Nanostructures and Nanostructuring
20. / 27. Sept 2011

- Bildungs- und Wachstumsmechanismen
- Oberflächendiffusion
- Wachstumsmoden (ballistisch, dendritisch)
- amorph, poly, einkristallin
- Epitaxie

Surface Physics 2010

Surface Diffusion

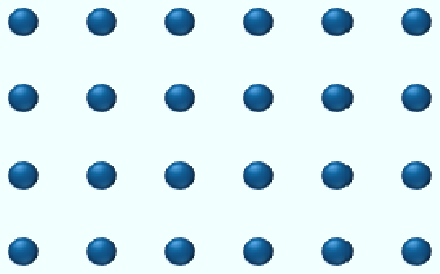
UNI
BASEL

Lecturer: Dr. Enrico Gnecco

NCCR Nanoscale Science

Random-Walk Motion

- Thermal motion of an adatom on an ideal crystal surface:



- Thermal excitation → the adatom can hop from one adsorption site to the next

- Mean square displacement at time *t*:

$$\boxed{\langle \Delta r^2 \rangle = \nu a^2 t}$$

a = jump distance; ν = hopping frequency

(Note that νt = number of hops!)

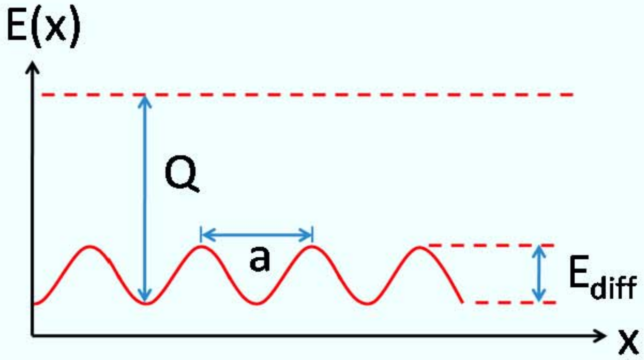
- **Diffusion coefficient**:

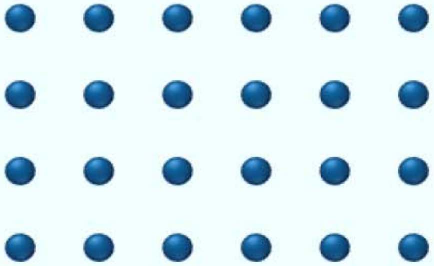
$$\boxed{D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}}$$

z = number of first neighbors = $\left[\begin{array}{l}\text{2 in 1D diffusion}\\ \text{4 on a square lattice}\\ \text{6 on a hexagonal lattice}\end{array}\right.$

Random-Walk Motion

- Hopping → surmounting a potential barrier





- **Arrhenius law**:

$$\boxed{\nu = \nu_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)}$$

ν_0 = oscillation frequency of the atom in the well;

E_{diff} = barrier height

Tipically E_{diff} ~ 5-20% of Q (heat of desorption)

- For chemisorbed species: $E_{diff} >> k_B T$
- If $E_{diff} < k_B T$: 2D gas (only a few physisorbed species)

Fick's Laws

- **Fick's First Law** (for 1D diffusion):

$$J = -D\frac{\partial c}{\partial x}$$

diffusion flux

concentration gradient

(flux → region of lower concentration)

- **Fick's Second Law** (for 1D diffusion):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

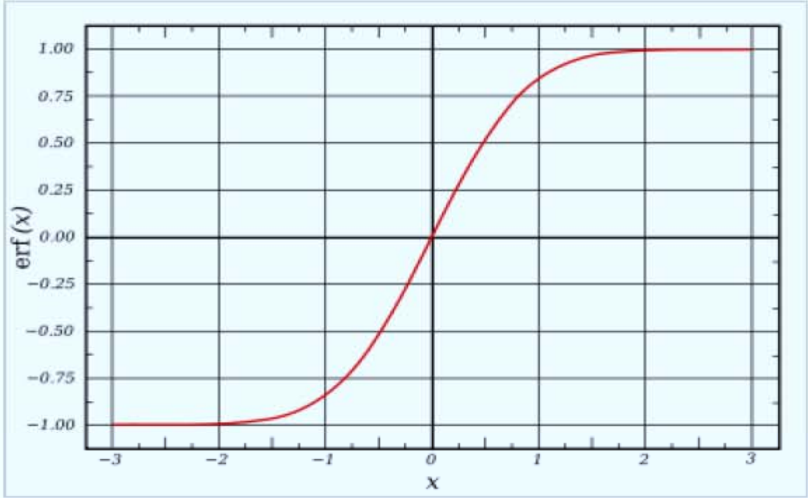
← from equation of continuity

- Analytical solutions can be found for specific initial and boundary conditions!

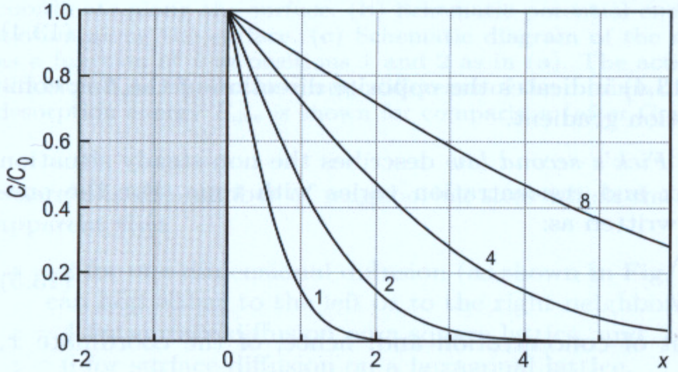
Analytical Solutions of Fick's Laws

- We introduce the **error function**

$$\boxed{\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\, dt}$$



- Source of constant concentration:



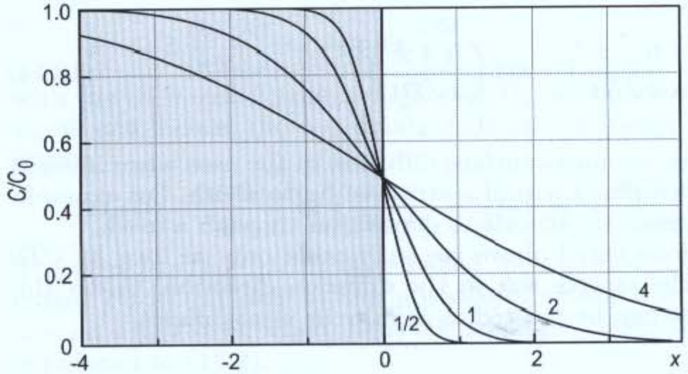
$$c(x,t) = c_0\left[1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$2\sqrt{Dt}$: **diffusion length**

- Example: Submonolayer film with 3D islands supplying mobile adatoms

Analytical Solutions of Fick's Laws

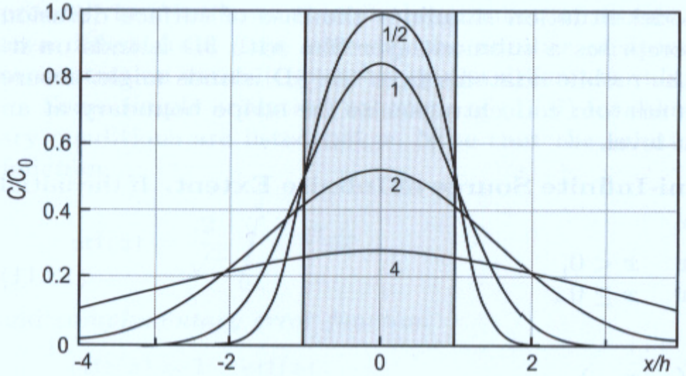
- Source of infinite extent:



$$c(x,t) = \frac{c_0}{2}\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

- Example: Submonolayer film

- Source of limited extent:



$$c(x,t) = \frac{c_0}{2}\left[\mathrm{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right]$$

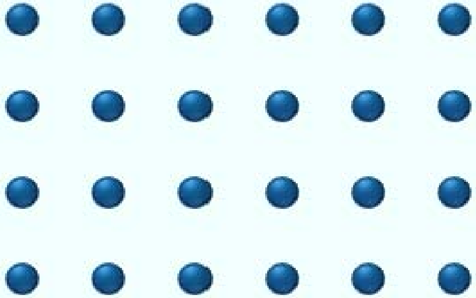
- Example: Submonolayer film confined in a stripe of finite width

Diffusion Mechanisms

- Depending on the <u>coverage</u> Θ:
  - Tracer diffusion (low Θ)
  - Chemical diffusion (intermediate to high Θ)

Tracer Diffusion

- **Tracer Diffusion:** - Low coverage (<0.01 ML)
  - Individual adparticles



- Fick's first law is valid:

$$D = \frac{\langle \Delta r^2 \rangle}{zt}$$

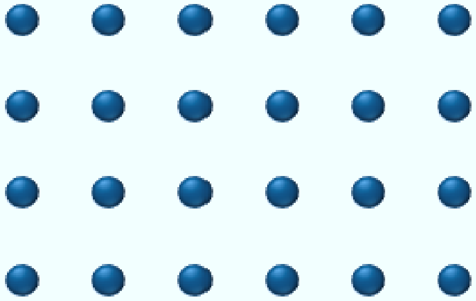
- For an ensemble of many particles:

$$D = \frac{1}{zNt} \sum_i \langle \Delta r_i^2 \rangle$$

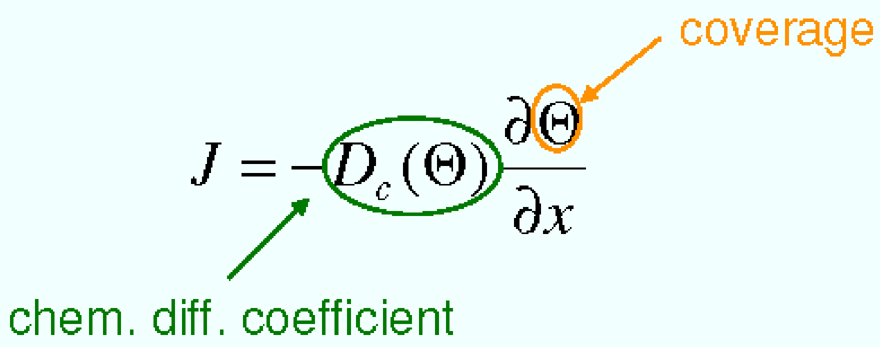
(no relation to radioactive tracers!)

Chemical Diffusion

- **Chemical Diffusion:** - Higher coverage
  - Attraction or repulsion between adatoms



- Fick's first law can be generalized:



$$J = -\underbrace{D_c(\Theta)}_{\text{chem. diff. coefficient}} \frac{\partial \overset{\text{coverage}}{\Theta}}{\partial x}$$

- <u>Strong dependence on</u> adsorbate <u>coverage</u> is expected, especially when ordered phases are formed (Naumovets-Vedula, 1986)

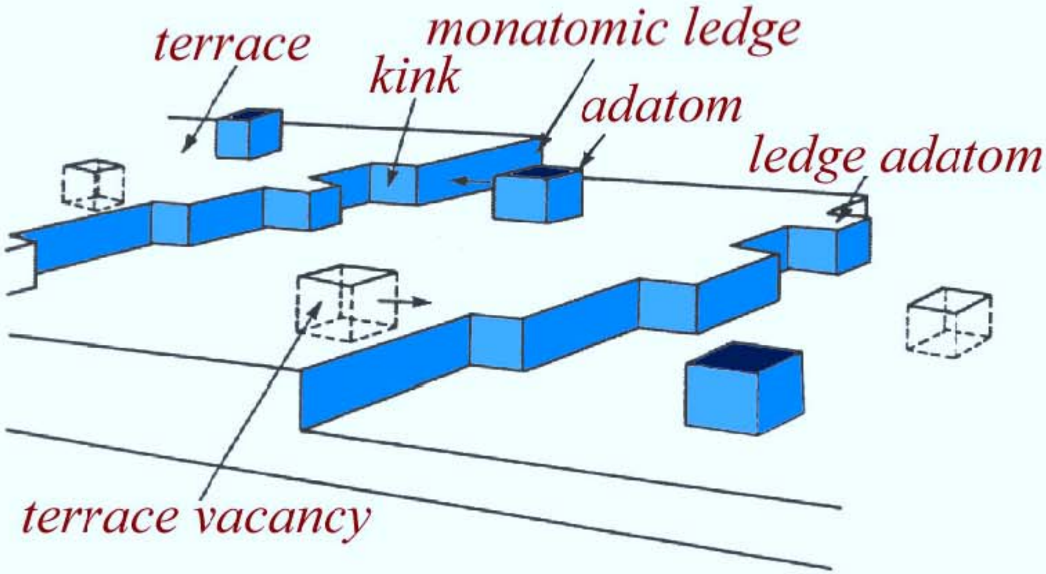
Diffusion Mechanisms

- Depending on the landscape**:**
  - Intrinsic diffusion (no sources and traps)
  - Mass transfer diffusion (generation and/or trapping)

