Repetition:

- Nanostrukturierung: Warum? Wo? Wie? -- Beispiele
- Bottom-Up vs. Top Down
  Sauberkeit: Clean-room vs. UHV
  'Total im Dreck' oder 'Total Sauber'
- Bottom-Up Nanostrukturieren:
  → Spielen mit Physikalischen / Chemischen WW
- Oberflaechen und Vakuum Warum? Wieviel?
- Atome und Molekuele sind Nanostrukturen
  → zu klein fuer die meisten technologischen Anwendungen
  → wie mit ihnen reden, wie Kontakt herstellen?

Nanostructures and Nanostructuring
2. Oct 2012

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

Nanostruktures: Important concepts

Dimensionality	'dot' vs 'wire' vs sheet
Ratio Bulk I vs Bulk II	'matrix & filler', ceramic
Controlling by size effects	'optic', 'electronic' etc.
Controlling by anisotropy	'polymer – polarizer'
Controlling contact area	'lotus effect'
Controlling by proximity @ Interface	'field effect transistor'
Sub-wavelength optics (diffraction)	'~ photons, $\varepsilon \sim 1$
...	

Important: Nanostructuring: Mostly 2D or pseudo 3D
3D: wishful thinking but enormous potential
('brain' vs 'processor')

Crucial: Control 'Surface / Interface active components'
→ need very clean materials (~d^3) / surfaces (d^2)

Surface Physics 2010

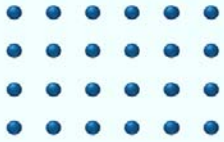
Surface Diffusion

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:

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

a = jump distance; ν = hopping frequency

(Note that νt = number of hops!)

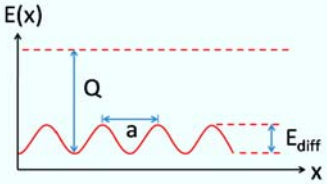
• **Diffusion coefficient**:

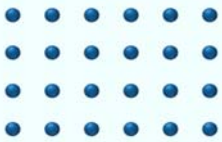
$$D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}$$

z = number of first neighbors = [2 in 1D diffusion; 4 on a square lattice; 6 on a hexagonal lattice]

Random-Walk Motion

- Hopping → surmounting a potential barrier





• **Arrhenius law**:

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

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):

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

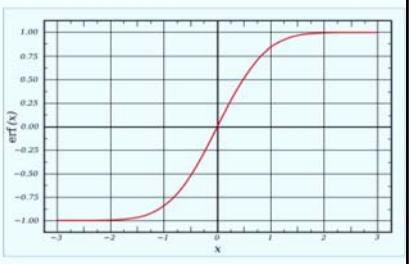
← from equation of continuity

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

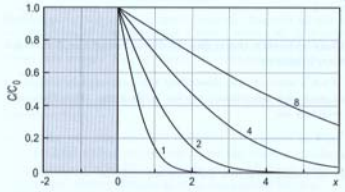
Analytical Solutions of Fick's Laws

- We introduce the **error function**

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



- Source of constant concentration:



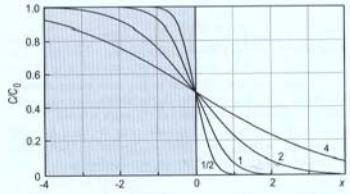
$$c(x,t) = c_0\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

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

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

Analytical Solutions of Fick's Laws

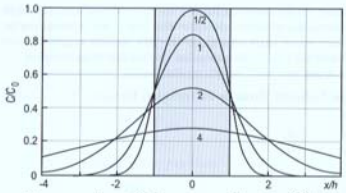
• Source of infinite extent:



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

- 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

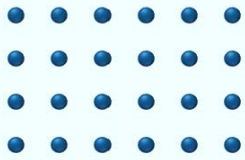
• Depending on the coverage Θ:

- 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:

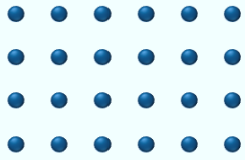
$$D = \frac{1}{zNt} \sum_i \langle \Delta r_i^2 \rangle$$

(no relation to radioactive tracers!)

Chemical Diffusion

• **Chemical Diffusion:** - Higher coverage

- Attraction or repulsion between adatoms



• Fick's first law can be generalized:

$$J = -D_c(\Theta)\frac{\partial \Theta}{\partial x}$$

coverage

chem. diff. coefficient

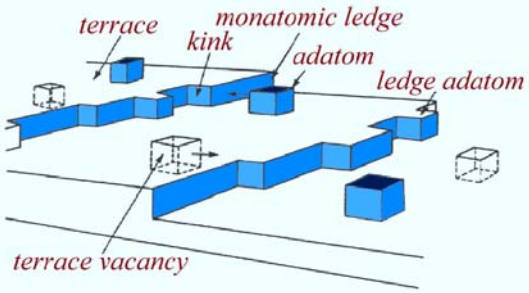
• Strong dependence on adsorbate coverage is expected, especially when ordered phases are formed (Naumovets-Vedula, 1986)

