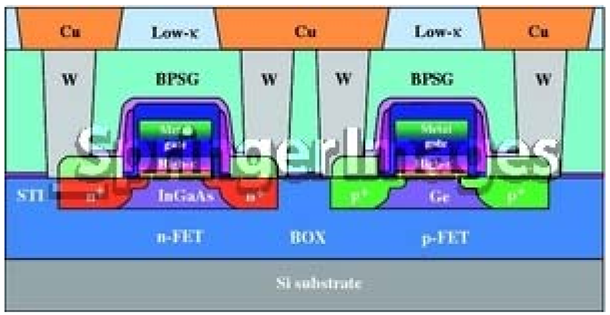


Fig 22
Ideal CMOS structure for high performance [120]

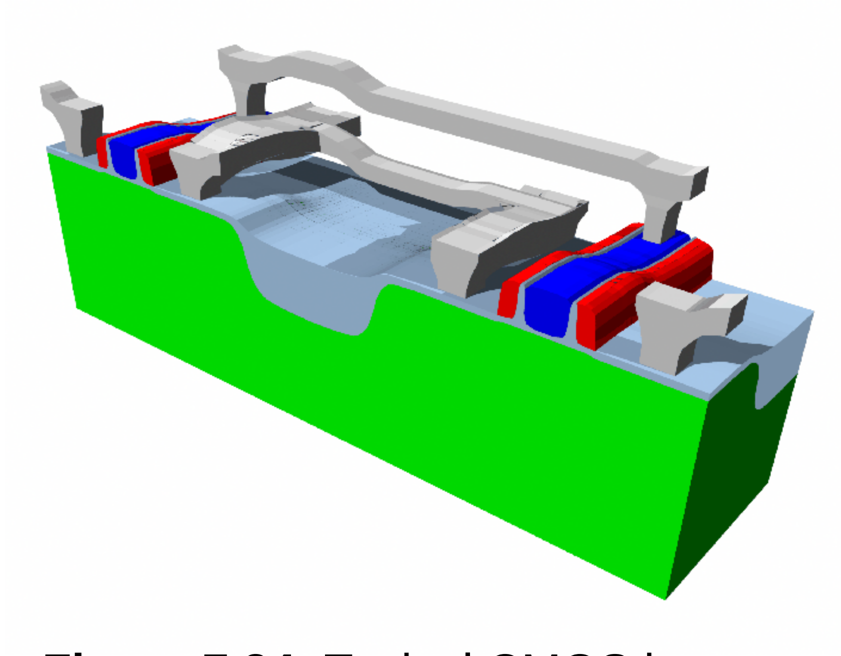


Figure 7.24: Typical CMOS inverter structure with two transistors.

Repetition:

- Nanostrukturierung: Warum? Wo? Wie? -- Beispiele
- Bottom-Up vs. Top Down
- Bottom-Up Nanostrukturieren:

    → Spielen mit Physikalischen / Chemischen WW
- Oberflaechen und Vakuum Warum? Wieviel?

Nanostructures and Nanostructuring
20. / 27. Sept 2011

- 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

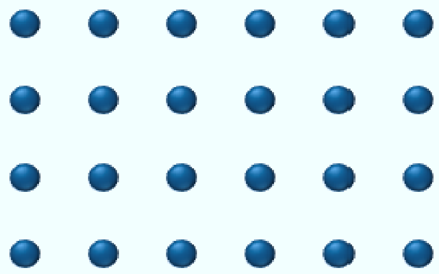
UNI
BASEL

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!)

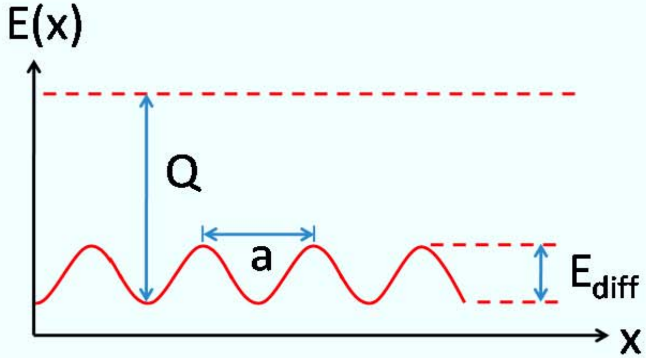
• **Diffusion coefficient**:

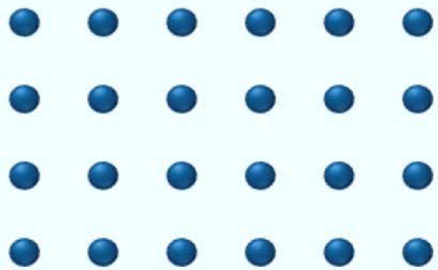
$$D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}$$

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):

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

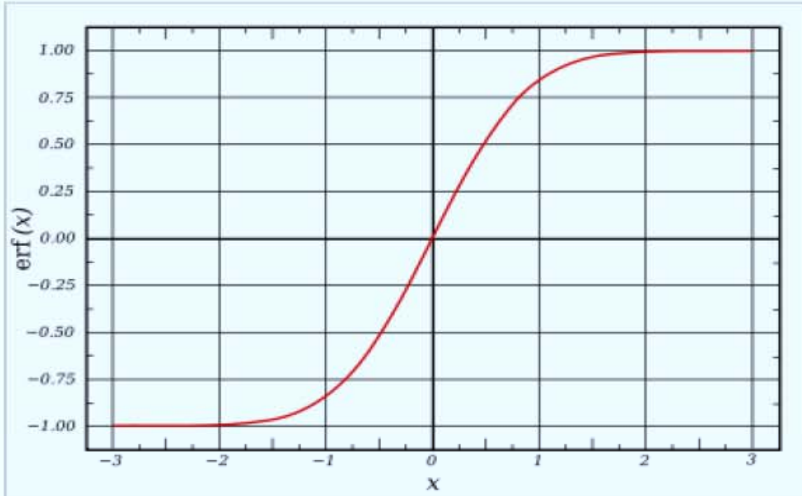
← from equation of continuity

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

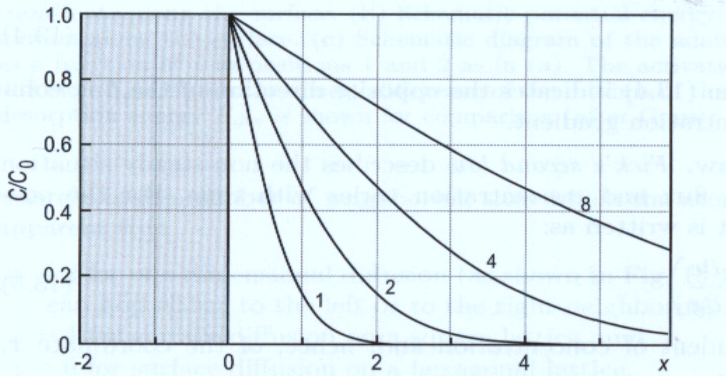
Analytical Solutions of Fick's Laws

- We introduce the **error function**

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



- Source of constant concentration:



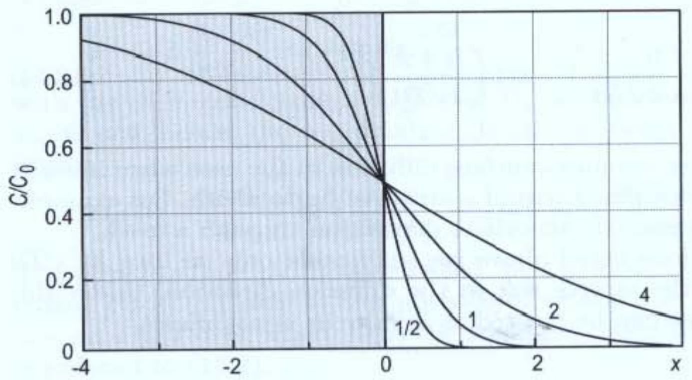
$$c(x,t) = c_0\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

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

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

Analytical Solutions of Fick's Laws

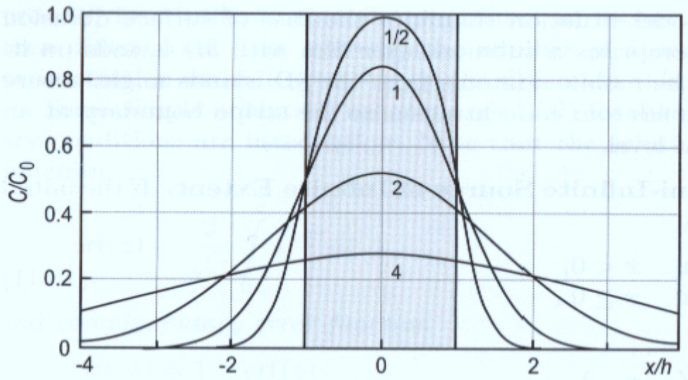
• Source of infinite extent:



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

- Example: Submonolayer film

• Source of limited extent:



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

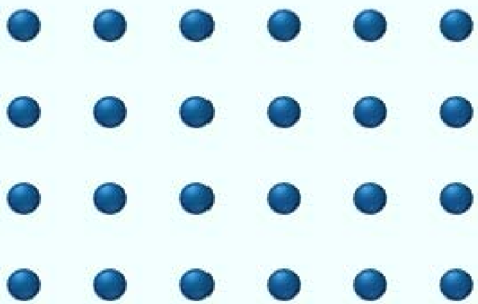
- Example: Submonolayer film confined in a stripe of finite width

Diffusion Mechanisms

- Depending on the <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:

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

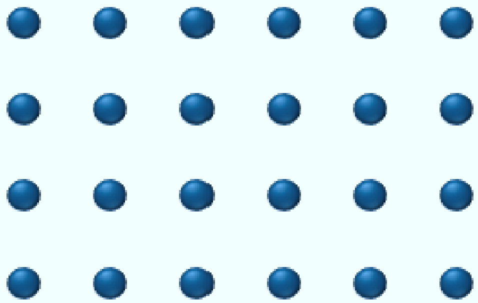
- For an ensemble of many particles:

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

(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

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

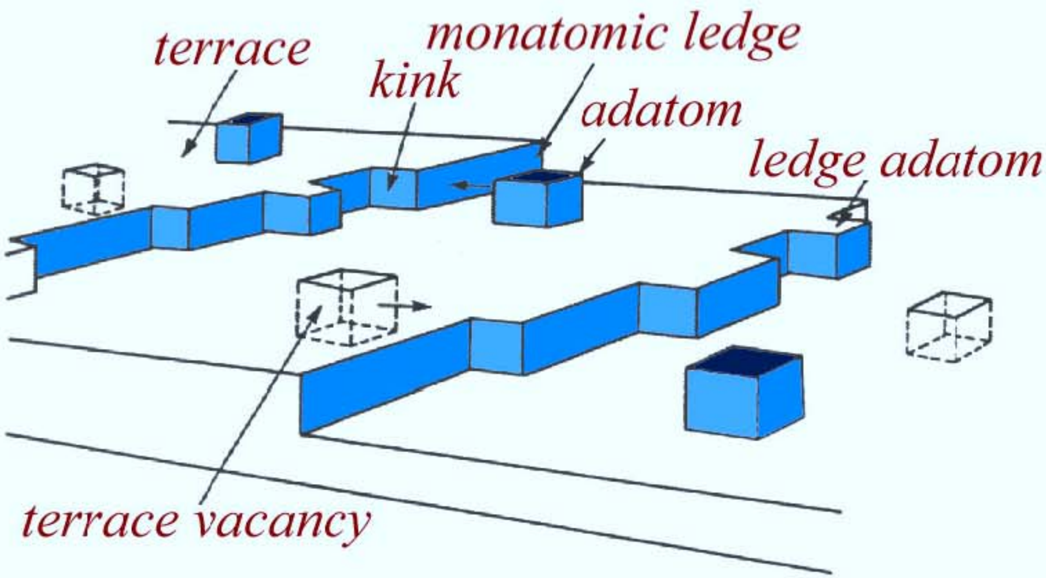
Diffusion Mechanisms

- 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:

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

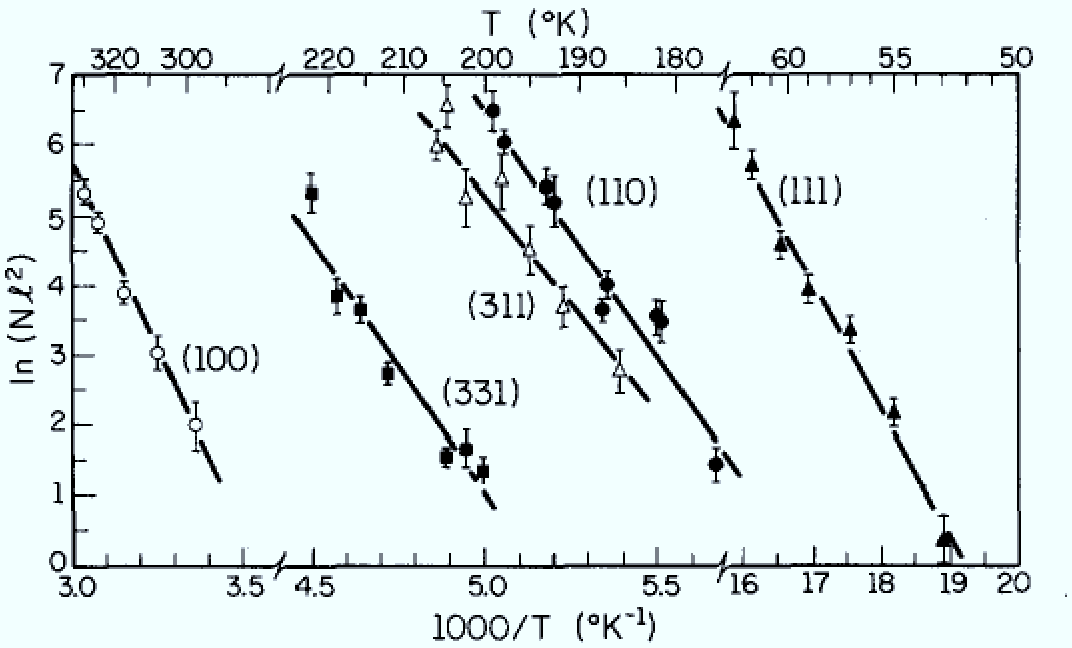
ΔG = energy of adatom formation

(→ 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

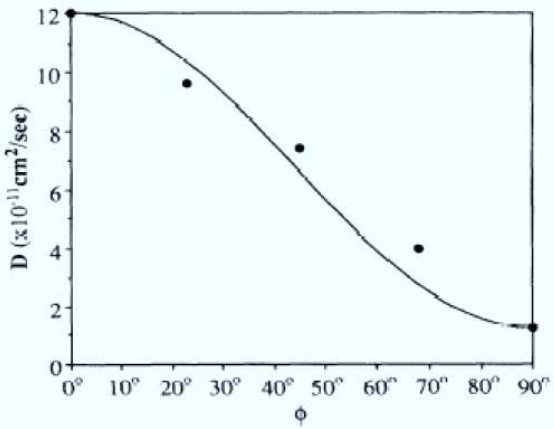
ℓ: jump distance

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

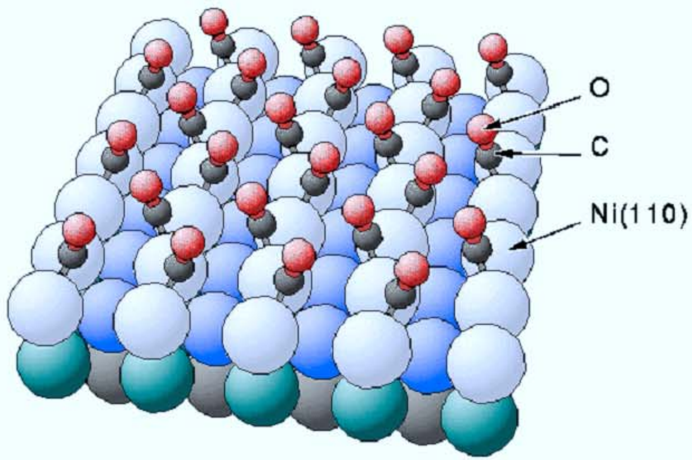
Anisotropy of Surface Diffusion

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

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