Intrinsic Diffusion

- Adparticle motion is monitored within a single terrace → Spatial limit ~ 100 nm

- In practice: no strong distinction from tracer diffusion



Mass Transfer Diffusion

- Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)

- If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent

- If adatoms and substrate are the same chemical species:

$$D = \frac{\nu_0 a^2}{z} \exp\left(- \frac{\boxed{\Delta G} + E_{diff}}{k_B T} \right)$$

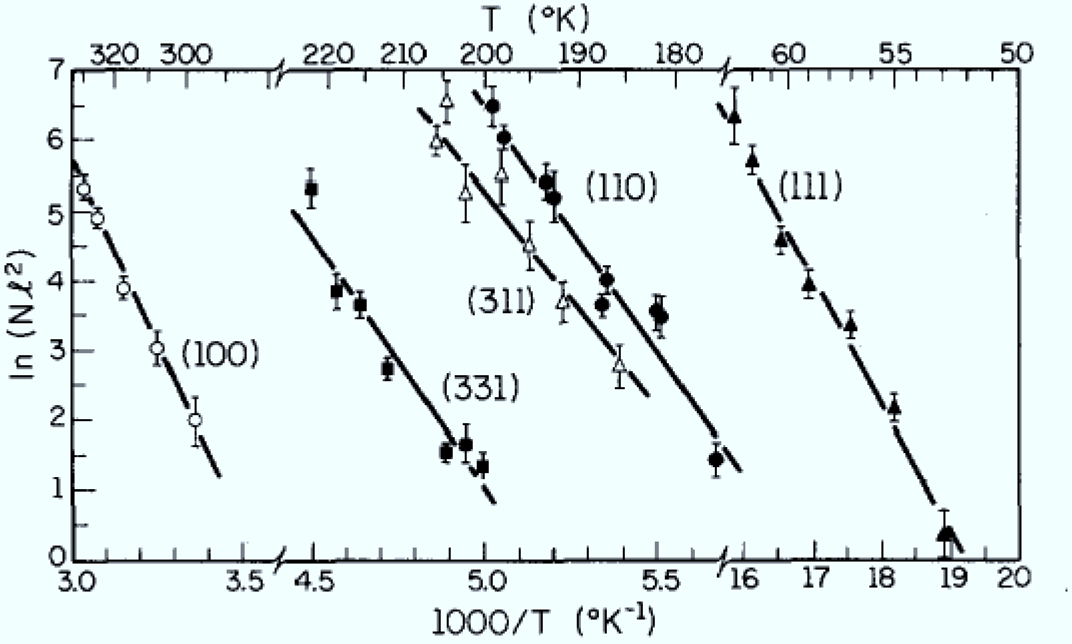
ΔG = energy of adatom formation

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

- **Orientational Anisotropy:** the diffusion coefficient depends on the <u>orientation of the surface</u>

- Example: Rh surfaces at different T (Ayrault & Ehrlich, JCP 1974)



N: number of jumps in 3 min

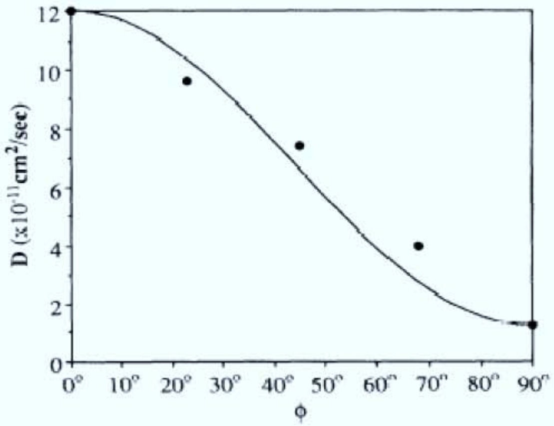
ℓ: jump distance

- At given T the differences in the diff. coeff. can be several orders of magnitude!

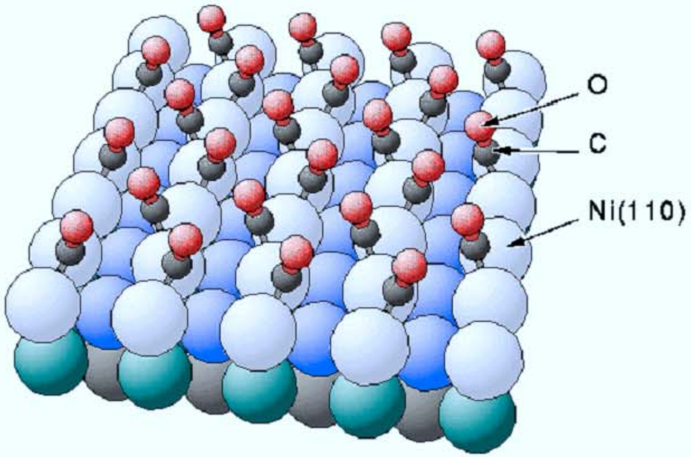
Anisotropy of Surface Diffusion

- **Directional Anisotropy:** the diffusion coefficient depends on the direction at the surface

- Rectangular lattice → directional anisotropy (Xiao et al., PRL 1991)

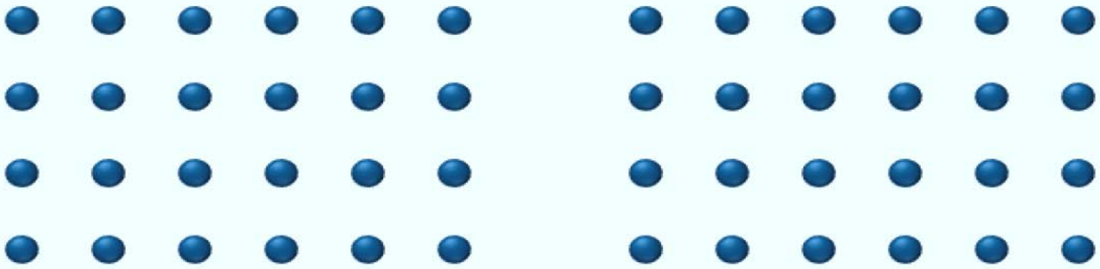


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

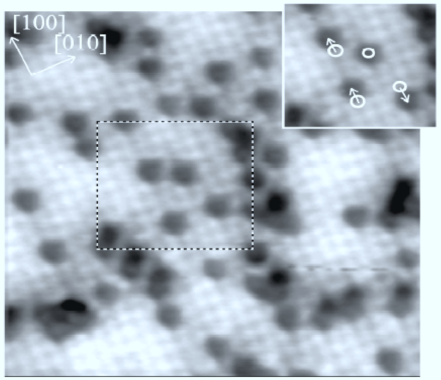


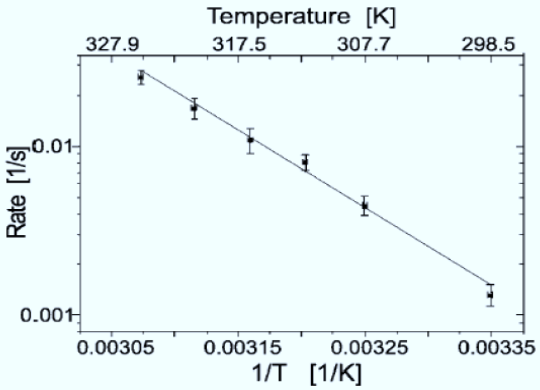
Atomistic Mechanisms

1) Hopping mechanism:



- Example: N adatoms on Fe(100) (Pedersen et al., PRL 2000)

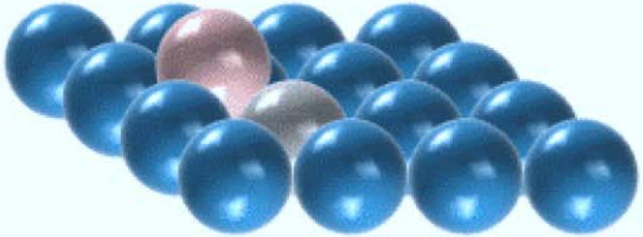


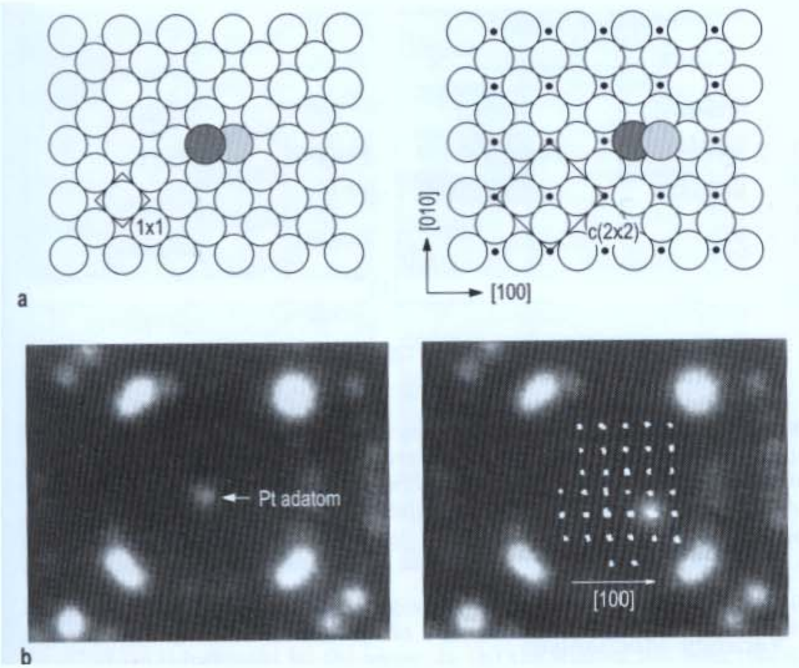


→ Arrhenius law with $\nu \sim 10^{12}\ \mathrm{s}^{-1}$, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:





- Example: Pt adatom on Pt(100) (Kellogg, SSR 1994)

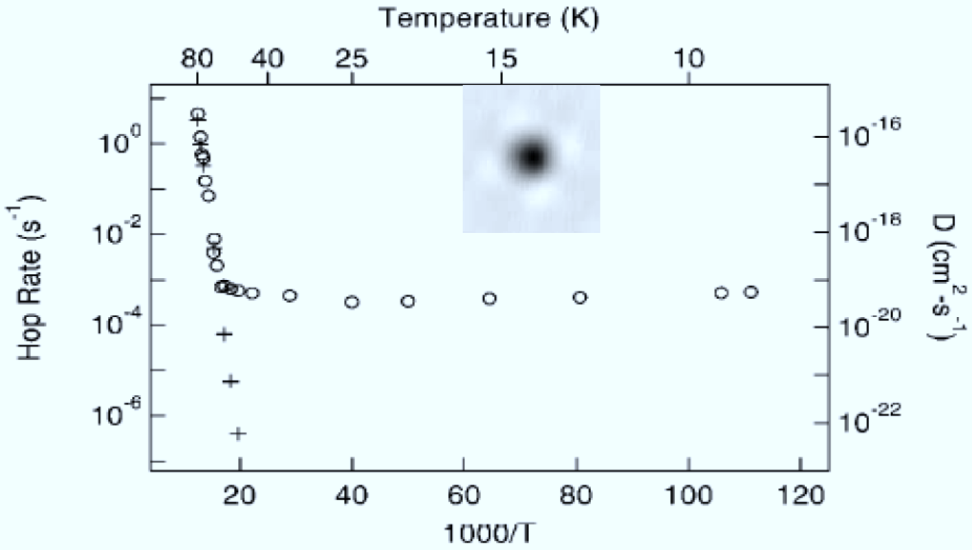
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

- Diffusing particle with small mass
- Low potential barrier against diffusion

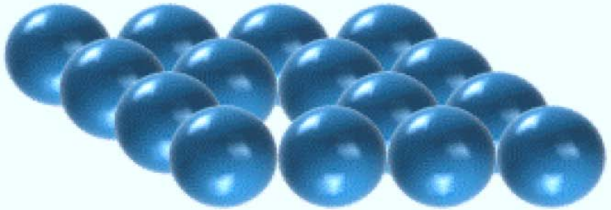
- Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