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:

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

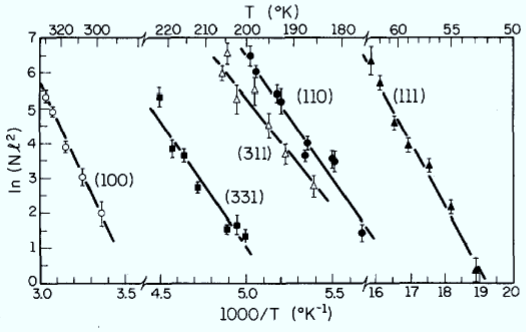
ΔG = energy of adatom formation

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

• **Orientational Anisotropy:** the diffusion coefficient depends on the orientation of the surface

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



N: number of jumps in 3 min

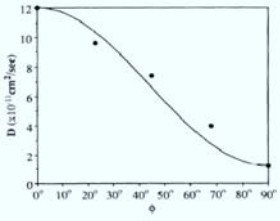
ℓ: jump distance

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

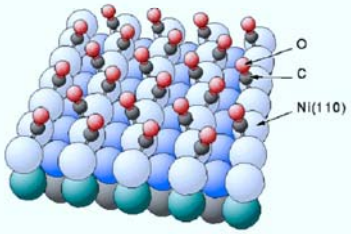
Anisotropy of Surface Diffusion

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

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

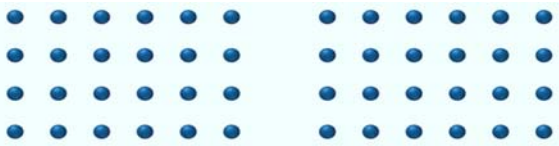


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

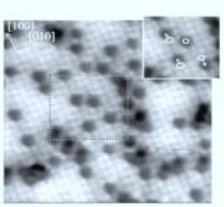


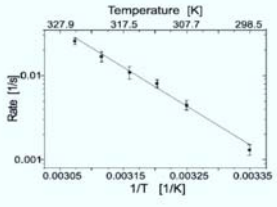
Atomistic Mechanisms

1) Hopping mechanism:



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

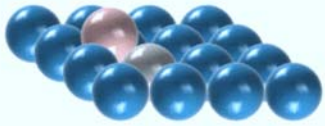


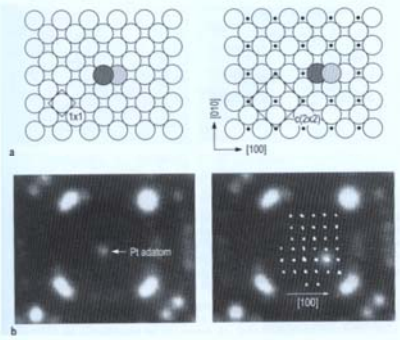


→ Arrhenius law with $\nu \sim 10^{12}$ s^{-1}, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:





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

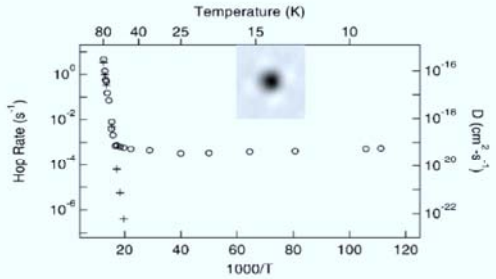
• Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

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

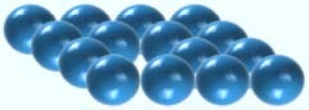
• Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



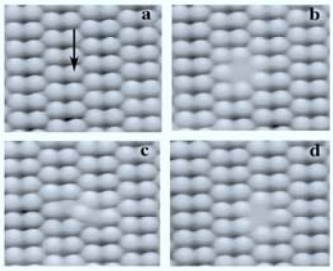
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}$ s^{-1}, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



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



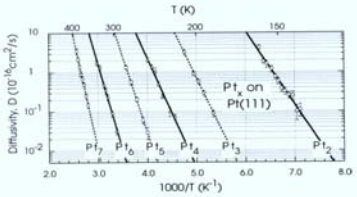
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

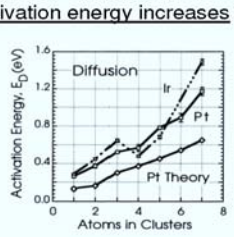
• Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

• The larger the cluster, the lower its mobility:

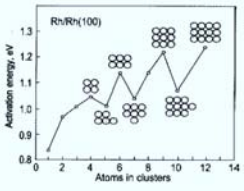


• Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

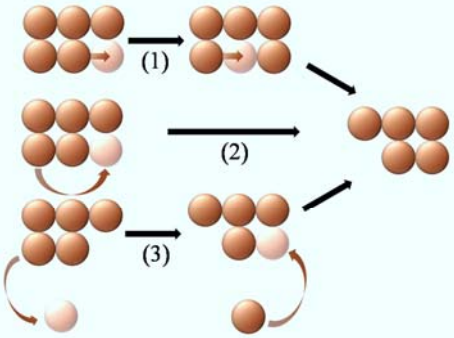
• Compact shapes are less mobile...