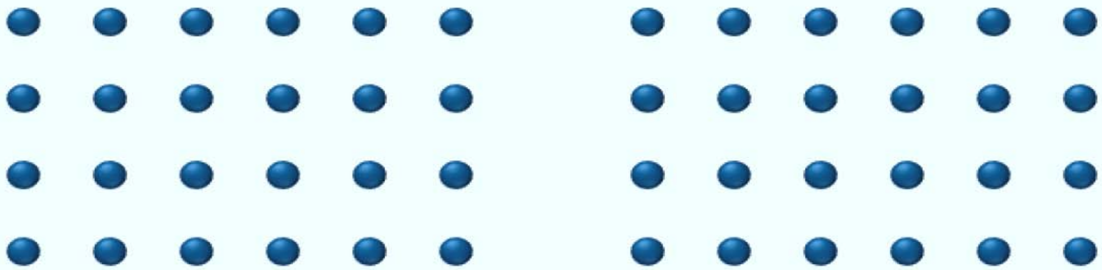


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

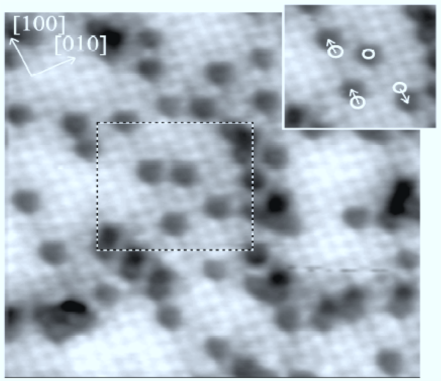


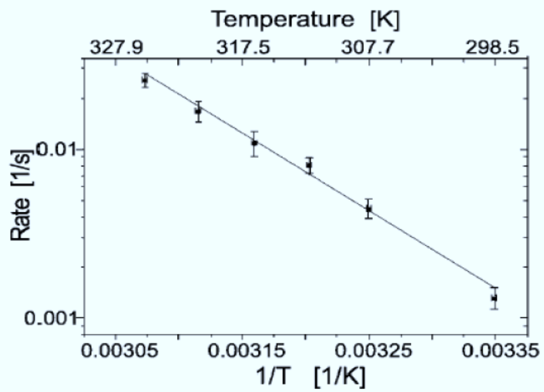
Atomistic Mechanisms

1) Hopping mechanism:



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

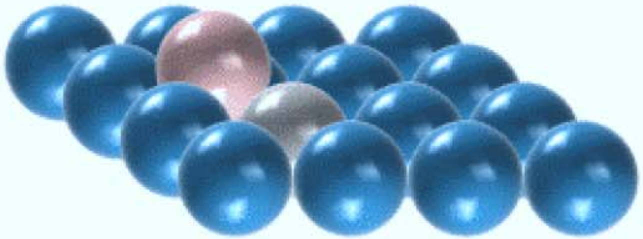


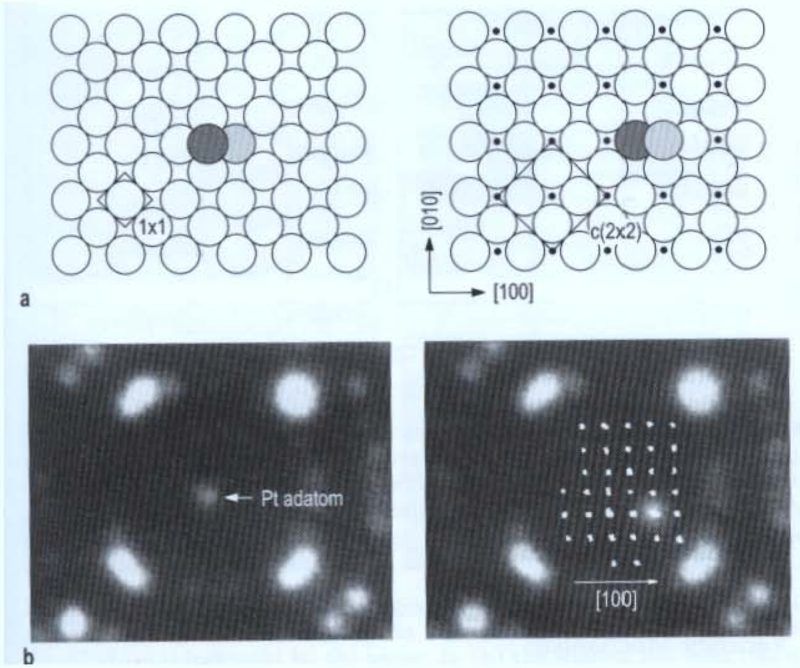


→ Arrhenius law with $\nu \sim 10^{12}\ s^{-1}$, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:





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

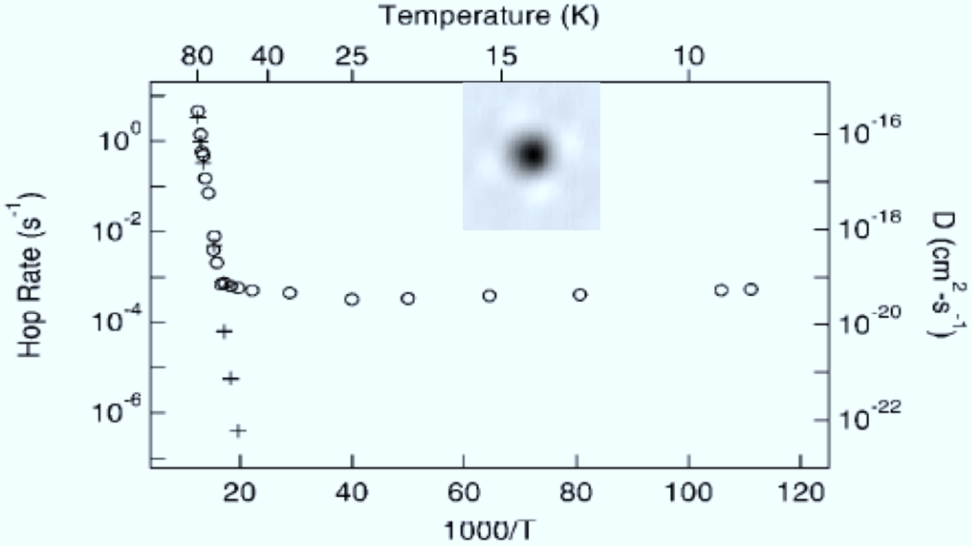
• Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

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

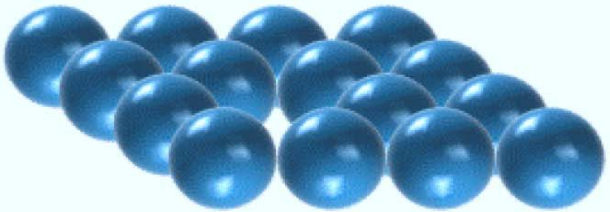
• Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



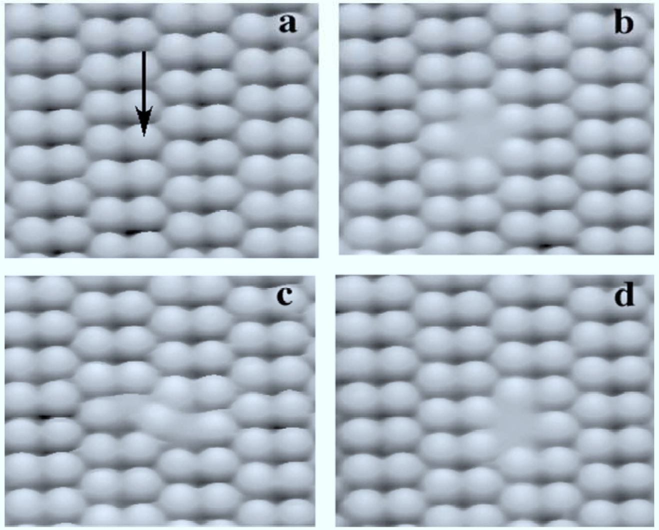
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}\ s^{-1}$, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



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



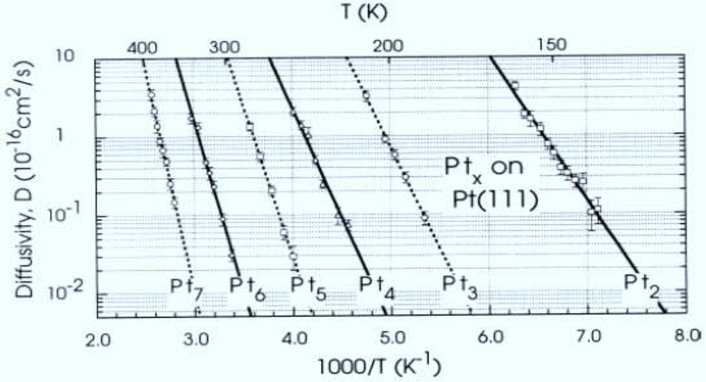
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