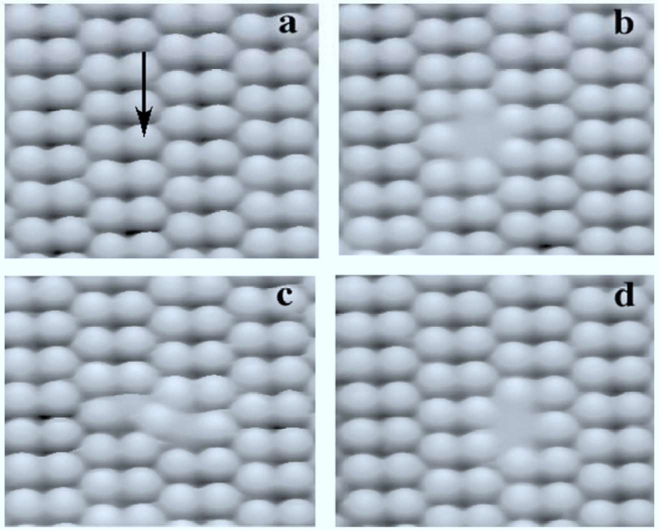
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}\ s^{-1}$, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



- Example: Ge(111)c(2x8) (Mayne et al., SS 2001)



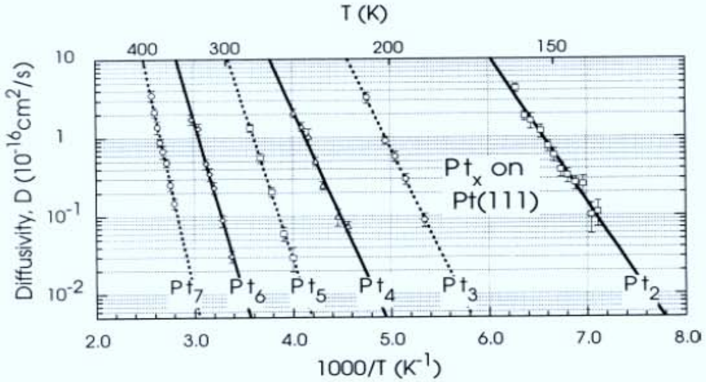
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

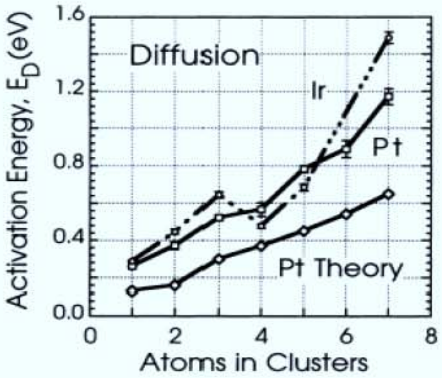
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

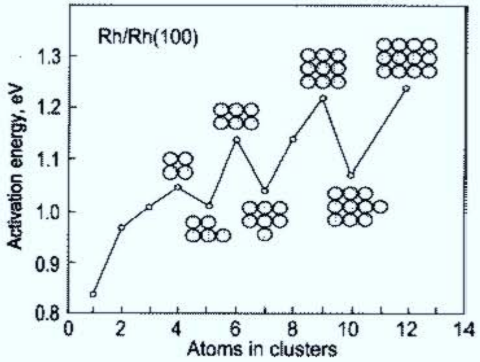


- Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

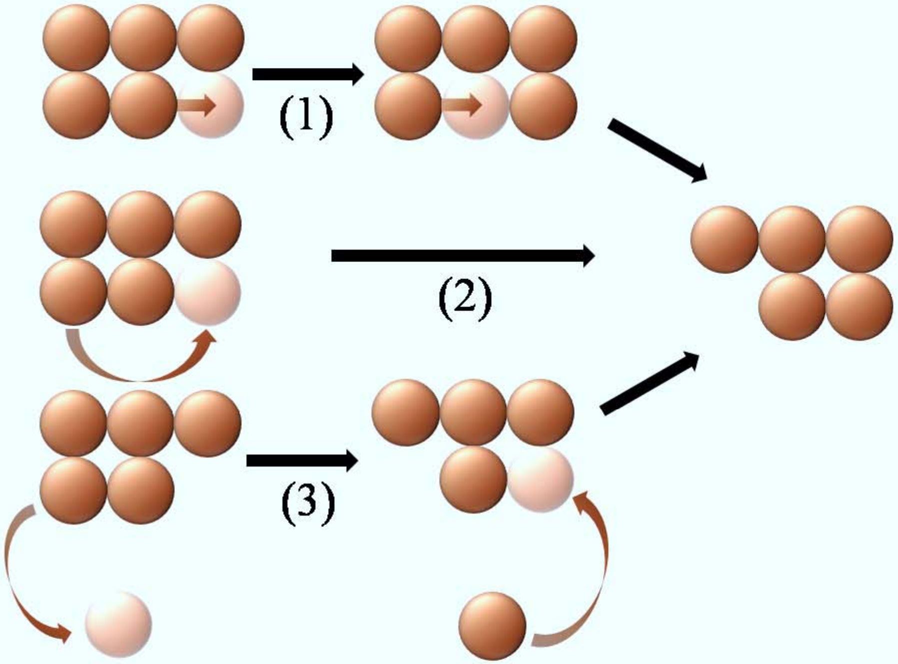
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

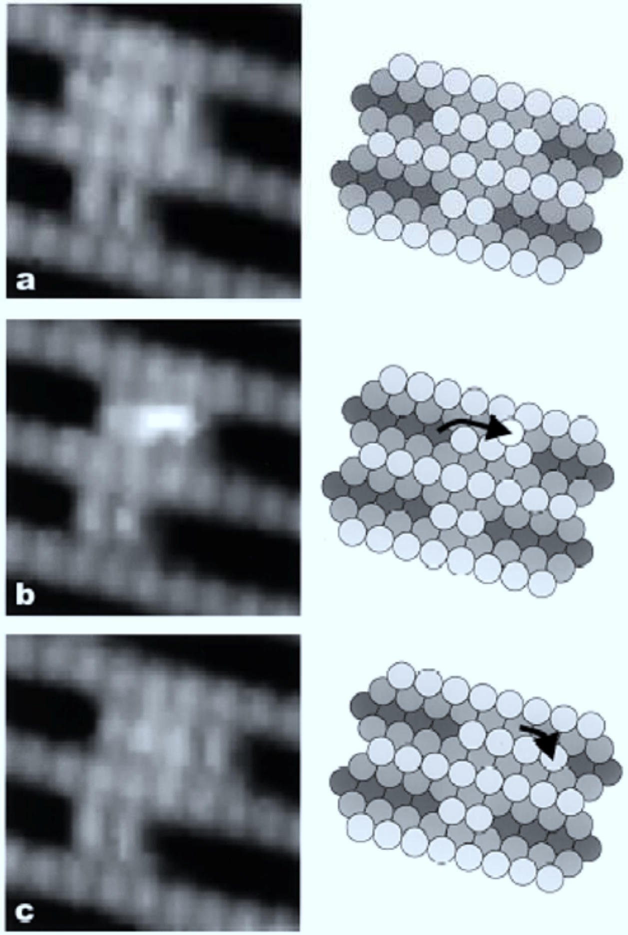
(2) Edge diffusion

(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) “Leapfrog” mechanism:

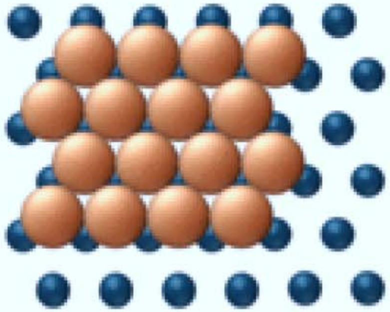


- Example: Pt(110)2x1
(Linderoth et al., PRL 1999)

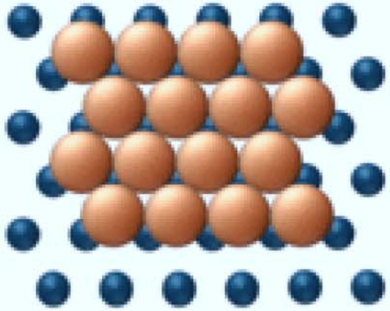
Cluster Diffusion

Concerted mechanisms:

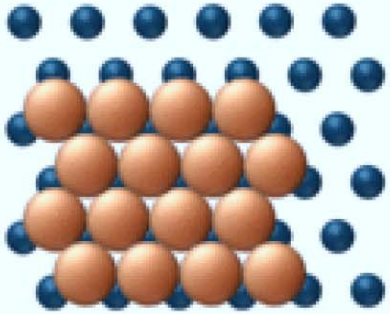
(1) Glide:



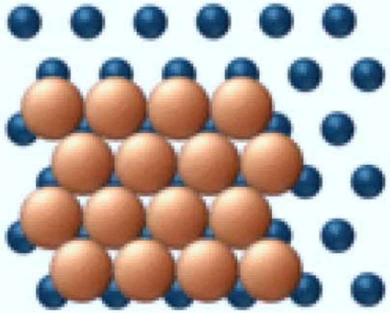
(2) Shear:



(3) Reptation:

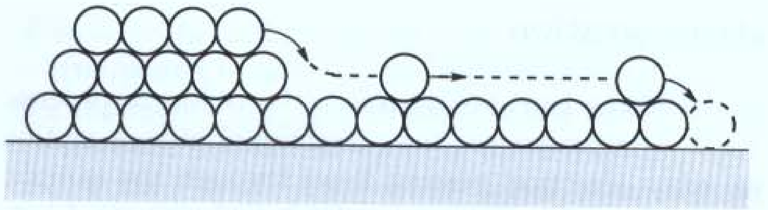


(4) Dislocation:



Phase Formation

- Coverage Θ ~ 0.1-1 ML→ formation of <u>surface phases</u>
- First layer atoms are usually immobile → “unrolling carpet” mechanism



Surface Electromigration

- Electric current through the sample → Directional atomic motion on the surface
- Self-electromigration → Changes in the step structure
- Hetero-electromigration → Mass transfer towards catode or anode

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
- G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1

Repetition:

- Nanostrukturierung: Warum? Wo? Wie? -- Beispiele
- Bottom-Up vs. Top Down
- Bottom-Up Nanostrukturieren:
  → Spielen mit Physikalischen / Chemischen WW
- Oberflaechen und Vakuum Warum? Wieviel?

- Diffusion
- Methoden zur Bestimmung
- Bedeutung fuer’s Wachstum
- Isotropie / Anisotropie