(Kellogg, PSS 1996

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

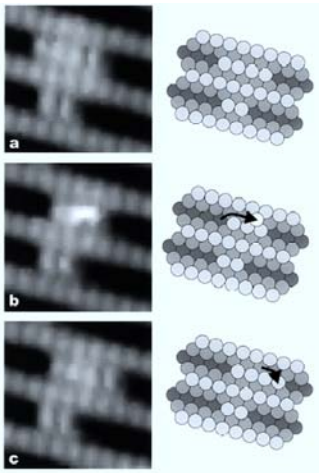
(2) Edge diffusion

(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) "Leapfrog" mechanism:

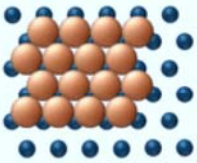


• Example: Pt(110)2x1
(Linderoth et al., PRL 1999)

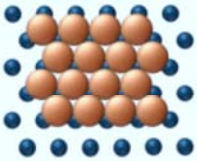
Cluster Diffusion

Concerted mechanisms:

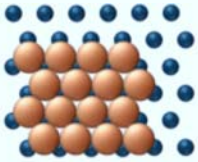
(1) Glide:



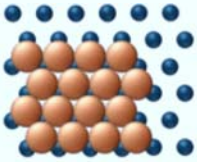
(2) Shear:



(3) Reptation:

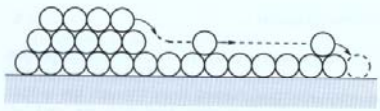


(4) Dislocation:



Phase Formation

- Coverage Θ ~ 0.1-1 ML→ formation of surface phases
- First layer atoms are usually immobile → "unrolling carpet" mechanism



Surface Electromigration

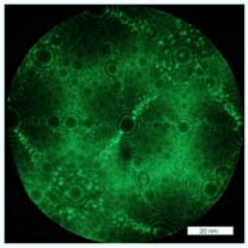
- Electric current through the sample → Directional atomic motion on the surface
- Self-electromigration → Changes in the step structure
- Hetero-electromigration → Mass transfer towards catode or anode

Experimental Techniques

1) Direct observation:

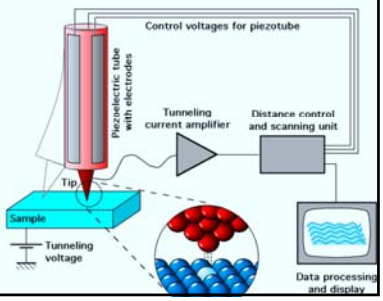
• Field ion microscopy (FIM)
→ "image-anneal-image" technique

- Limited to refractory or noble metal surfaces



• Scanning tunneling microscopy (STM)
→ "image-while-hot" technique

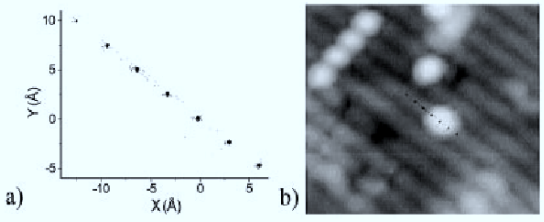
- STM "movies" can be recorded
(at 0.01-1 frames per second)



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!

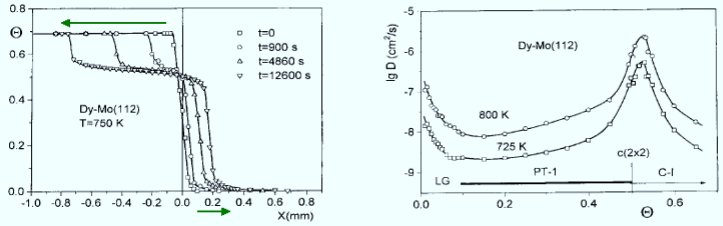
Experimental Techniques

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:

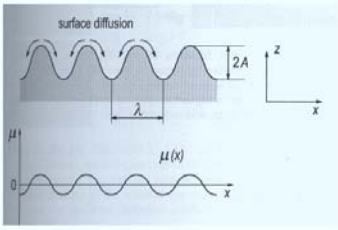
- A surface is perturbed from its lowest energy configuration...

