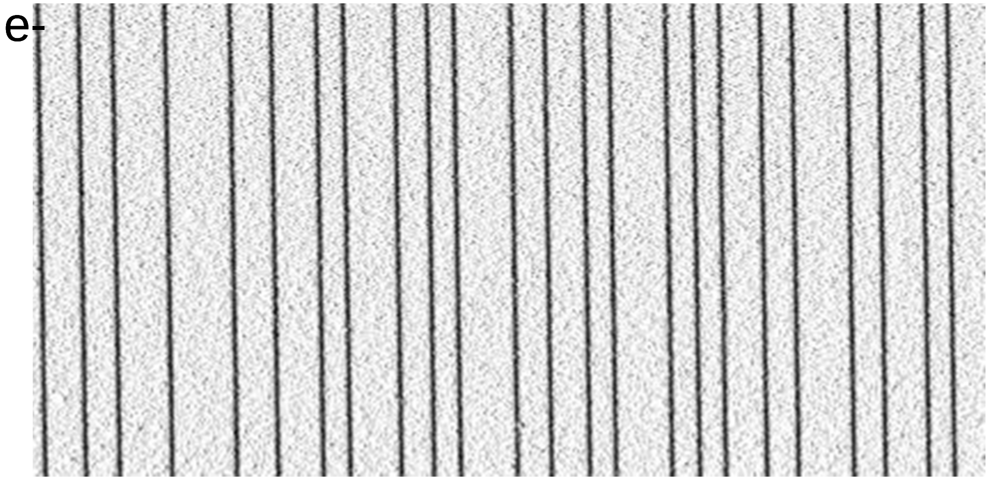


(a) **Layer-by-layer** or **Frank-van der Merve** mode → 2D islands
(b) **Island** or **Vollmer-Weber** mode → 3D islands
(c) **Layer plus island** or **Stranski-Krastanov** mode → 2D layer + 3D islands

‘Physical’ Self Assembly of e.g. Nanowires





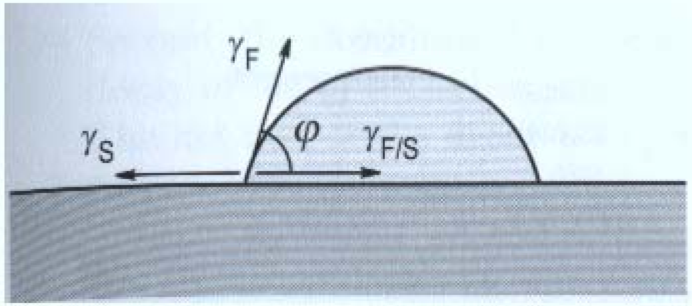


F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

Growth Modes

- **Surface tension** γ = work required to build a surface of unit area

  (≡ force per unit length)

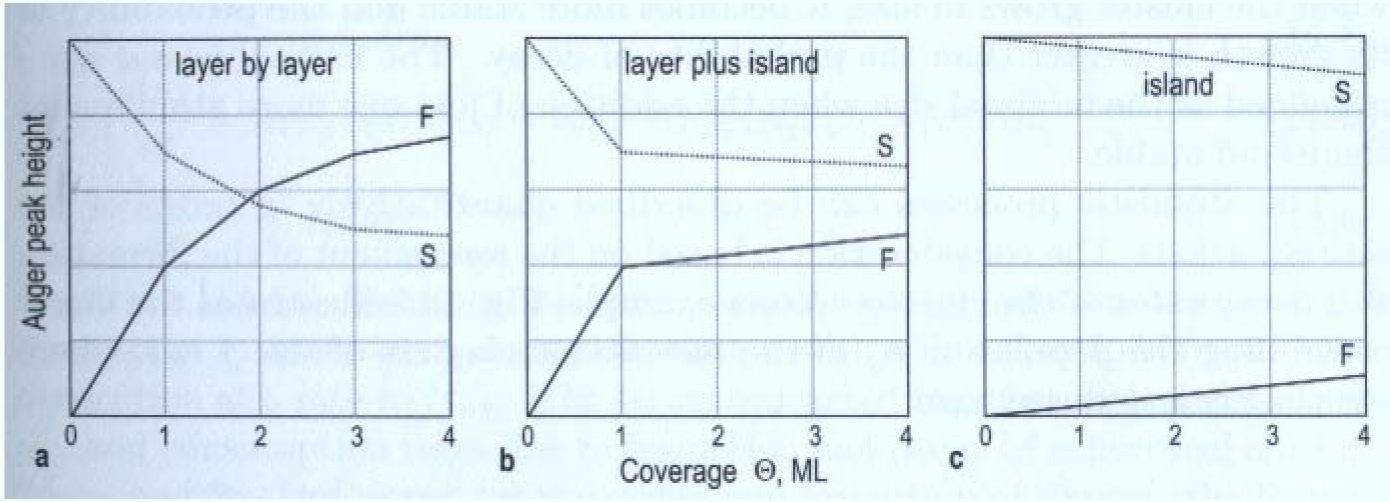


$$\gamma_S = \gamma_{SF} + \gamma_F \cos\varphi$$

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

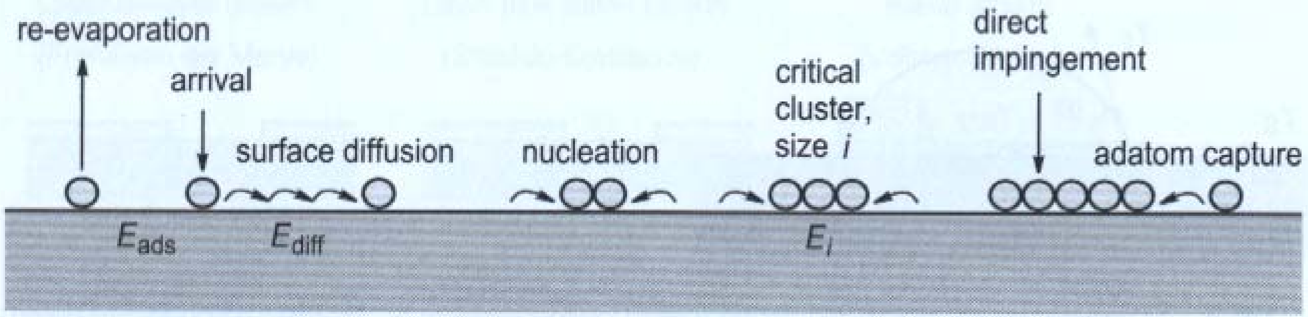
Growth Modes

- Exp: Monitor <u>Auger signals</u> from film and substrate while depositing...