Surface Physics 2010

Growth of Thin Films

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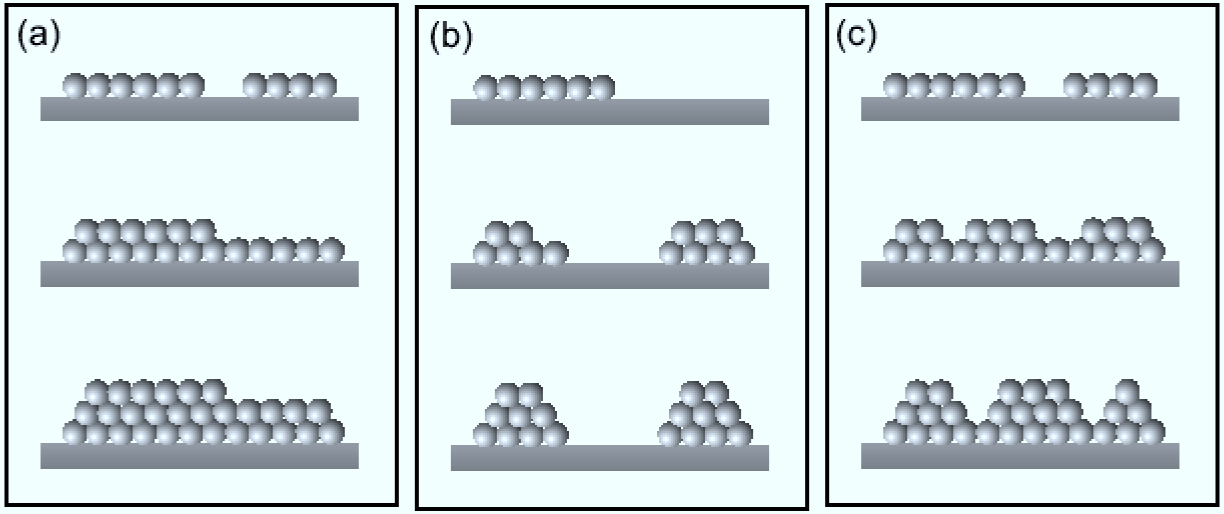
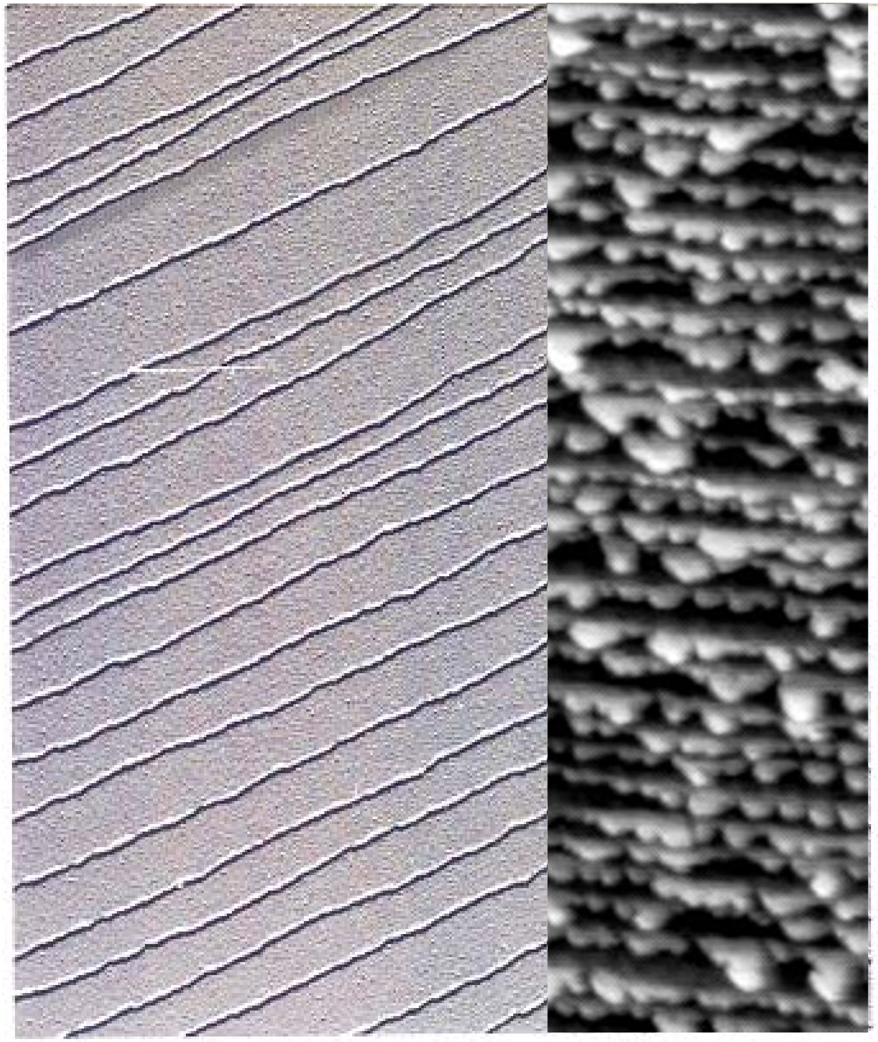
NCCR Nanoscale Science

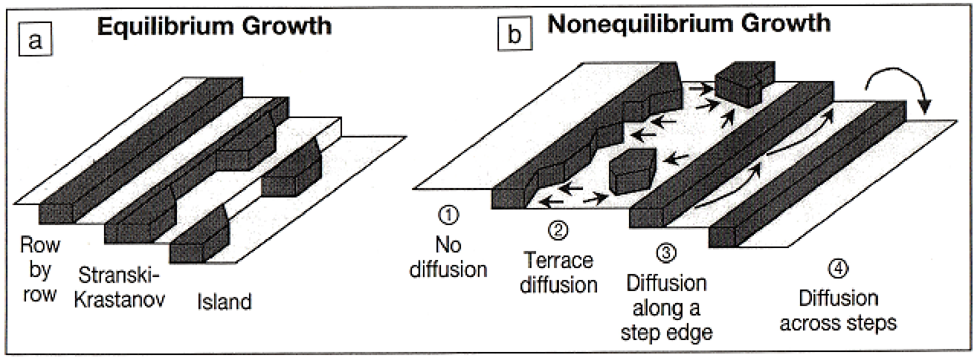
Growth Modes

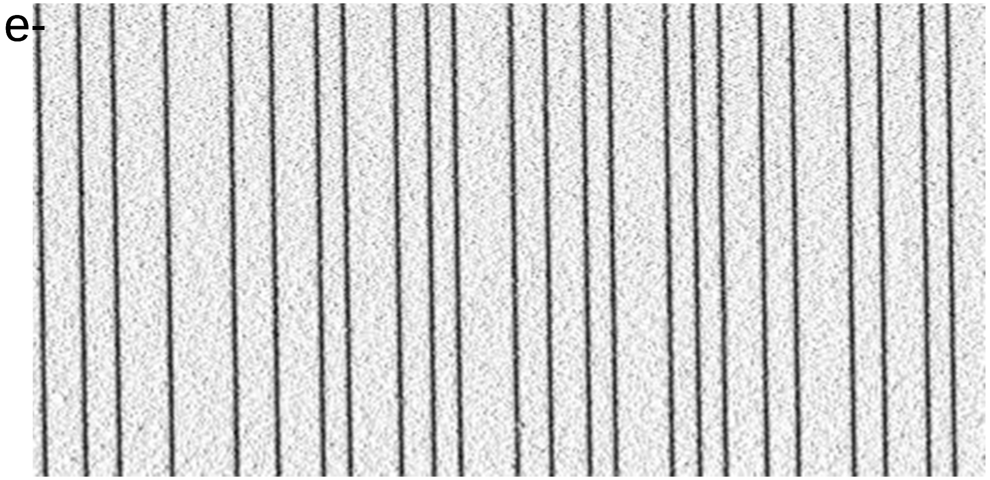


(a) **Layer-by-layer** or **Frank-van der Merve** mode → 2D islands
(b) **Island** or **Vollmer-Weber** mode → 3D islands
(c) **Layer plus island** or **Stranski-Krastanov** mode → 2D layer + 3D islands

‘Physical’ Self Assembly of e.g. Nanowires



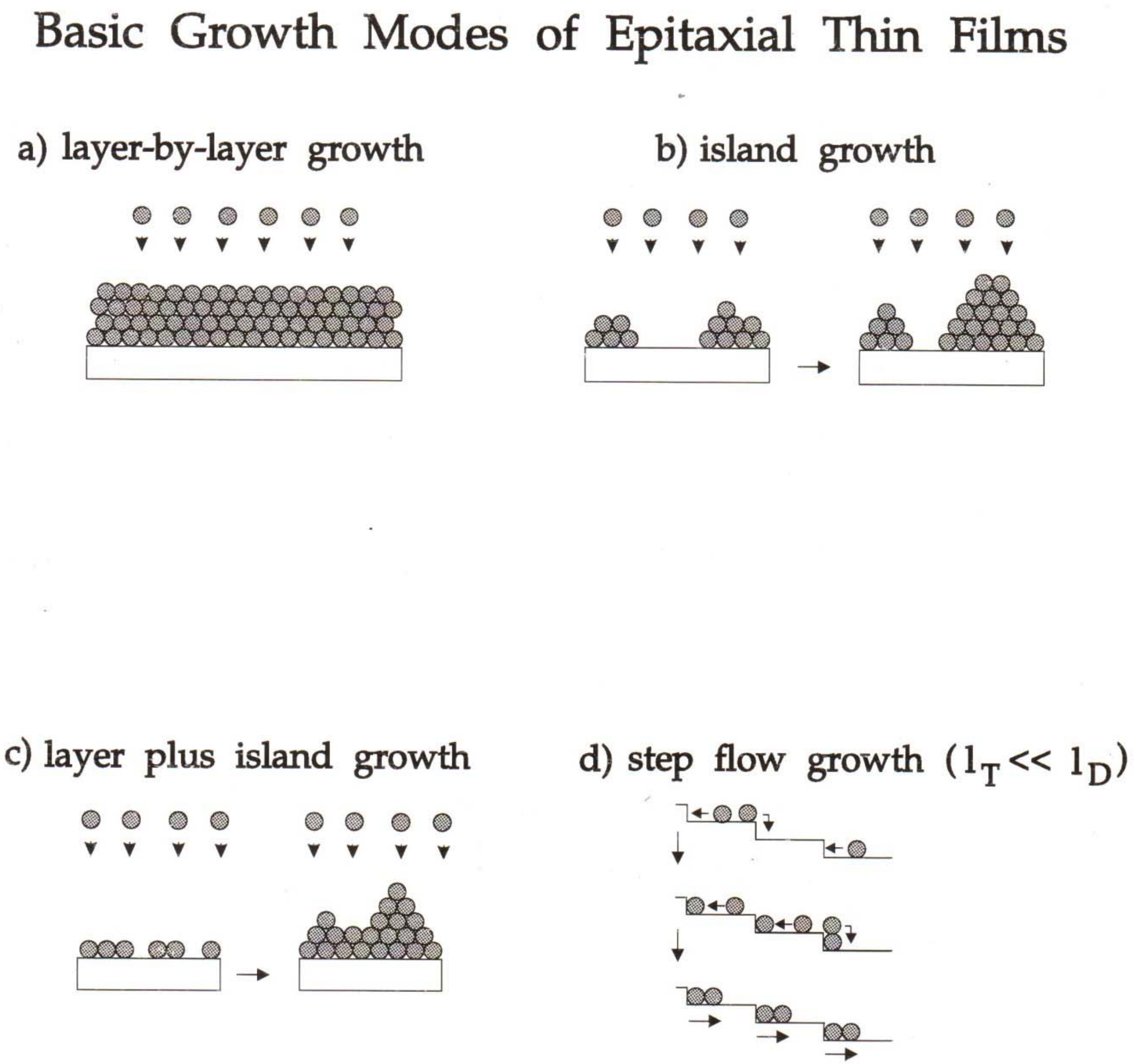


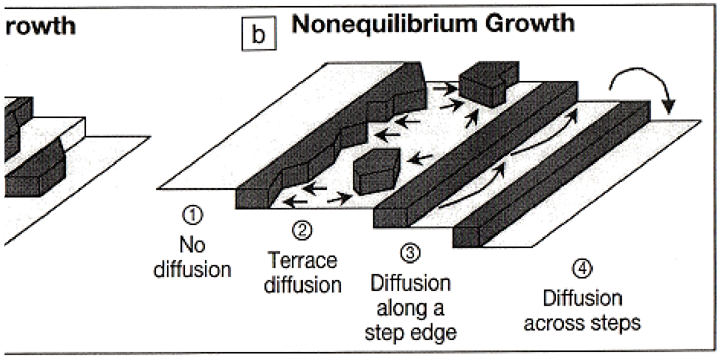


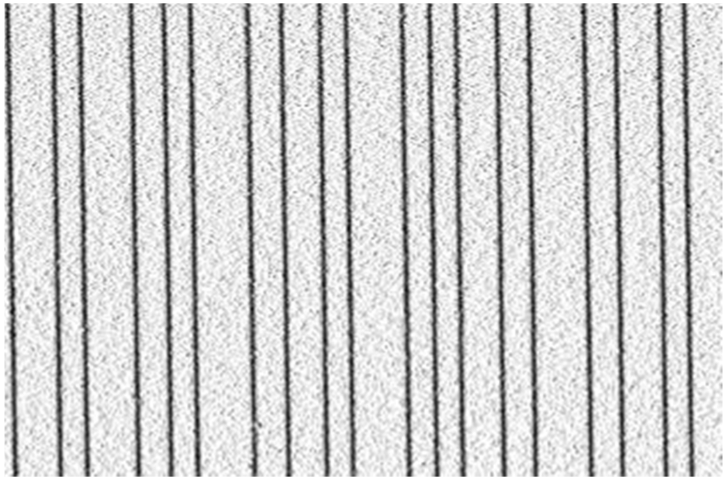
F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

‘Physical’ Self Assembly of e.g. Nanowires

jumping from 3D to 2D







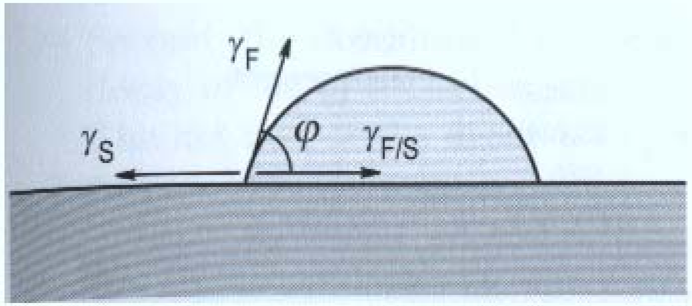
Th. Jung et al.

n **24**, 20--24 (1999).