... and allowed to relax via diffusion

- Relaxation rate → Coefficient of diffusion

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

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

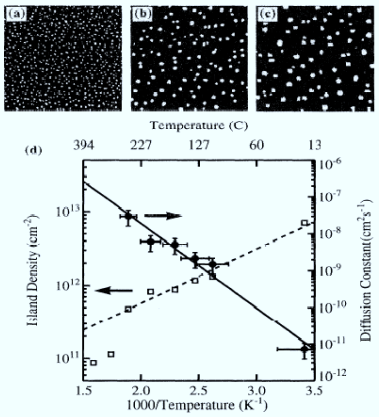


γ = surface tension; V = atomic volume; n_0 = surface density

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)



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

deposition rate

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

Surface Physics 2010

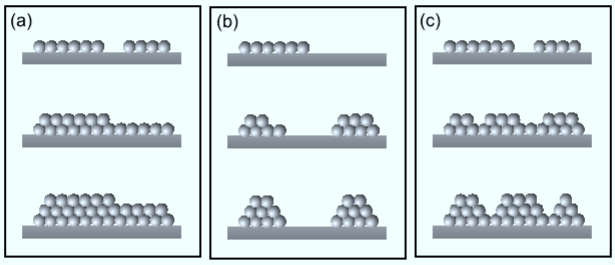
Growth of Thin Films

UNI BASEL

Lecturer: Dr. Enrico Gnecco

NCCR Nanoscale Science

Growth Modes

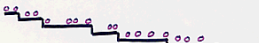


(a) **Layer-by-layer** or **Frank-van der Merve** mode → 2D islands
(b) **Island** or **Vollmer-Weber** mode → 3D islands
(c) **Layer plus island** or **Stranski-Krastanov** mode → 2D layer + 3D islands

"NANOWIRES" assly in parallel by Step Decoration & Controlling Growth.

Sample prepavation.

Adsorbate deposition



Annealing $T<T_s$

DIFFUSION ⟷

Annealing $T>T_s$

DIFFUSION ⟷ ↕

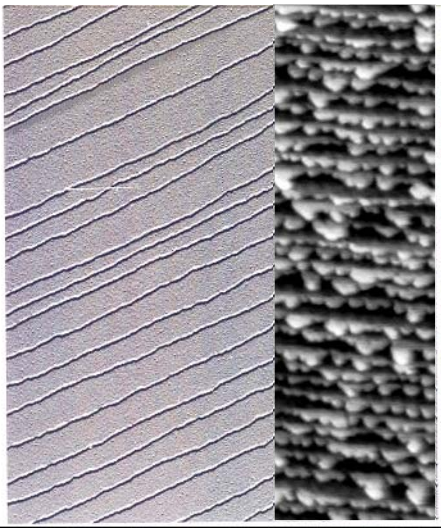
CONTROLLING GROWTH KINETICS:

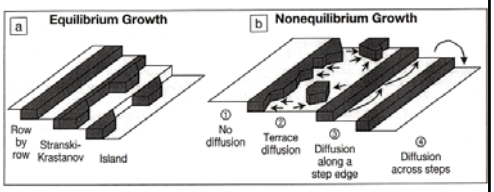
Diffusion Anisotropy

⇝ Preferential Growth in certain Direction

⇝ Special Shapes of Grown Islands

'Physical' Self Assembly of e.g. Nanowires





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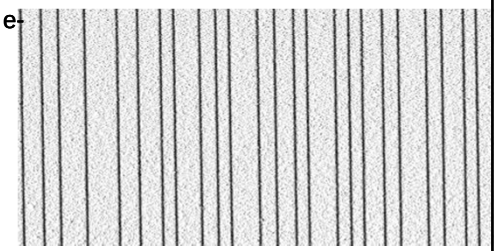
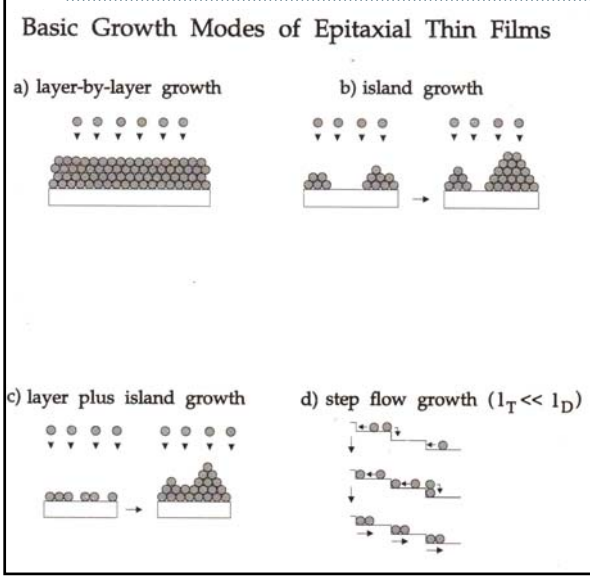
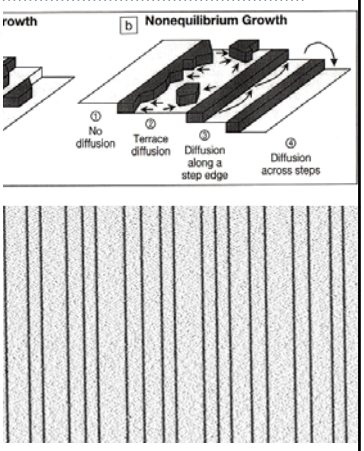