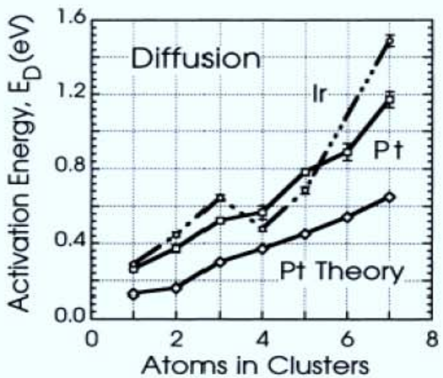
• Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

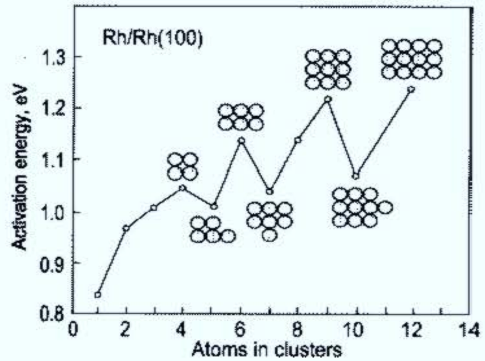


- Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

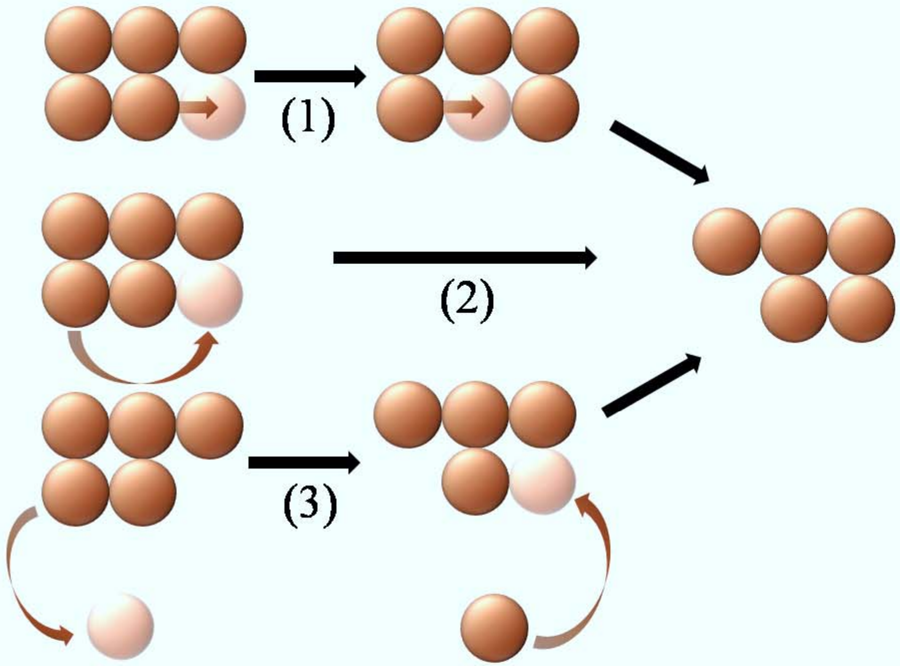
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