Island Number Density

- Nucleation and growth on surfaces:



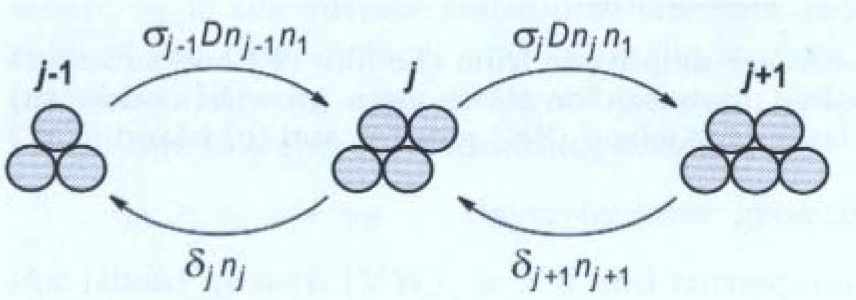
- Diffusion coefficient: $$D = \frac{\nu}{4n_0}\exp\left(-\frac{E_{diff}}{k_B T}\right)$$

- 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:

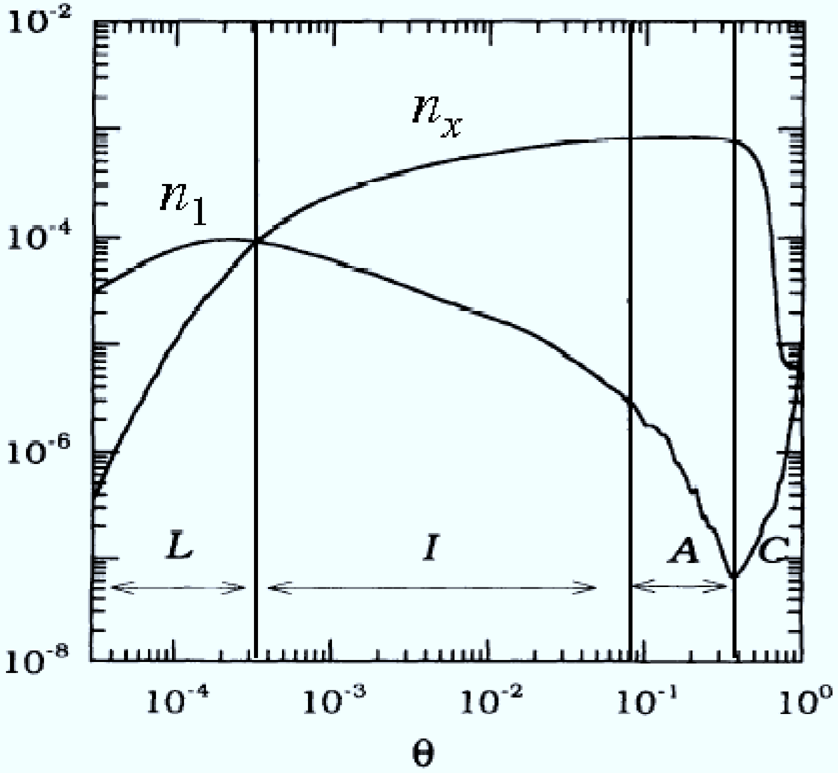
$$\frac{d\overset{\text{adatom density}}{n_1}}{dt} = \underset{\text{deposition rate}}{R} - \frac{n_1}{\tau_{ads}} + \overset{\text{subcritical clusters}}{\boxed{\left(2\delta_2 n_2 + \sum_{j=3}^{i}\delta_j n_j - 2\sigma_1 D n_1^2 - n_1\sum_{j=2}^{i}\sigma_j D n_j\right)}} - \underset{\text{stable clusters}}{\boxed{n_1\sigma_x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

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

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

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):

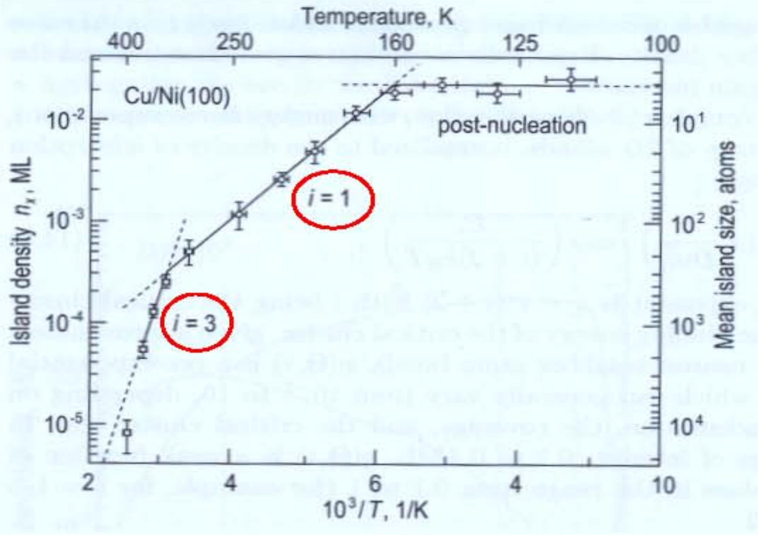
χ

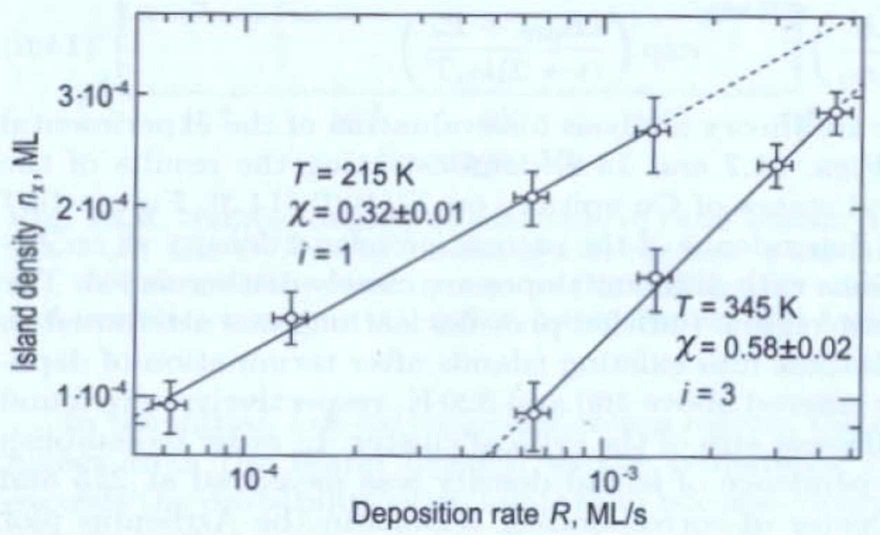
binding energy
of critical cluster

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

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

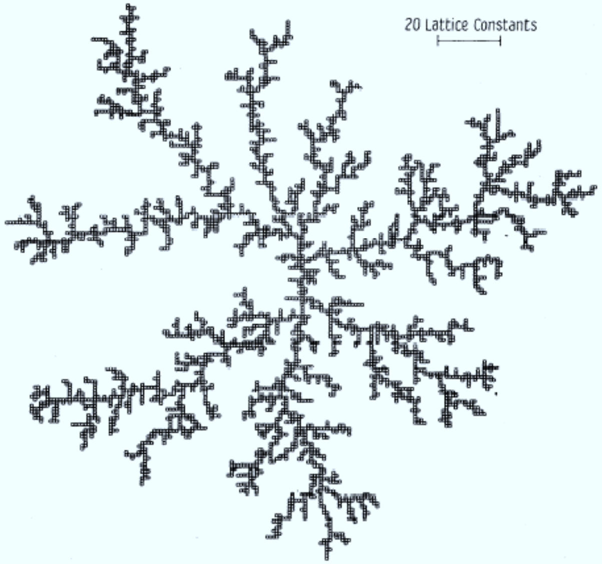
- Example: Cu on Ni(100) (Müller et al., PRB 1996)