F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

‘Physical’ Self Assembly of e.g. Nanowires
jumping from 3D to 2D





Th. Jung et al.
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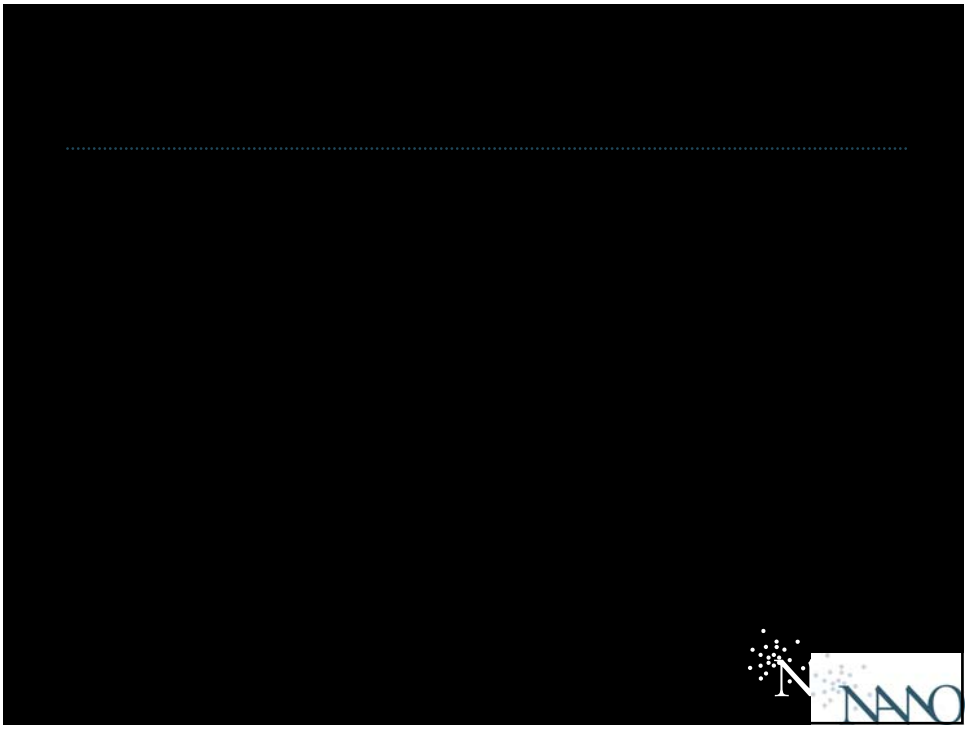


Vorlesung
Analysemethoden II
Andrij Romanyuk

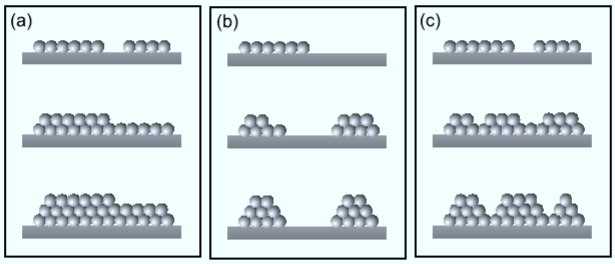
- Di 18.10. statt 8.15 ab 15.00
- Fr 21.10. ganzer Tag

Repetition:

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

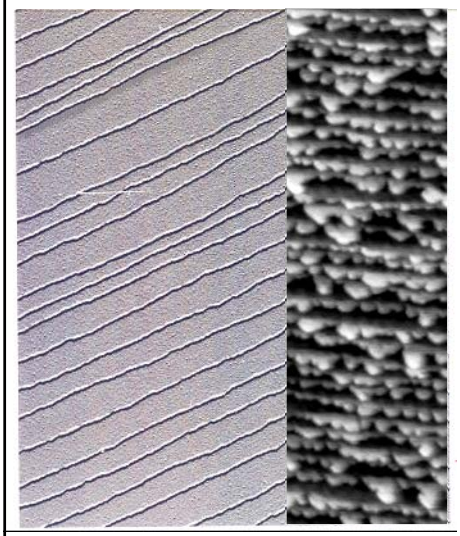
- Diffusion
- Methoden zur Bestimmung
- Bedeutung fuer's Wachstum
- Isotropie / Anisotropie

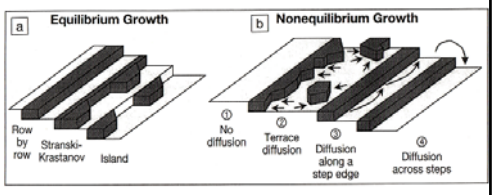
Growth Modes



(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





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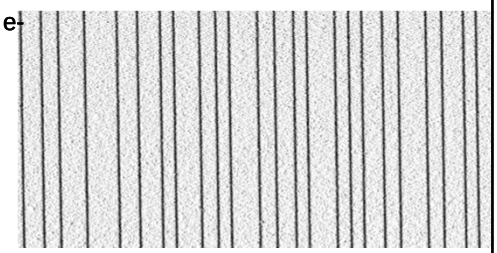