Growth Modes

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

  ($\equiv$ force per unit length)

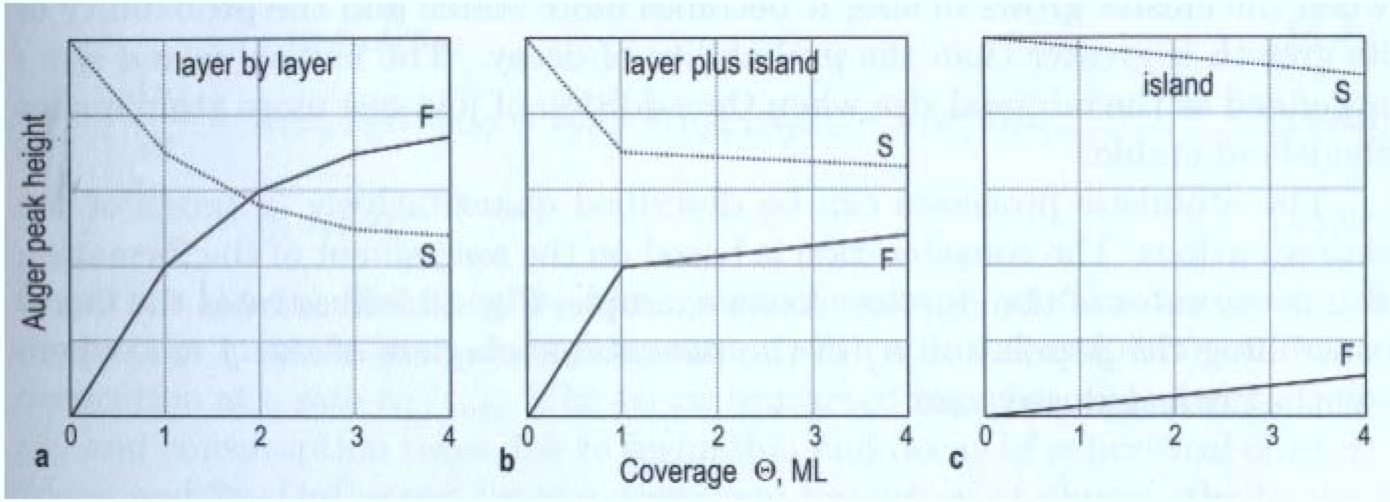


$$\gamma_S = \gamma_{SF} + \gamma_F \cos\varphi$$

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

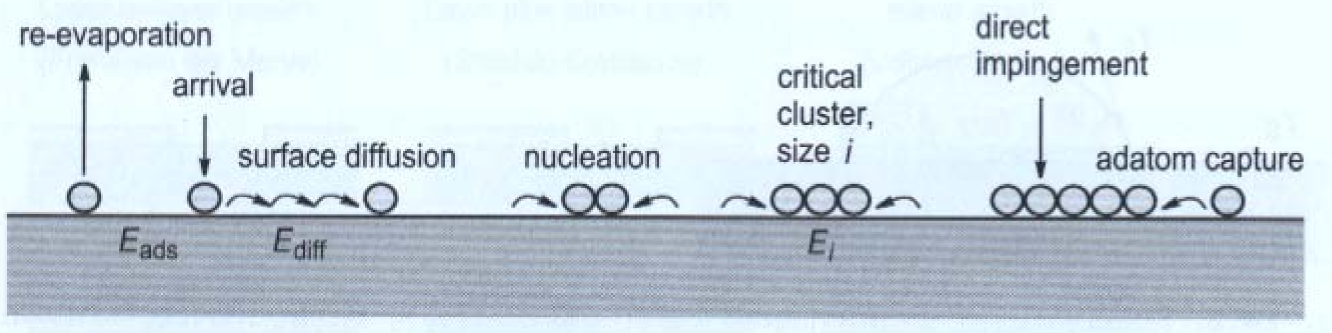
Growth Modes

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



Island Number Density

- Nucleation and growth on surfaces:



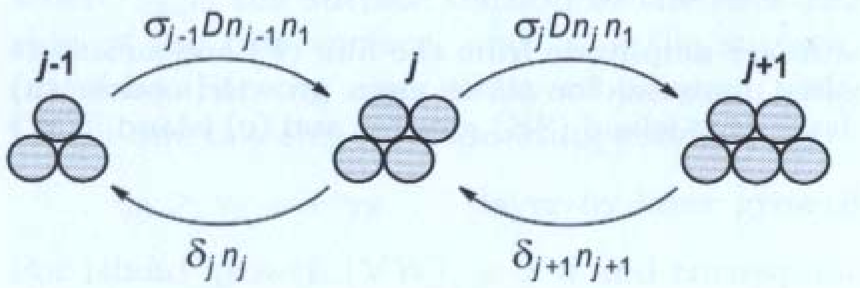
- Diffusion coefficient: $$D = \frac{\nu}{4n_0}\exp\left(-\frac{E_{diff}}{k_B T}\right)$$

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

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

Island Number Density

- Capture and decay processes → cluster size



- Rate equations:

adatom density

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

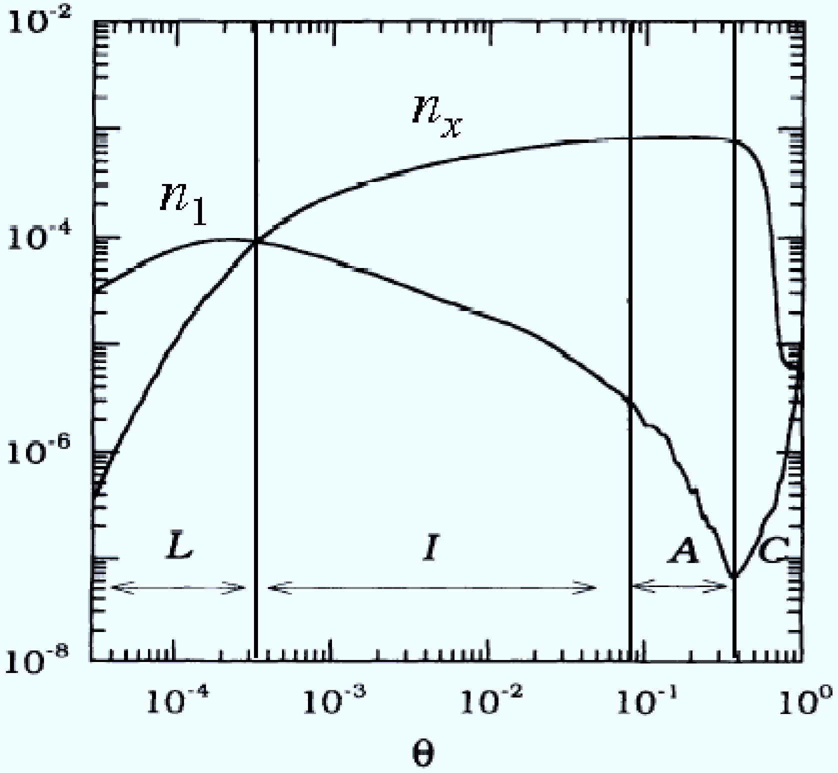
deposition rate

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

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

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

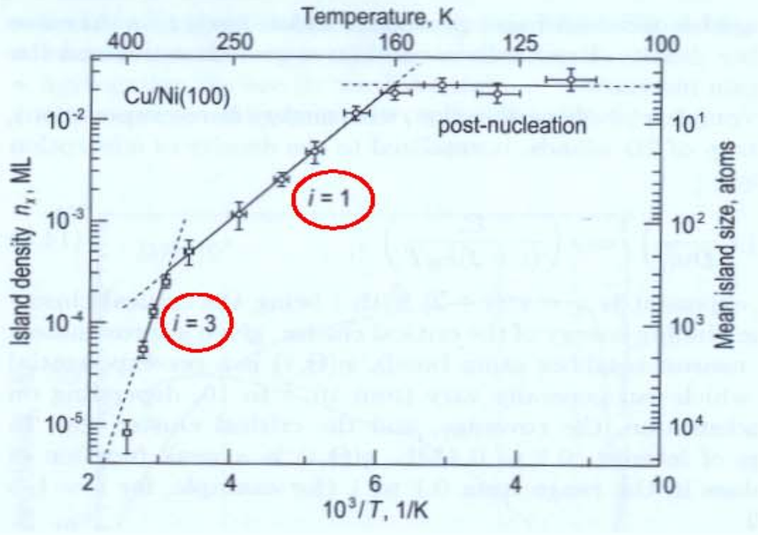
- Saturation density (Venables et al., 1984):

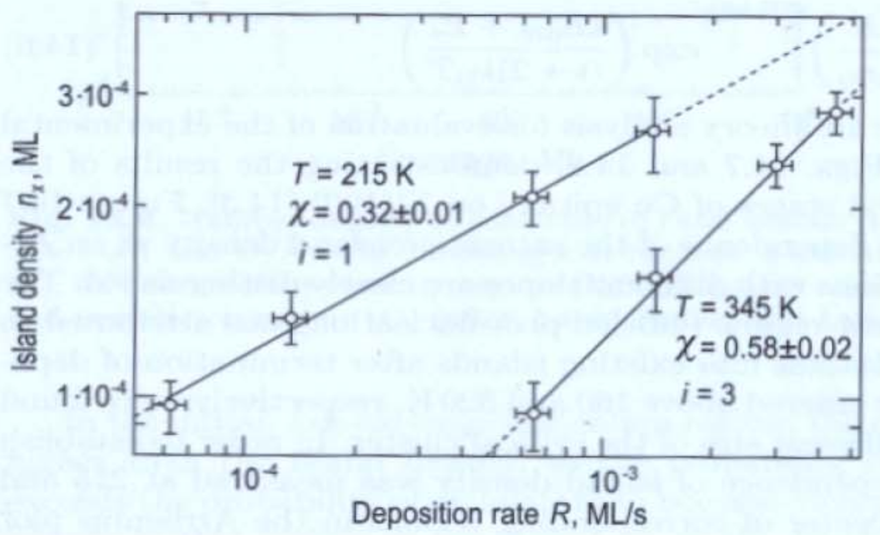
$$\boxed{n_x = n_0\,\eta(\Theta, i)\left(\frac{4R}{\nu_0 n_0}\right)^{\overset{\chi}{\frac{i}{i+2}}} \exp\left(\frac{iE_{diff} + E_i}{(i+2)k_B T}\right)},$$

binding energy
of critical cluster

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

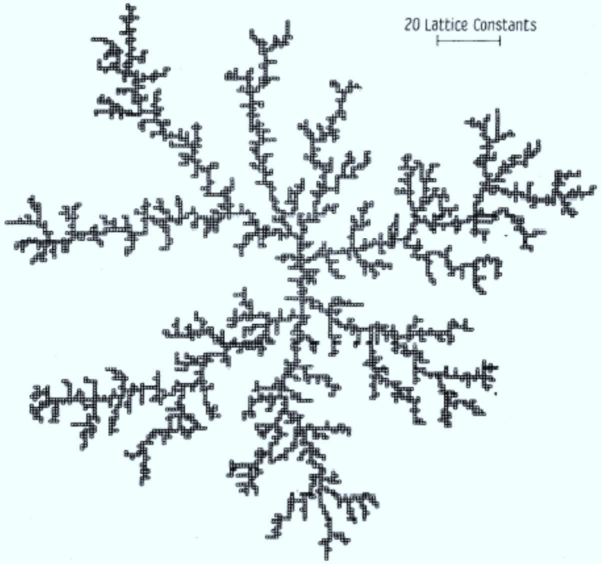
- Example: Cu on Ni(100) (Müller et al., PRB 1996)





Island Shape

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



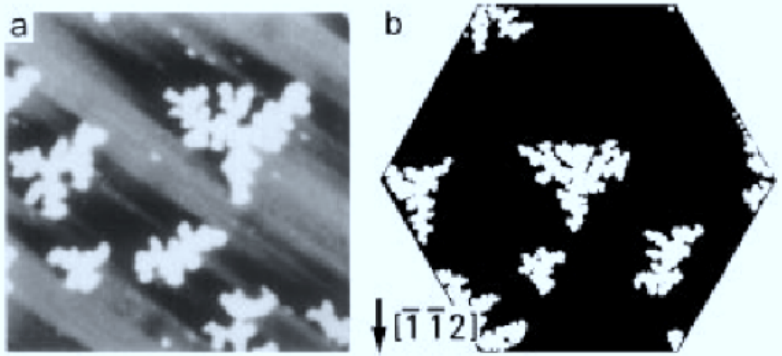
- Adatoms stick at islands
- Fractal shape
- Branch thickness ~ 1 atom
- No influence of lattice geometry

- In real growth (STM experiments):