Island Shape

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

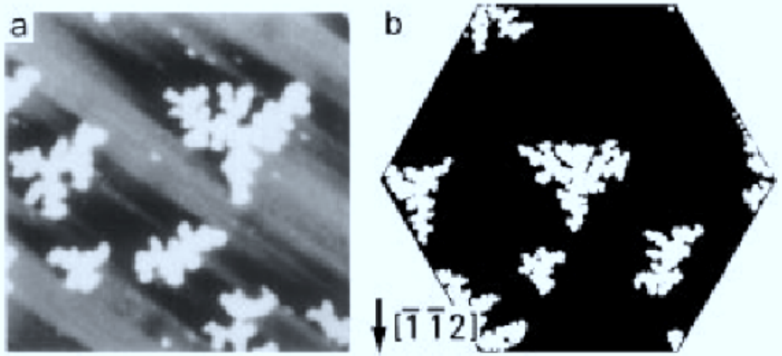


- Adatoms stick at islands
- Fractal shape
- Branch thickness ~ 1 atom
- No influence of lattice geometry

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

Island Shape

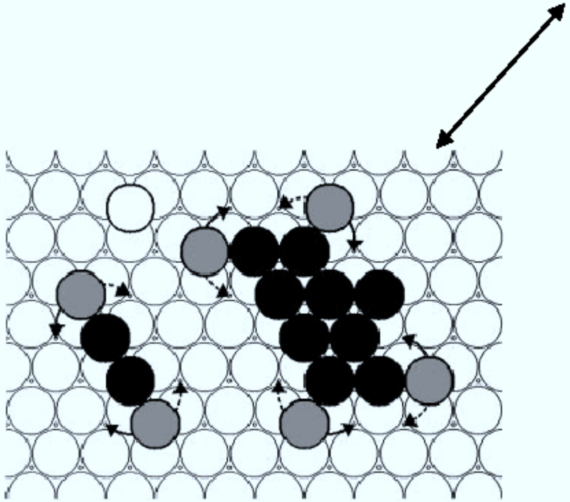
- Example: Pt/Pt(111) (Hohage et al., PRL 1996)



experiment

simulation

- Branch thickness ~ 4 atoms
- Trigonal symmetry

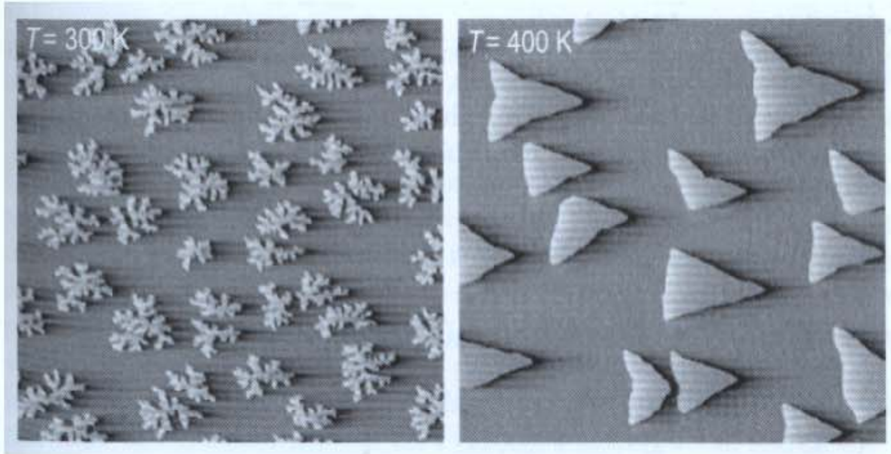


- Higher coordination is preferred

Island Shape

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

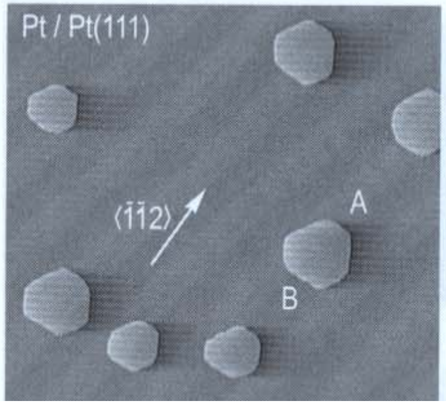
300 K



400 K

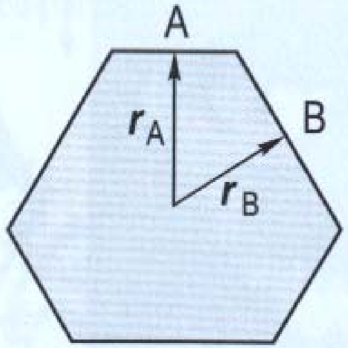
- The equilibrium shape is hexagonal:

(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



$$\frac{|r_B|}{|r_A|} = \frac{\gamma_B}{\gamma_A} = 0.87 \pm 0.02$$

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

Island Size Distribution

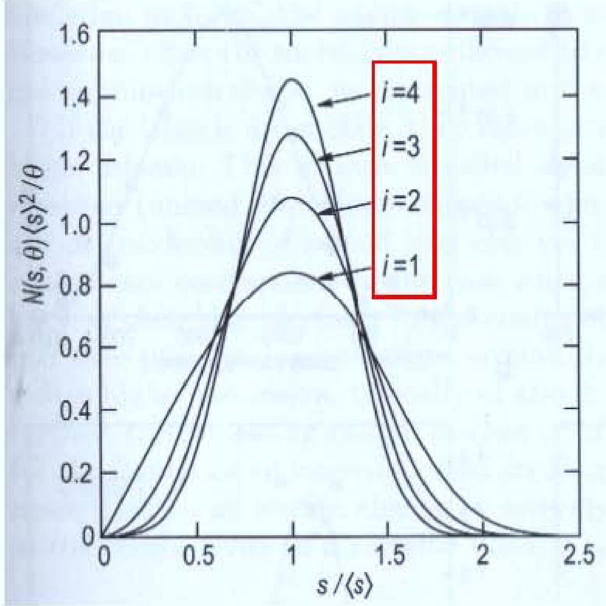
- **Island size distribution** depends on:
  - Critical island size
  - Coverage
  - Substrate structure
  - “Coarsening” (at high Θ)