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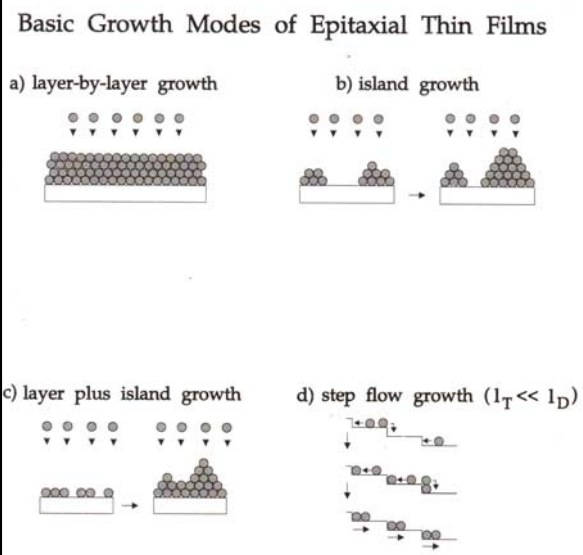
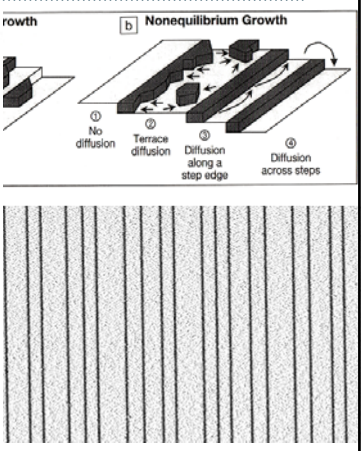
‘Physical’ Self Assembly of e.g. Nanowires
jumping from 3D to 2D

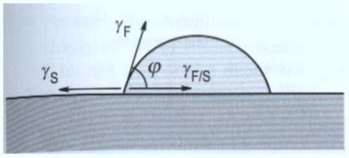




Th. Jung et al.
ı **24**, 20--24 (1999).

Growth Modes

- **Surface tension** (γ) = work required to build a surface of unit area
  (≡ force per unit length)

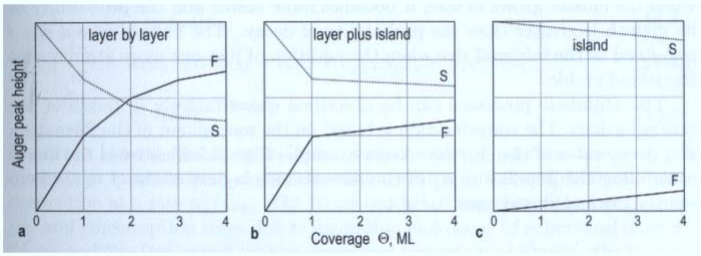


$$\gamma_S = \gamma_{SF} + \gamma_F \cos\varphi$$

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

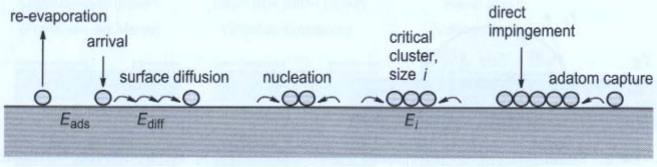
Growth Modes

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



Island Number Density

• Nucleation and growth on surfaces:



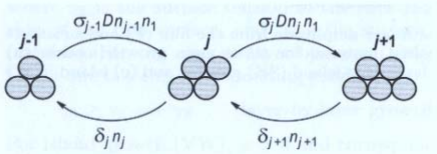
- Diffusion coefficient: $D = \frac{\nu}{4n_0}\exp\left(-\frac{E_{diff}}{k_B T}\right)$

- 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:

adatom density

subcritical clusters

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{ads}} + \left(2\delta_2 n_2 + \sum_{j=3}^{i} \delta_j n_j - 2\sigma_1 Dn_1^2 - n_1 \sum_{j=2}^{i} \sigma_j Dn_j \right) - n_1\sigma_x Dn_x$$

deposition rate

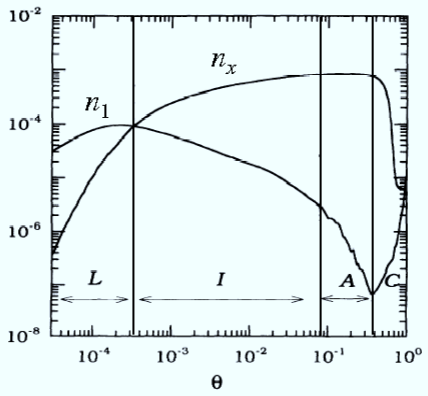
stable clusters

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

$$\frac{dn_x}{dt} = n_1\sigma_i Dn_i$$ → 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** (Θ ~ 0.1-0.4 ML)