- Fractal shape
- Branch thickness > 1 atom
- Influence of lattice geometry

Island Shape

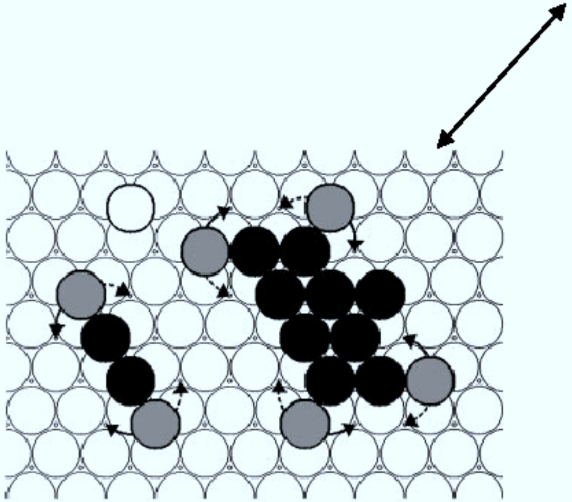
- Example: Pt/Pt(111) (Hohage et al., PRL 1996)



experiment

simulation

- Branch thickness ~ 4 atoms
- Trigonal symmetry

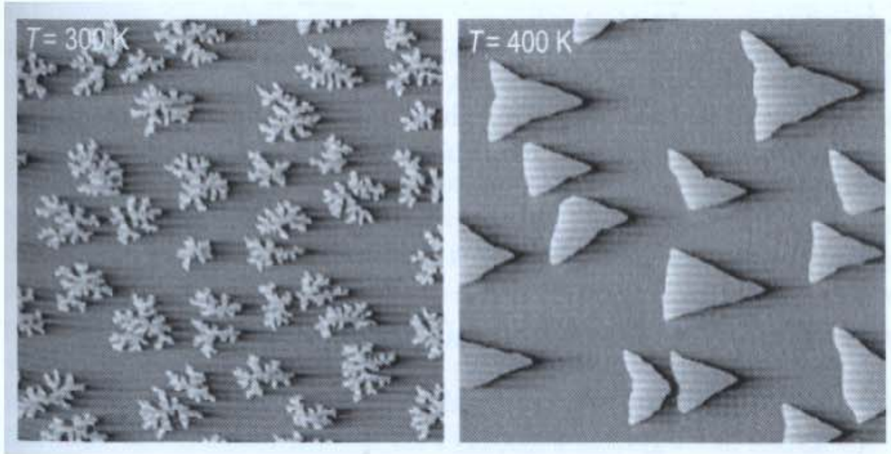


- Higher coordination is preferred

Island Shape

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

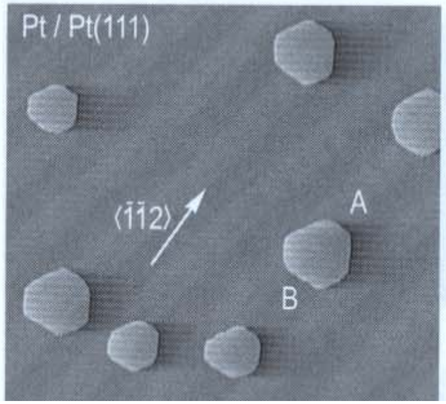
300 K



400 K

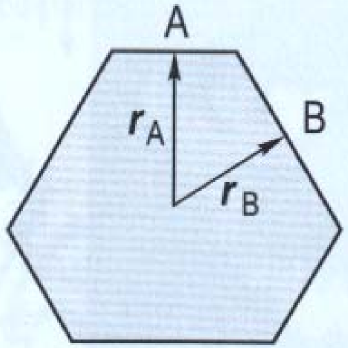
- The equilibrium shape is hexagonal:

(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



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

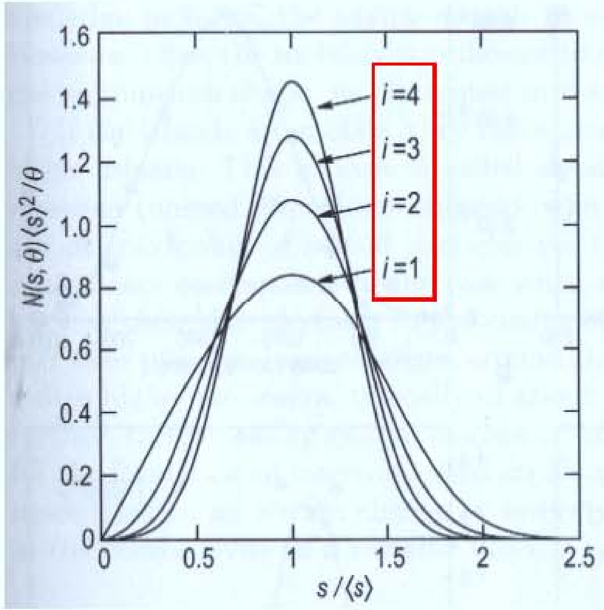
- For Pt(111): B/A ~ 0.87

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):

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

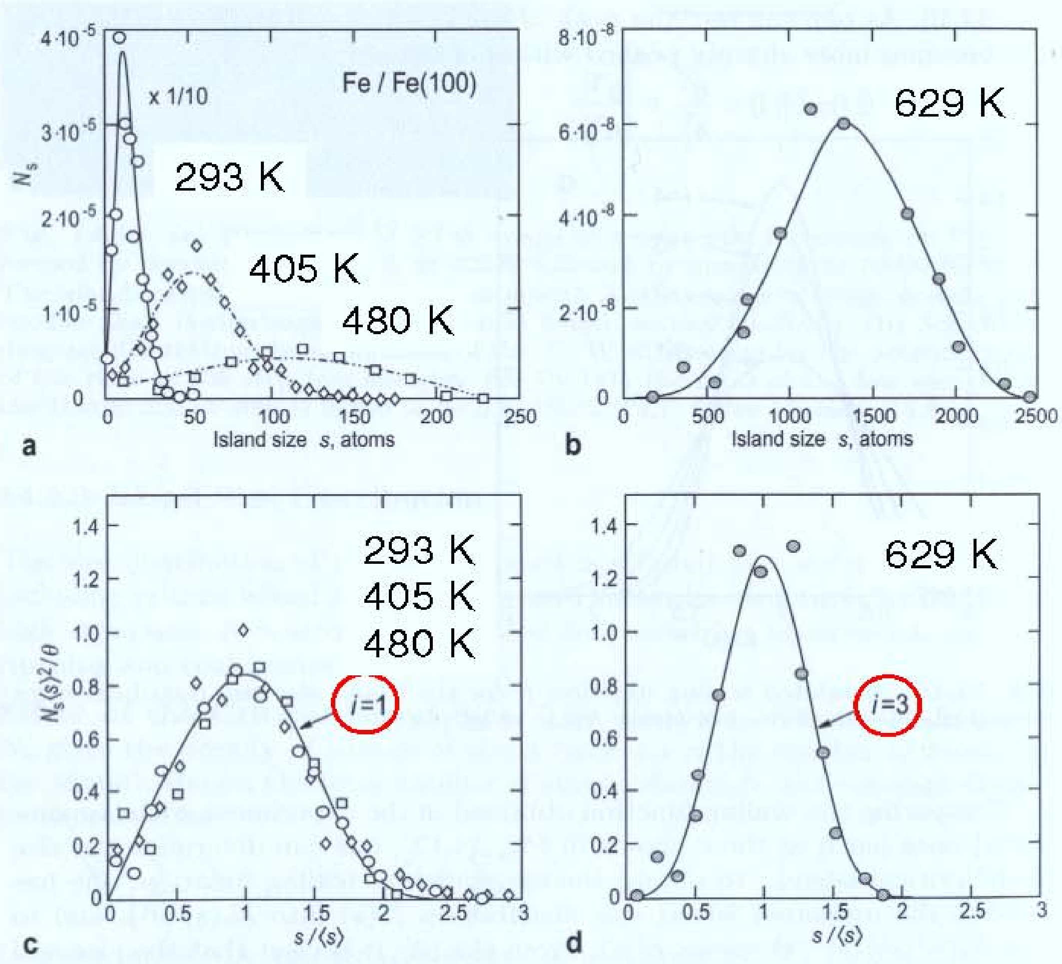


- Comparing with experimental results

→ critical island size

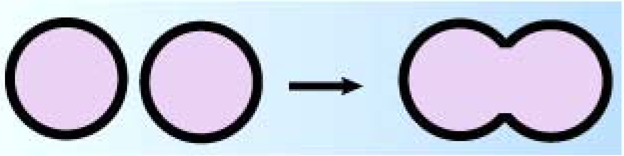
Island Size Distribution

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



Coarsening Phenomena

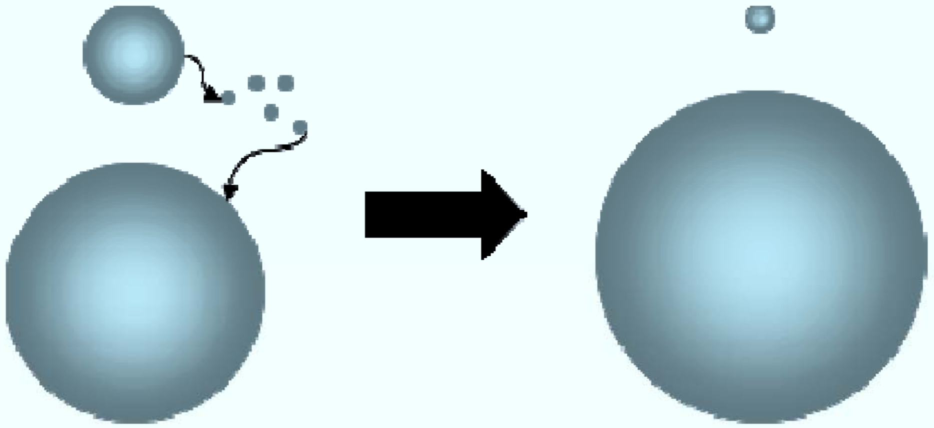
1) Coalescence:



- 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:



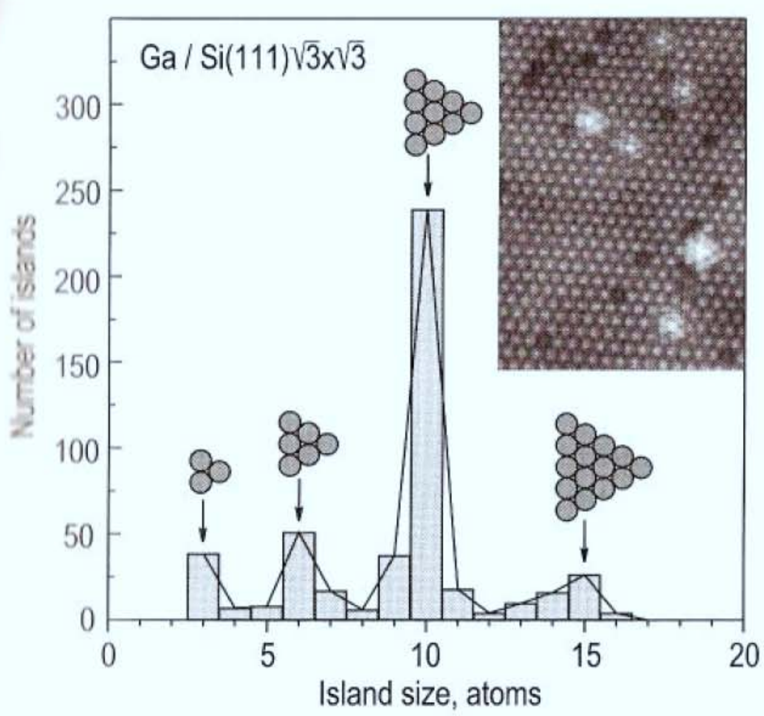
- Chemical potential of a circular island:

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

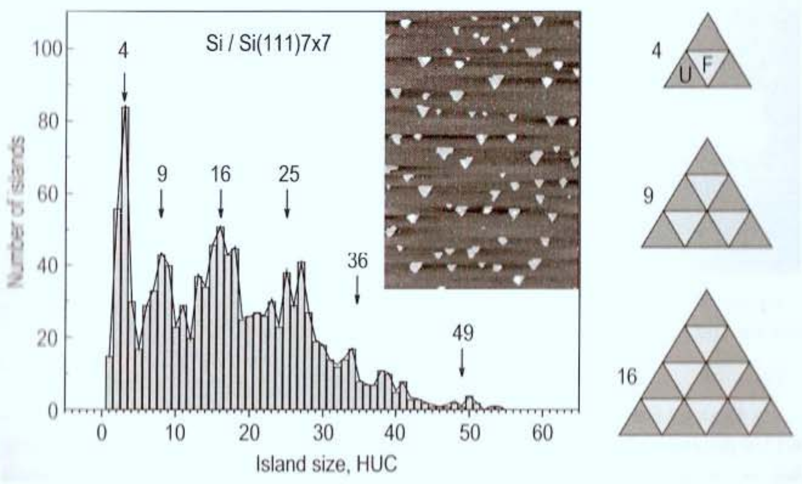
Reducing free energy → net flow from smaller to larger islands!