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

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

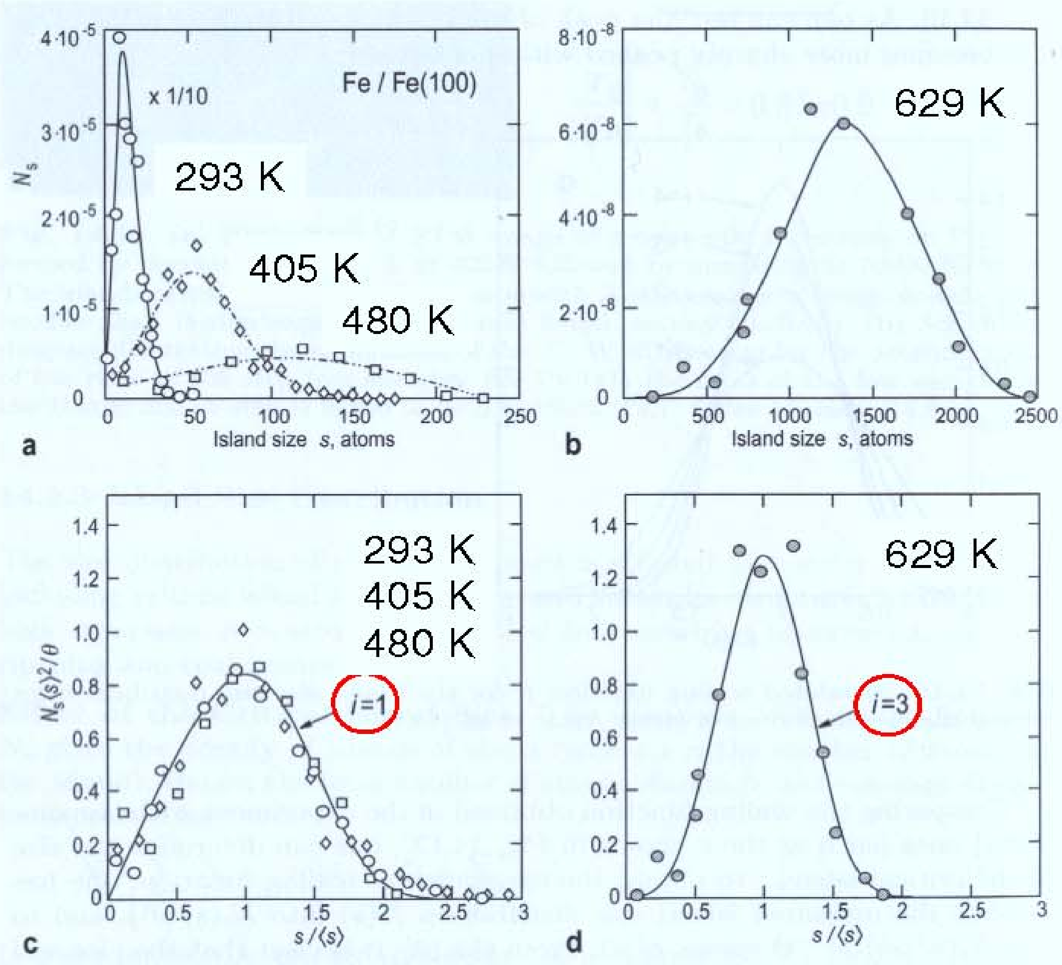
- Comparing with experimental results

→ critical island size



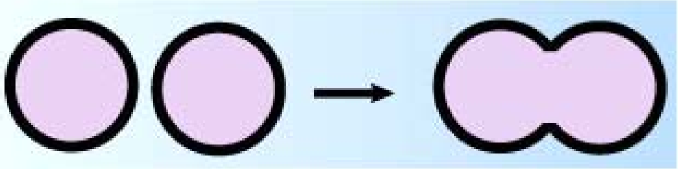
Island Size Distribution

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



Coarsening Phenomena

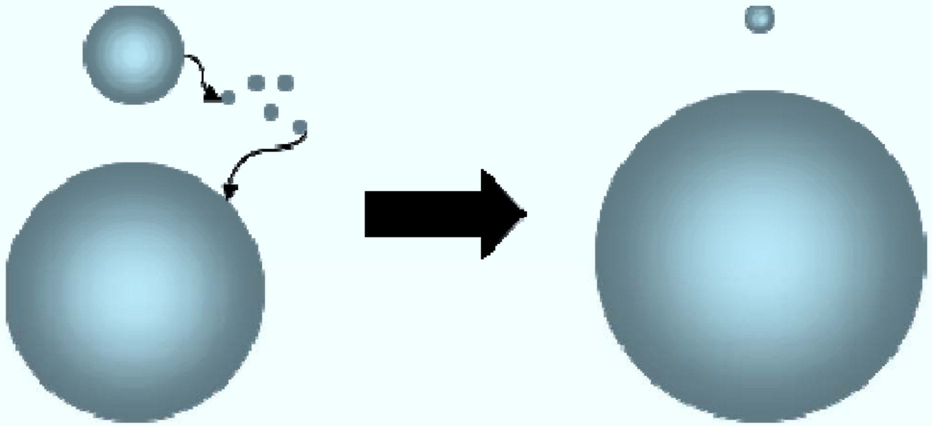
1) Coalescence:



- 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:



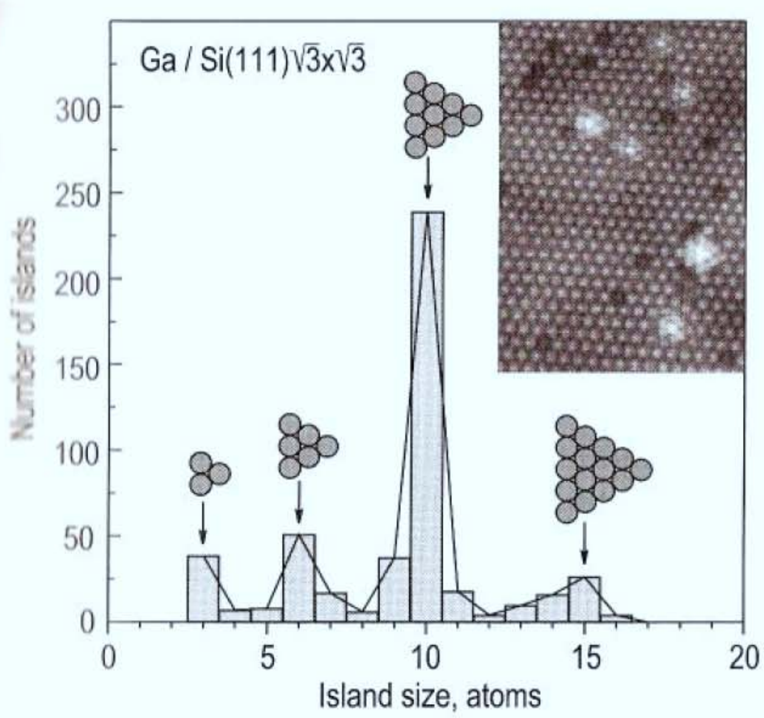
- Chemical potential of a circular island:

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

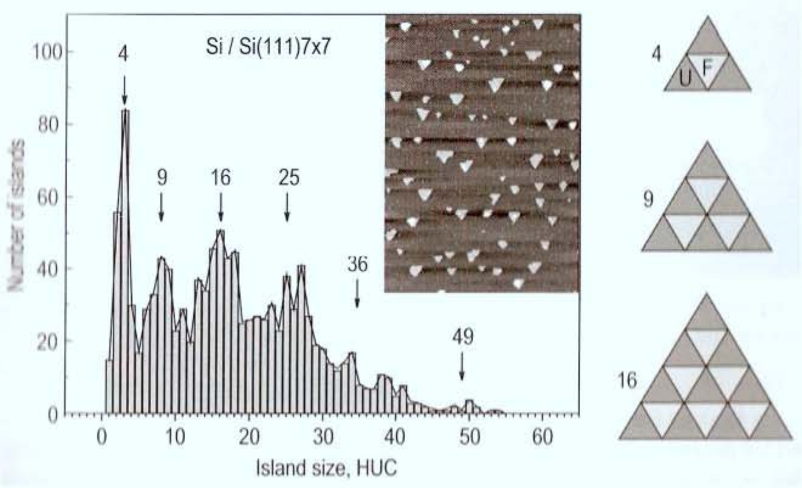
Reducing free energy → net flow from smaller to larger islands!

Magic Islands

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



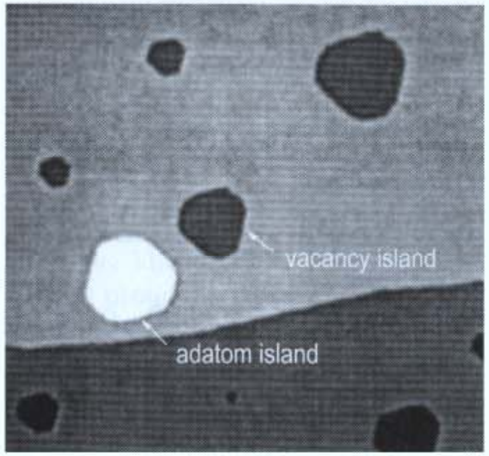
- Si on Si(111)7x7 (Voigtländer et al., PRL 199



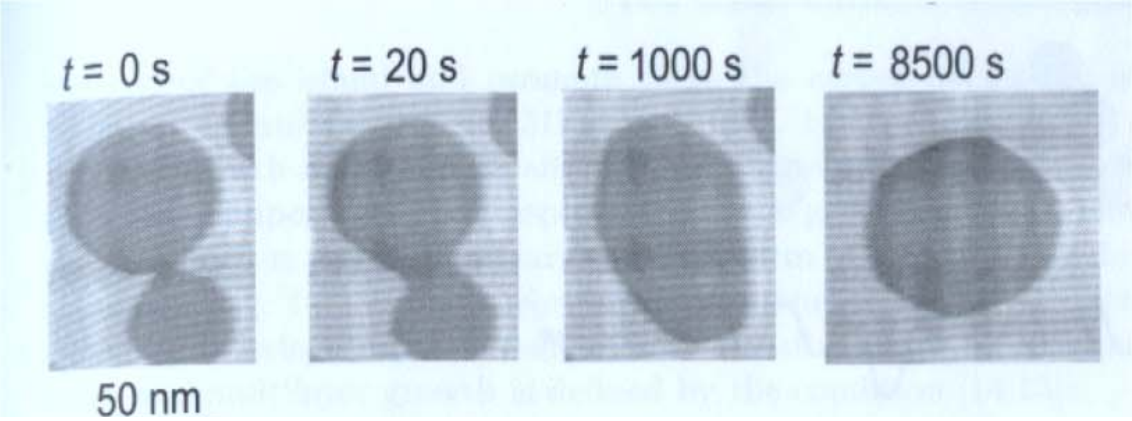
Formation of a new row → high energy cost!

Vacancy Islands

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

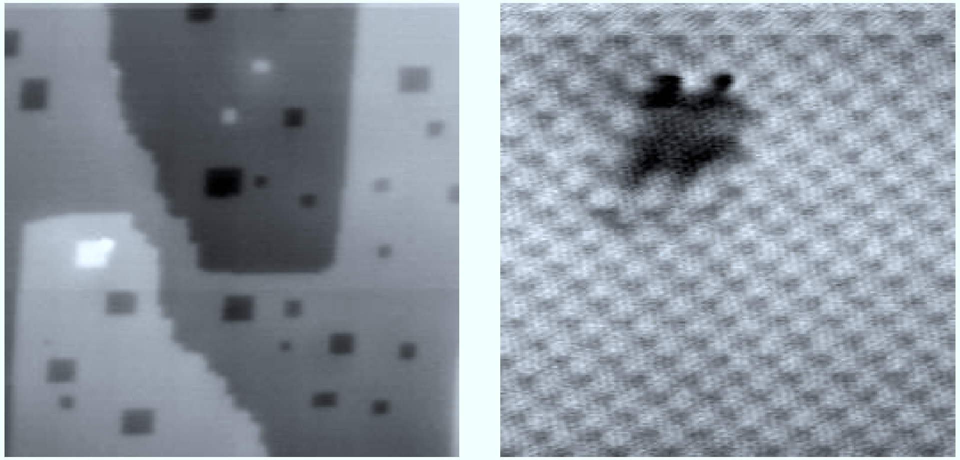


- Analogies with adatom islands



Vacancy Islands

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



KBr(100)