When the island join together

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

Island Number Density

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

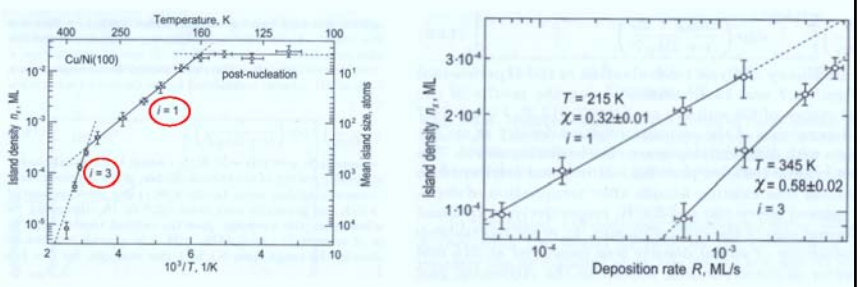
$$n_x = n_0 \eta(\Theta, i) \left(\frac{4R}{\nu_0 n_0} \right)^{\frac{i}{i+2}} \exp\left(\frac{i E_{diff} + E_i}{(i+2) k_B T} \right)$$

χ

binding energy of critical cluster

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

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



Island Shape

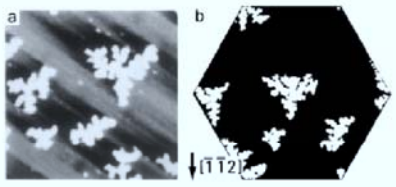
- At low T (slow edge diffusion): **ramified islands**
- **Diffusion-limited-aggregation (DLA) model** (Witten & Sander, PRL 1981):

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

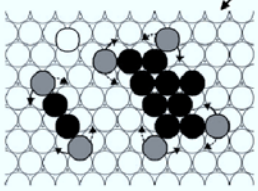
- In real growth (STM experiments):
  - Fractal shape
  - Branch thickness > 1 atom
  - Influence of lattice geometry

Island Shape

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



experiment simulation

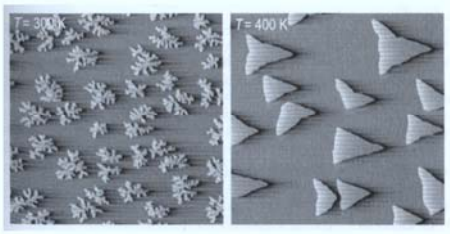


- Branch thickness ~ 4 atoms
- Trigonal symmetry

- Higher coordination is preferred

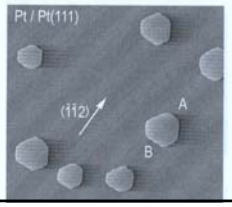
Island Shape

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

300 K  400 K

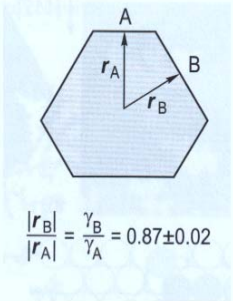
- The equilibrium shape is hexagonal:

(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

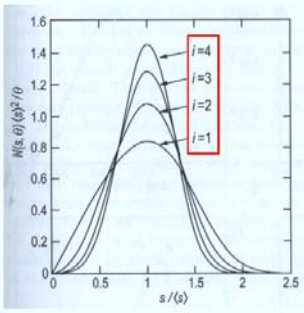
- **Island size distribution** depends on:
  - Critical island size
  - Coverage
  - Substrate structure
  - "Coarsening" (at high Θ)

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

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

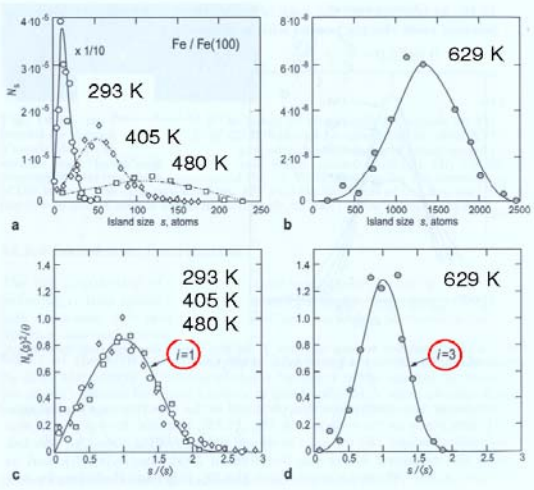
- Comparing with experimental results

→ critical island size



Island Size Distribution

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



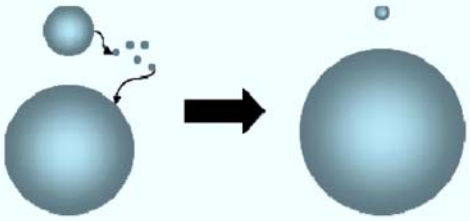
Coarsening Phenomena

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:



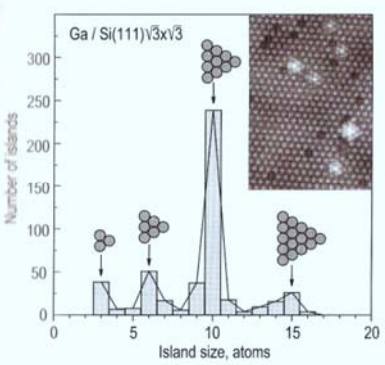
- Chemical potential of a circular island:

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

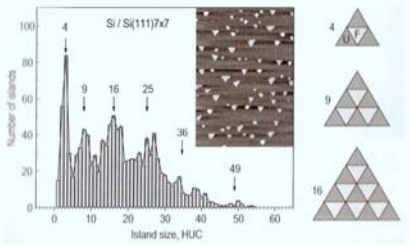
Reducing free energy → net flow from smaller to larger islands!