Magic Islands

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



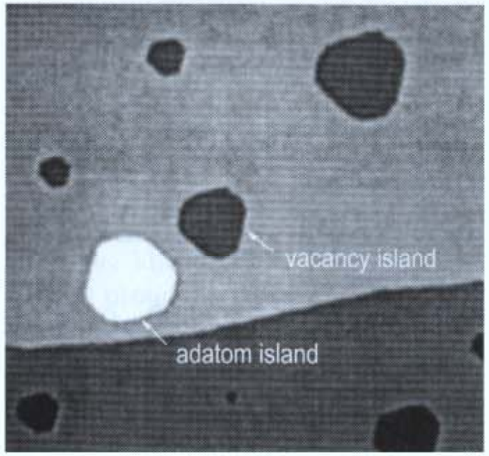
- Si on Si(111)7x7 (Voigtländer et al., PRL 199



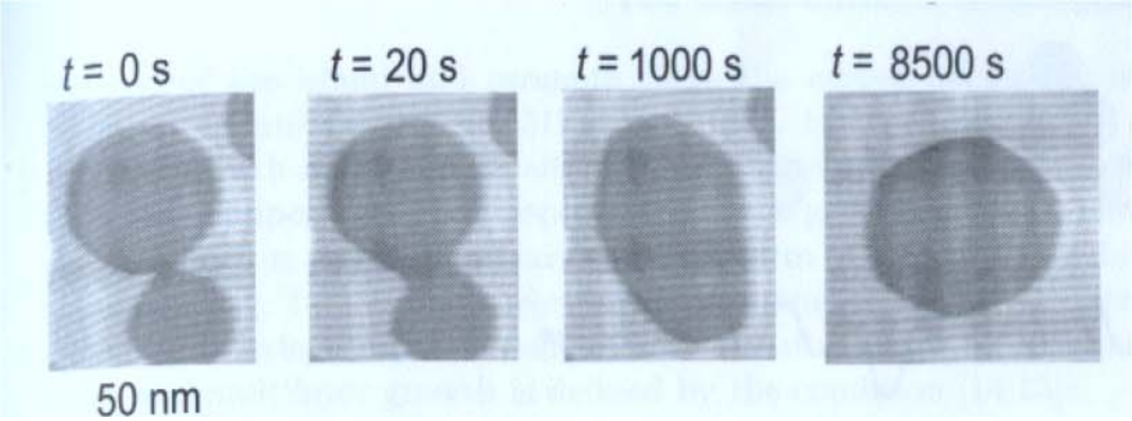
Formation of a new row → high energy cost!

Vacancy Islands

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

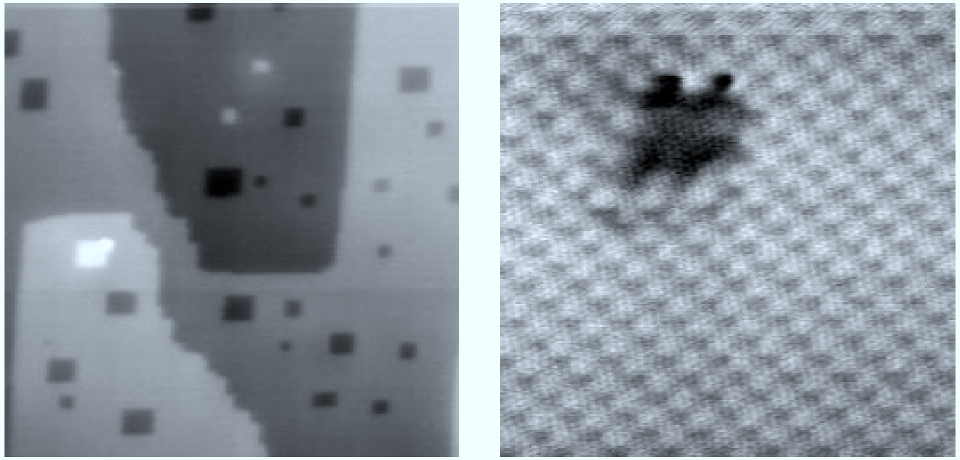


- Analogies with adatom islands



Vacancy Islands

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



KBr(100)

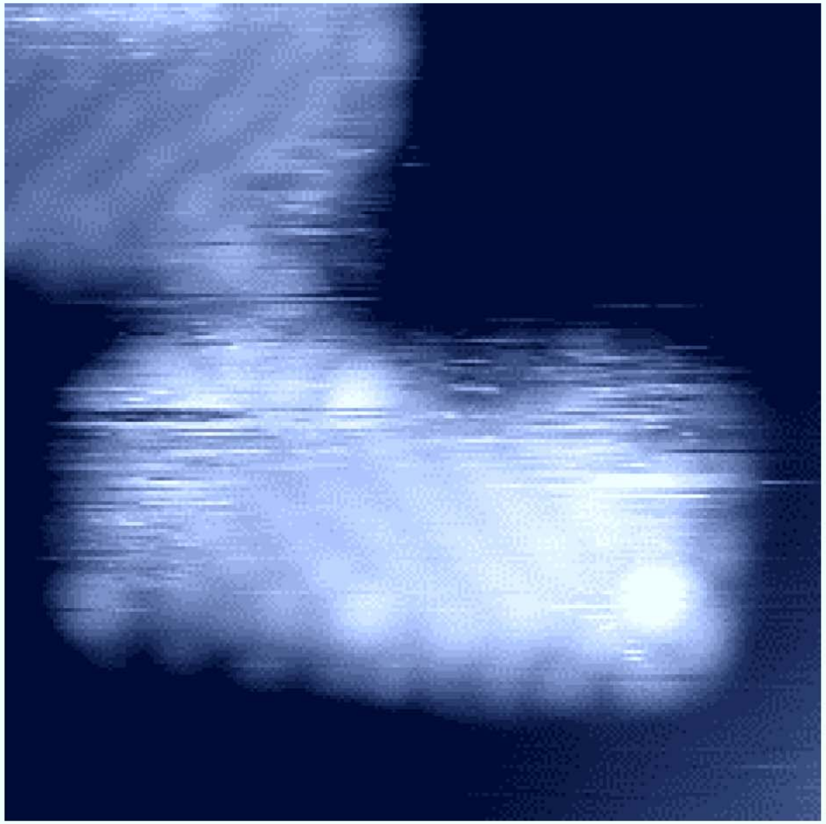
- Irradiation with 1 keV electrons at 130 ºC

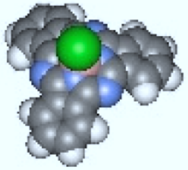
- Rectangular pits with area of 1x1 nm^2 up to 30x30 nm^2

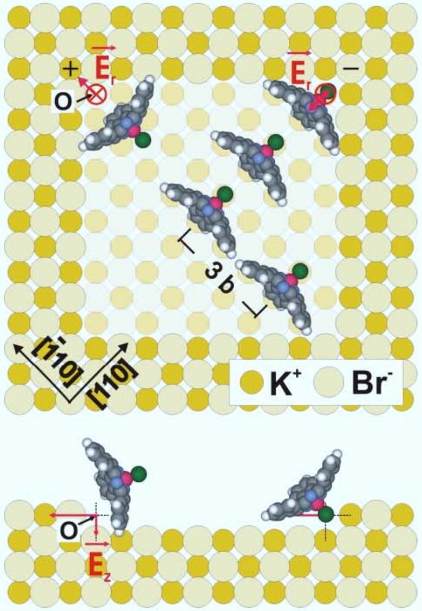
- 1 ML deep (0.33 nm)

Vacancy Islands

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

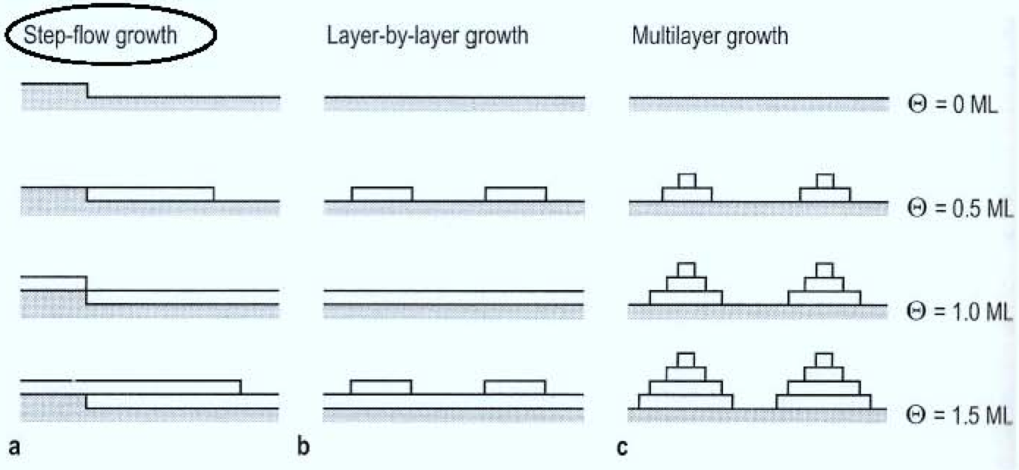




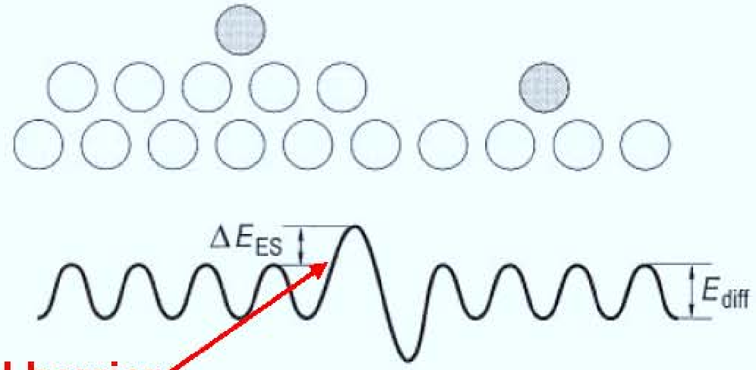


Kinetic Effects in Homoepitaxy

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



- **Interlayer** mass transport:

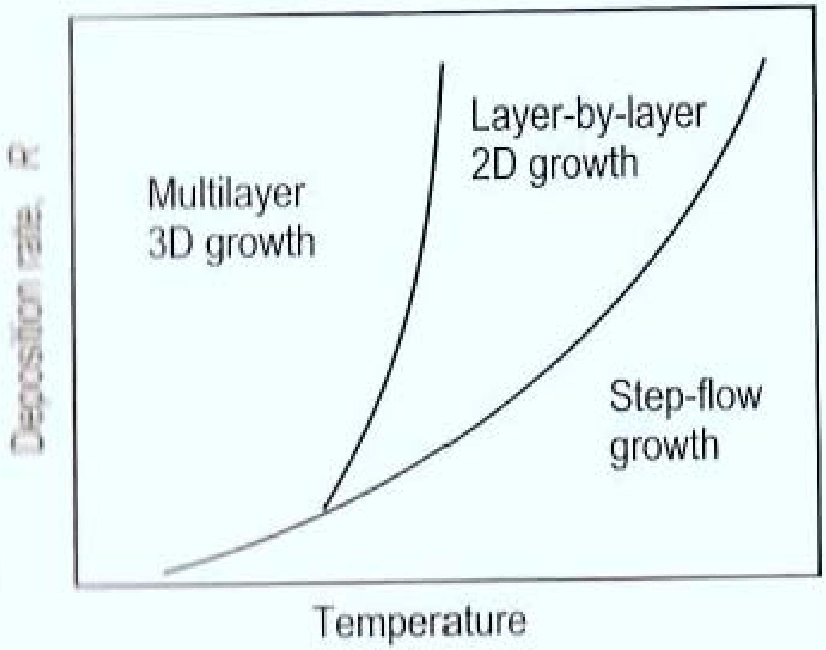


Ehrlich-Schwöbel barrier

Kinetic Effects in Homoepitaxy

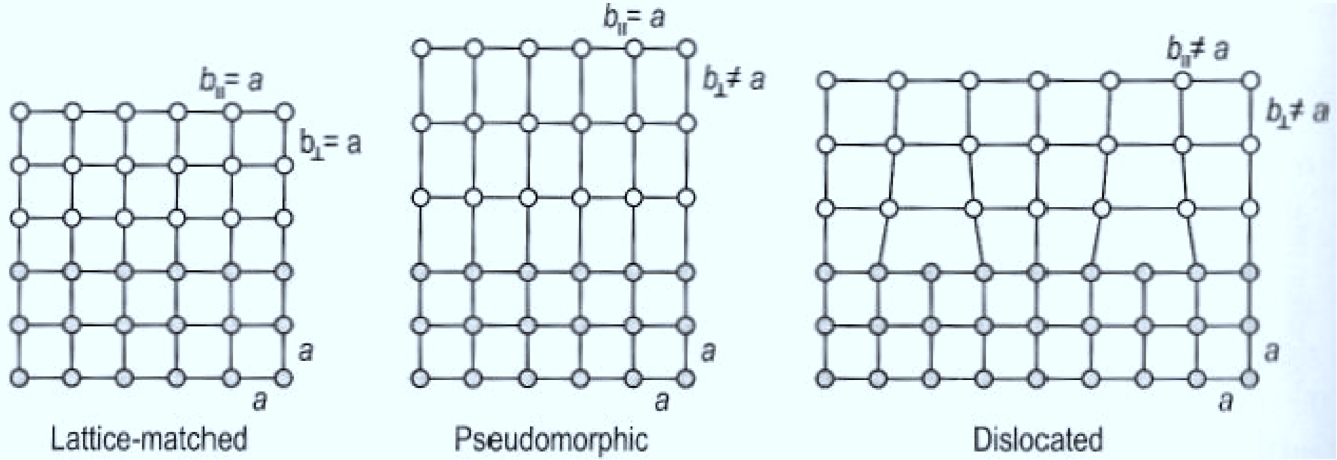
- Deposition rate and Temperature are important!