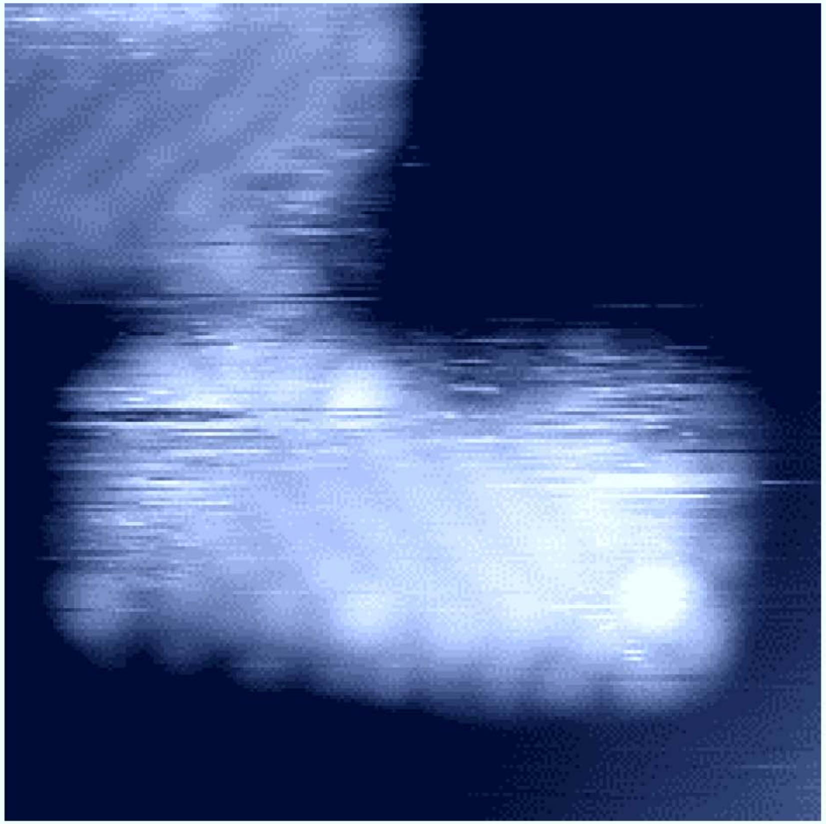
- Irradiation with 1 keV electrons at 130 ºC

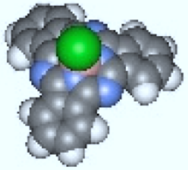
- Rectangular pits with area of 1x1 nm^2 up to 30x30 nm^2

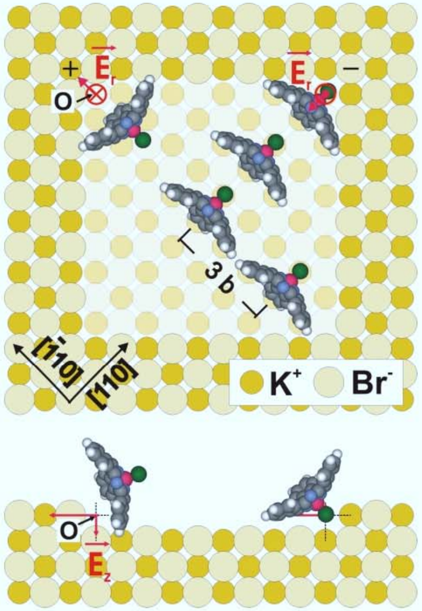
- 1 ML deep (0.33 nm)

Vacancy Islands

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

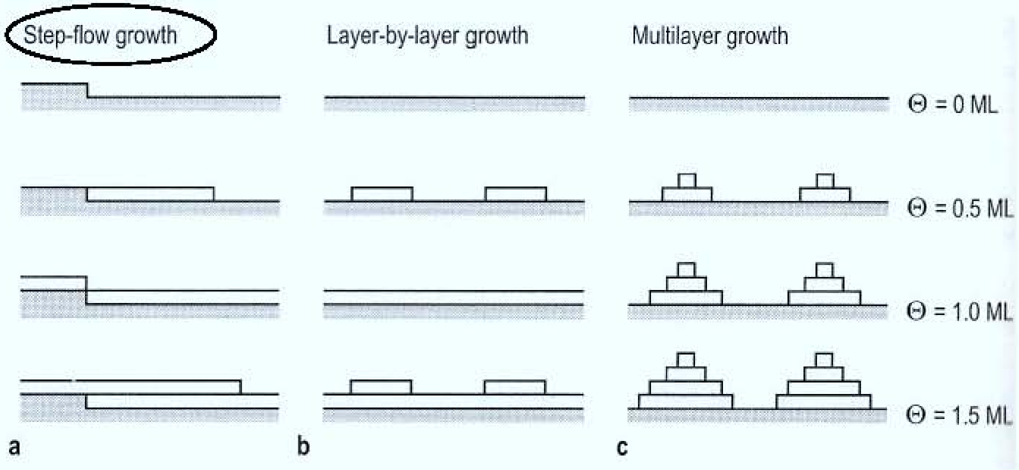




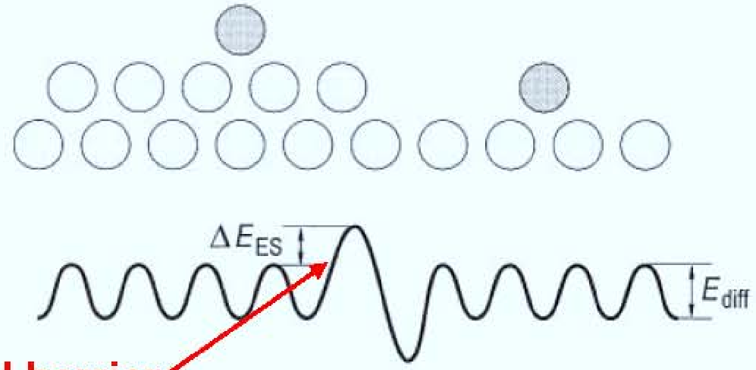


Kinetic Effects in Homoepitaxy

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



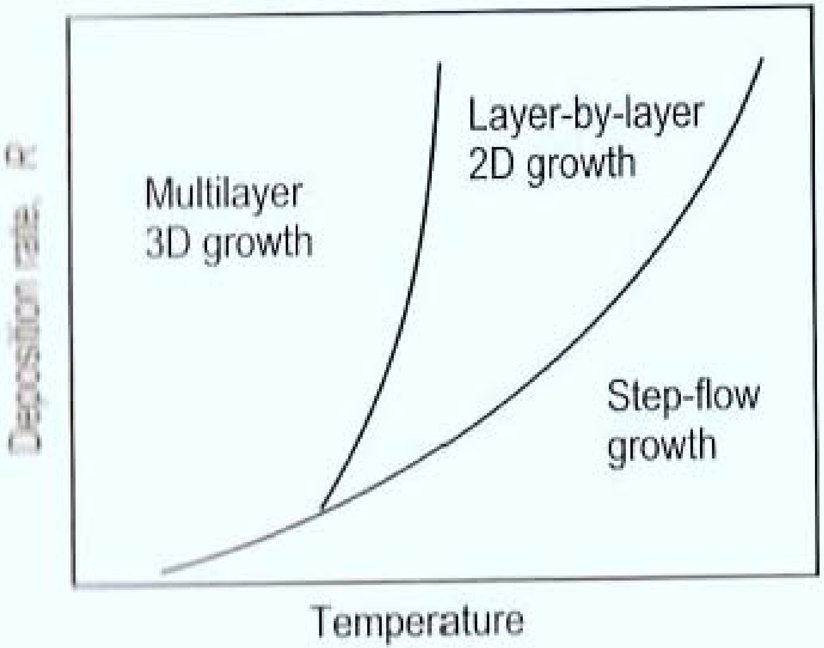
- **Interlayer** mass transport:



Ehrlich-Schwöbel barrier

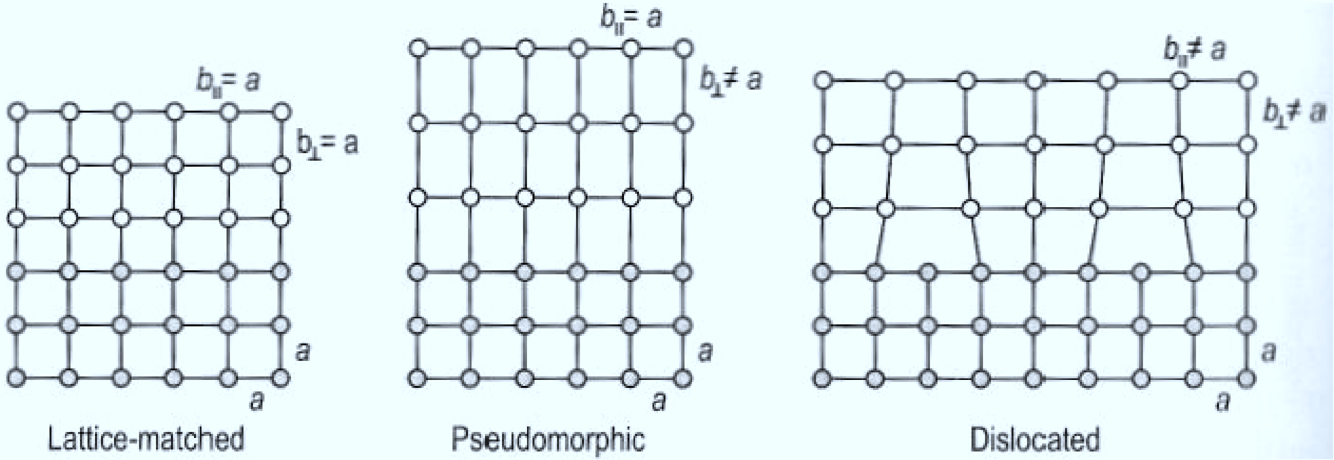
Kinetic Effects in Homoepitaxy

- Deposition rate and Temperature are important!
- Growth mode diagram (Rosenfeld et al., 1997):



Strain Effects in Heteroepitaxy

- Heteroepitaxy growth modes:

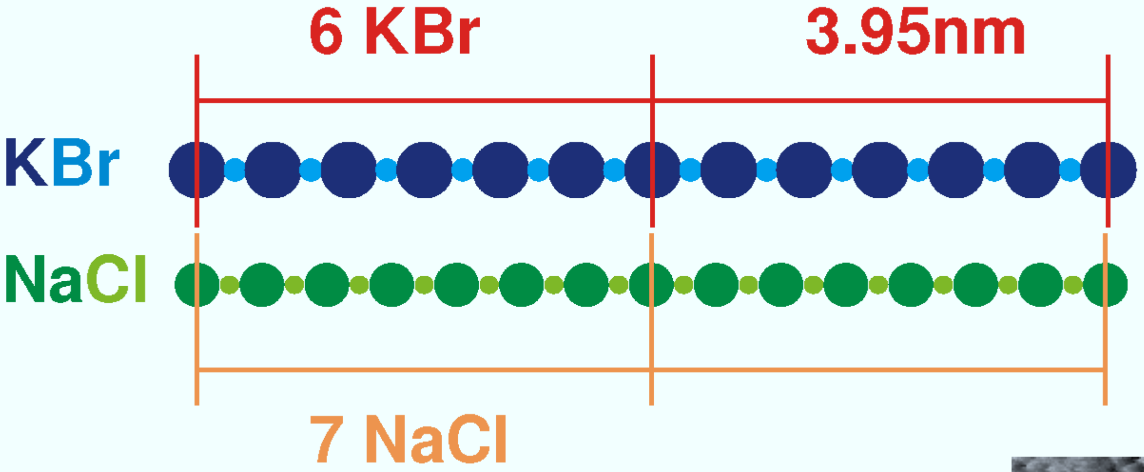


- Lattice **misfit** → elastic strain and dislocations

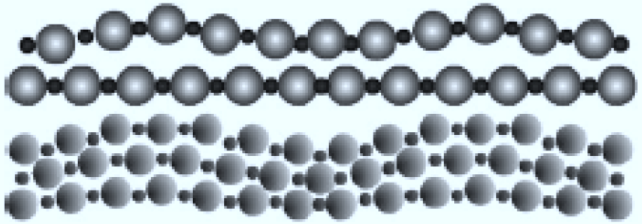
- Pseudomorphic growth below critical misfit and film thickness