Magic Islands

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



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

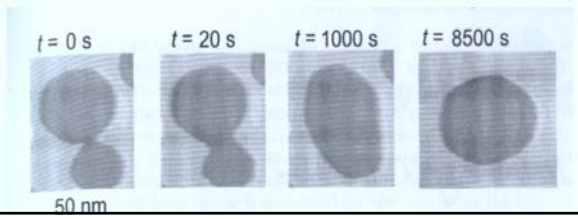


Formation of a new row → high energy cost!

Vacancy Islands

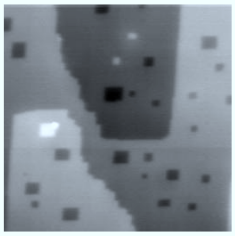
• Ion bombardment → formation of **vacancy islands**

• Analogies with adatom islands



Vacancy Islands

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

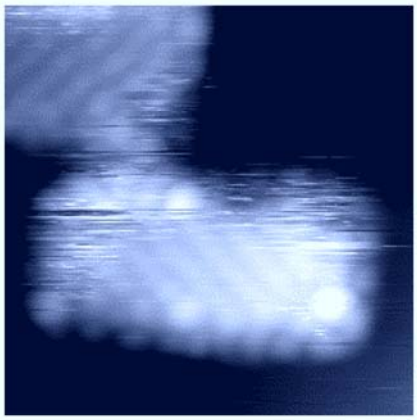


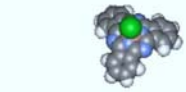
KBr(100)

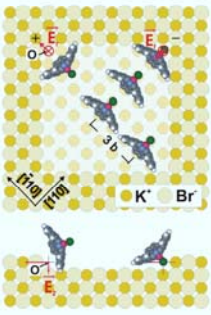
- Irradiation with 1 keV electrons at 130 ºC
- Rectangular pits with area of 1x1 nm^2 up to 30x30 nm^2
- 1 ML deep (0.33 nm)

Vacancy Islands

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

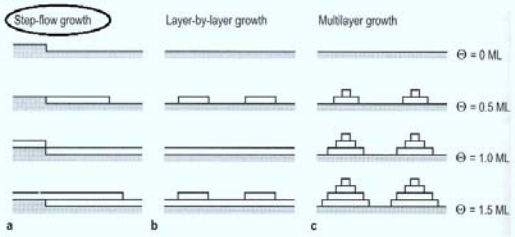




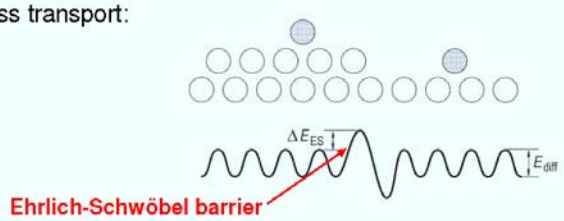


Kinetic Effects in Homoepitaxy

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

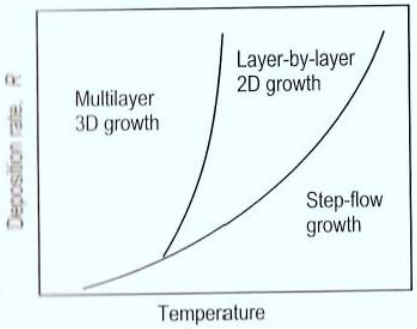


- **Interlayer** mass transport:



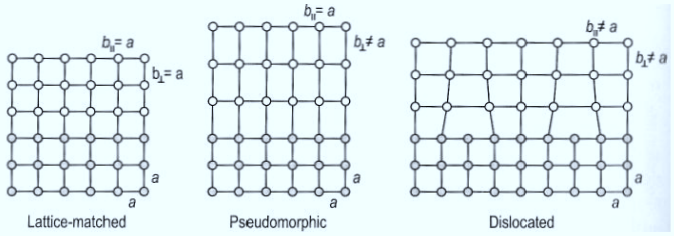
Kinetic Effects in Homoepitaxy

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



Strain Effects in Heteroepitaxy

• Heteroepitaxy growth modes:

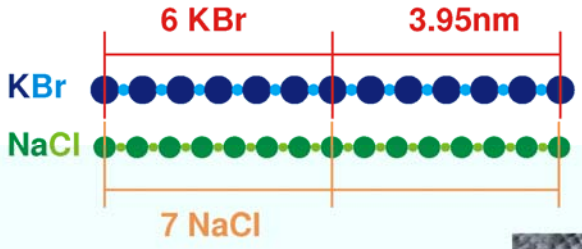


• Lattice **misfit** → elastic strain and dislocations

• 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?)