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



Strain Effects in Heteroepitaxy

- Heteroepitaxy growth modes:



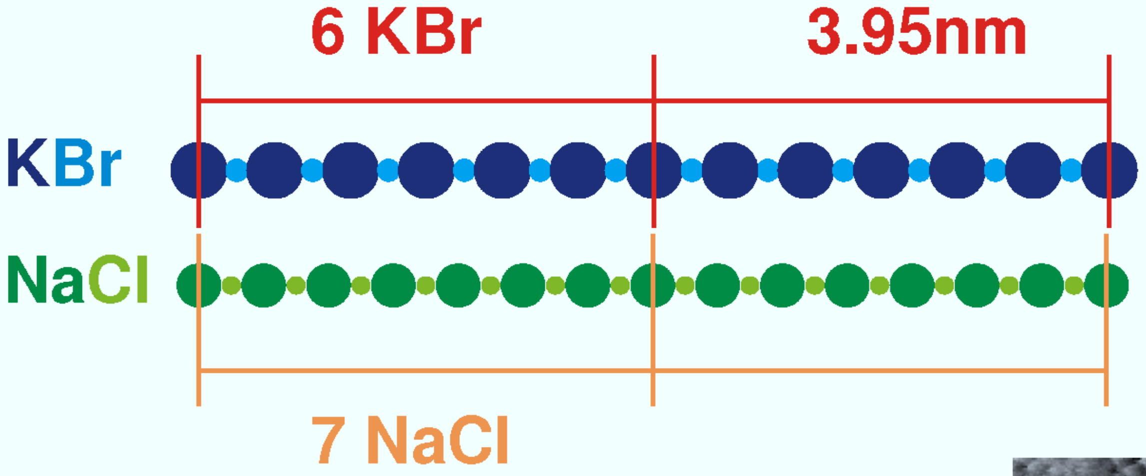
Lattice-matched Pseudomorphic Dislocated

- Lattice **misfit** → <u>elastic strain</u> and <u>dislocations</u>

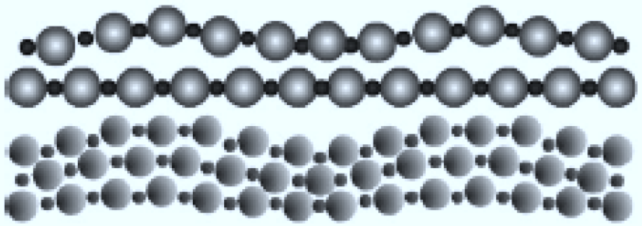
- Pseudomorphic growth below critical misfit and film thickness

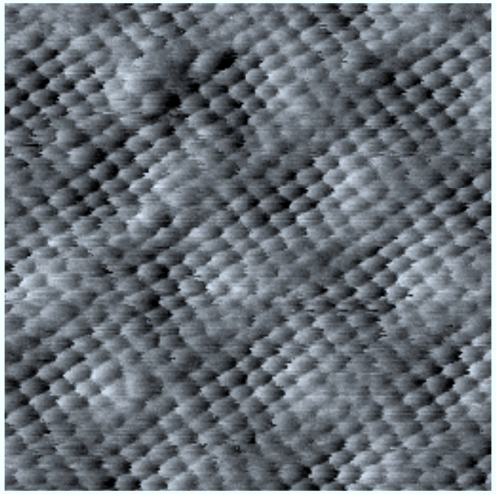
Strain Effects in Heteroepitaxy

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

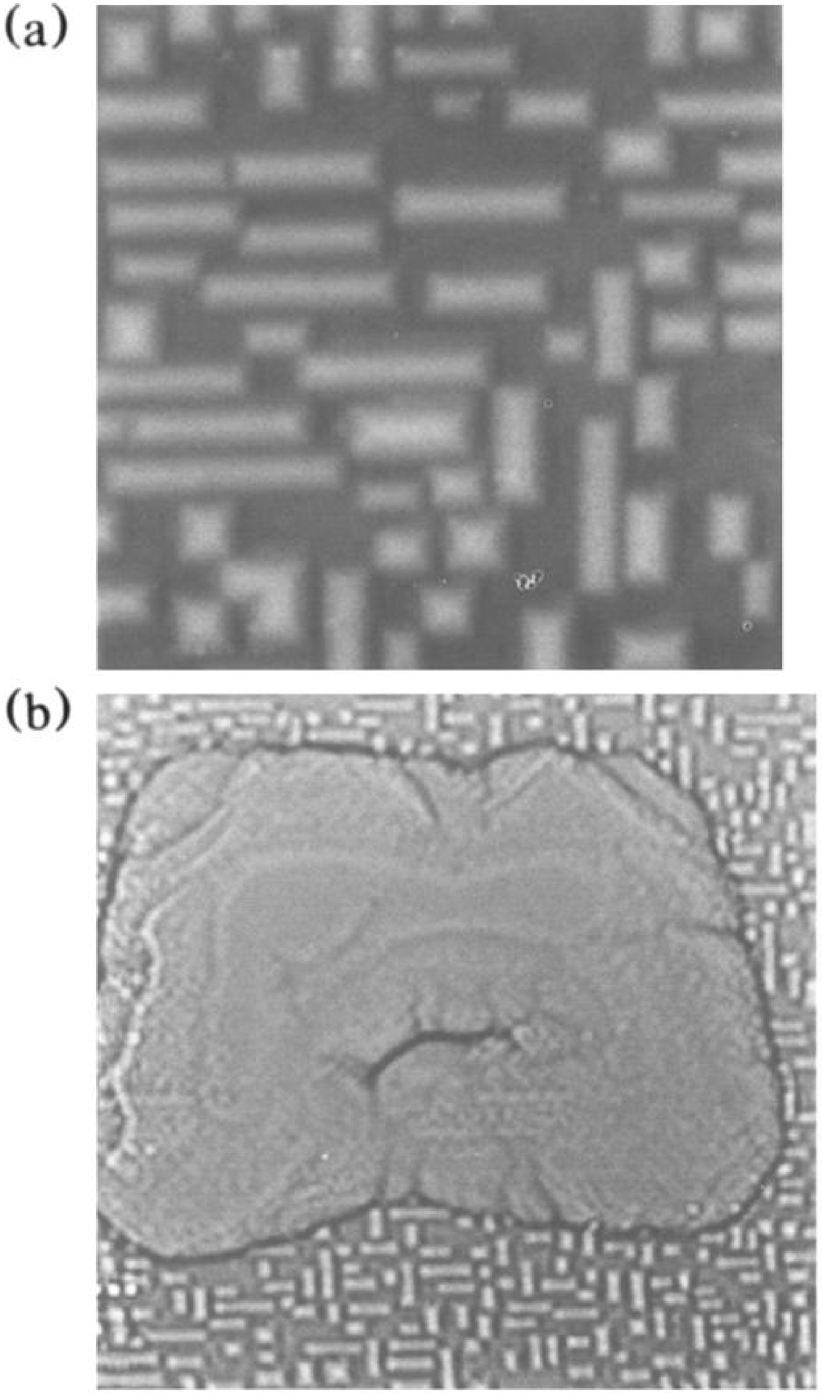


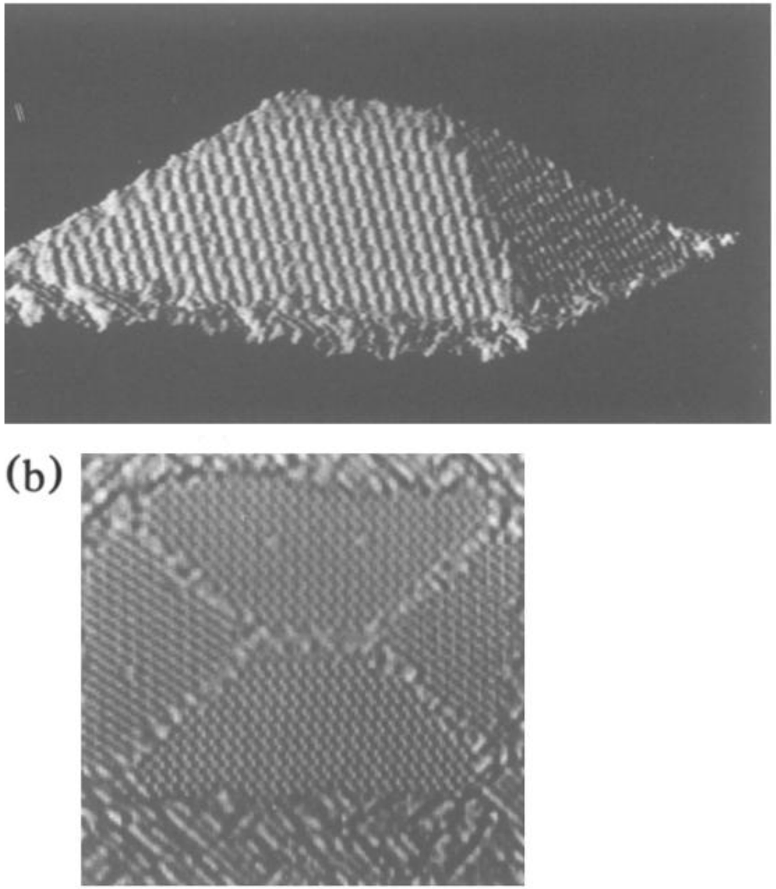
- A “Moiré pattern” appears (also in the substrate?)





Ge @ Si(100)

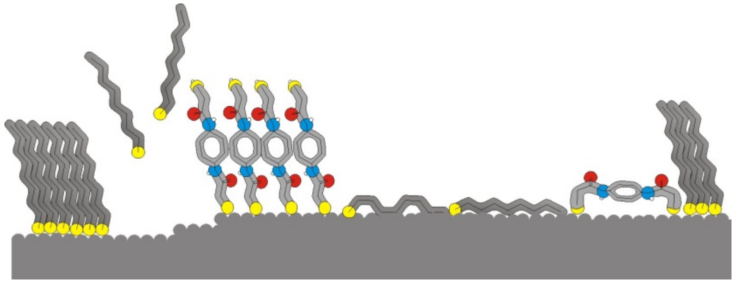


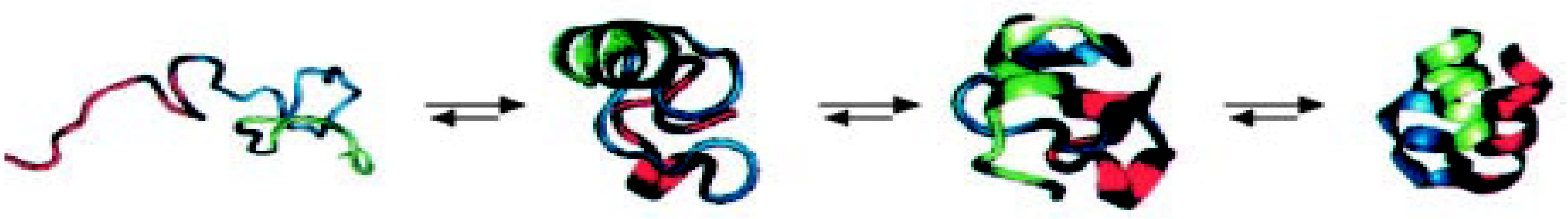


Molecular Self-Assembly

> “Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds. Molecular self-assembly is ubiquitous in biological systems and underlies the formation of a wide variety of complex biological structures.”

G.M. Whitesides, J.P. Mathias and C.T. Seto, *Science* **254**, 1312 (1991)





Fragen, Kommentare