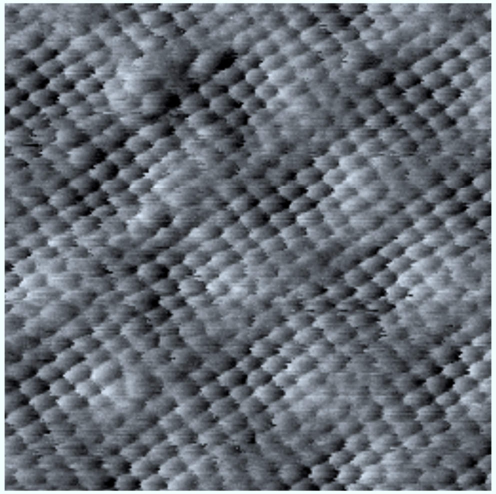
Strain Effects in Heteroepitaxy

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

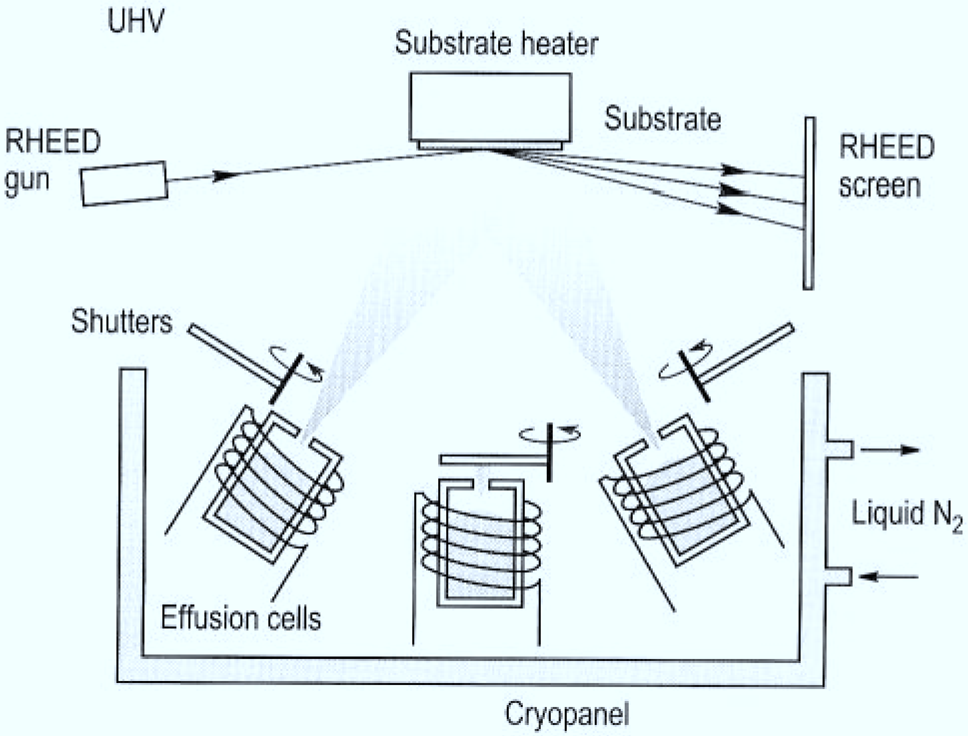


- A “Moiré pattern” appears (also in the substrate?)





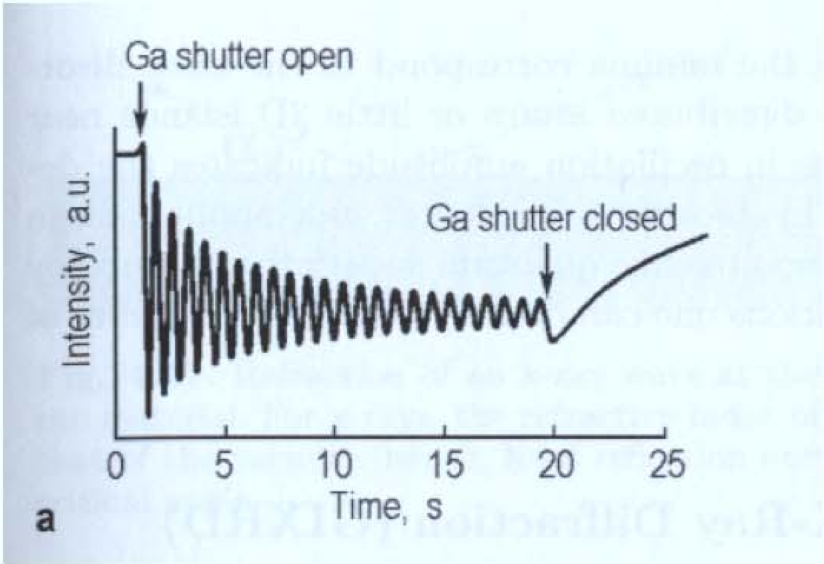
Molecular Beam Epitaxy

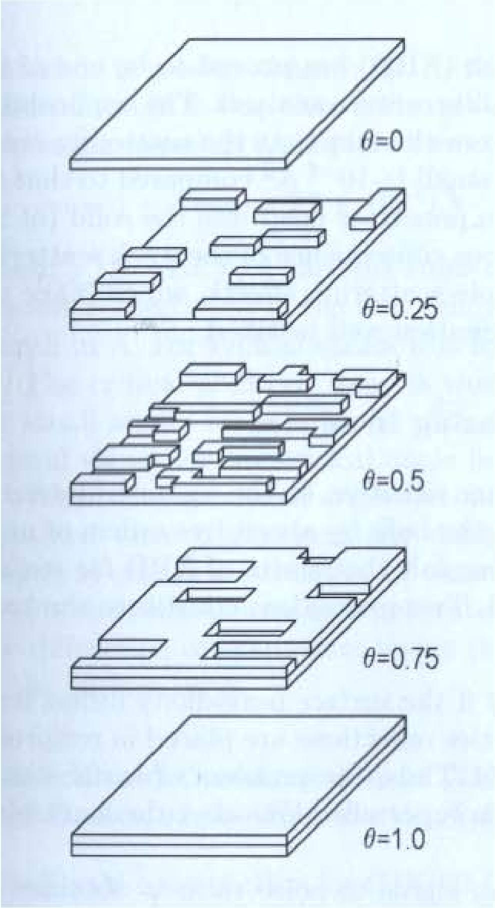


- Used both in research and in semiconductor device fabrications

Molecular Beam Epitaxy

- The growth process can be monitored by RHEED:





Solid Phase Epitaxy

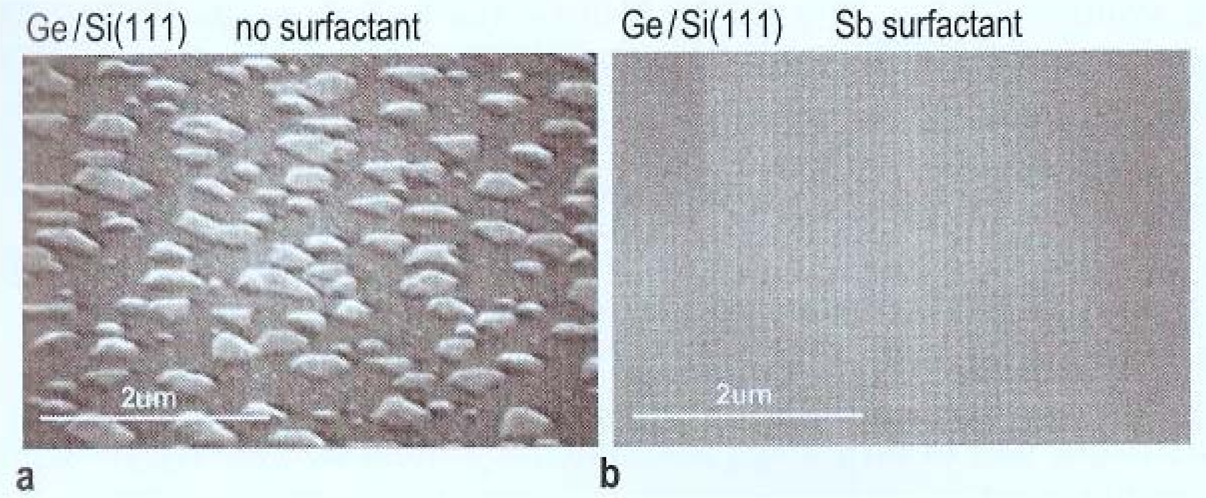
- Amorphous film deposited at low T and then crystallized upon heating at high T
- Lower crystallinity than MBE
- Used in semiconductor industry

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