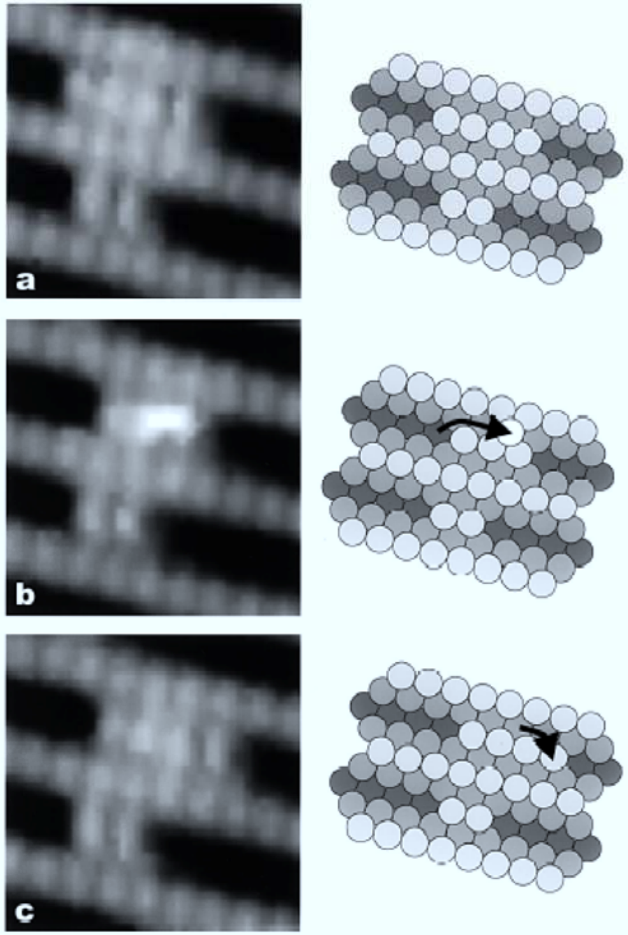
(2) Edge diffusion

(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) "Leapfrog" mechanism:

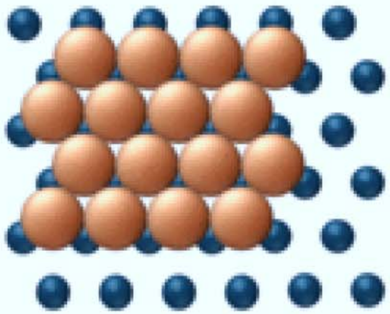


• Example: Pt(110)2x1
(Linderoth et al., PRL 1999)

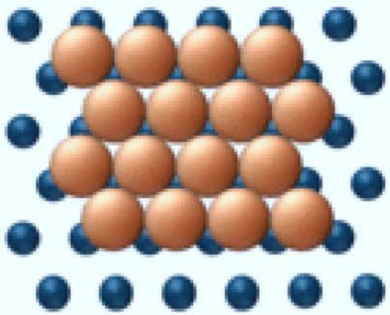
Cluster Diffusion

Concerted mechanisms:

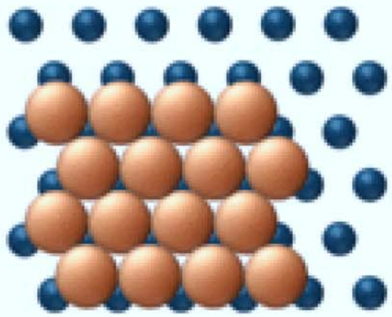
(1) Glide:



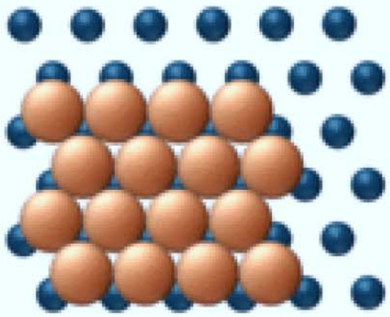
(2) Shear:



(3) Reptation:

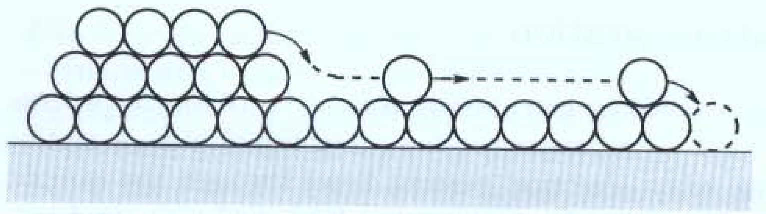


(4) Dislocation:



Phase Formation

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

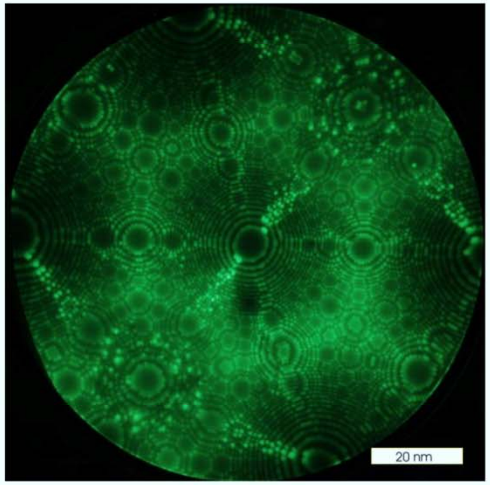


Surface Electromigration

- 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

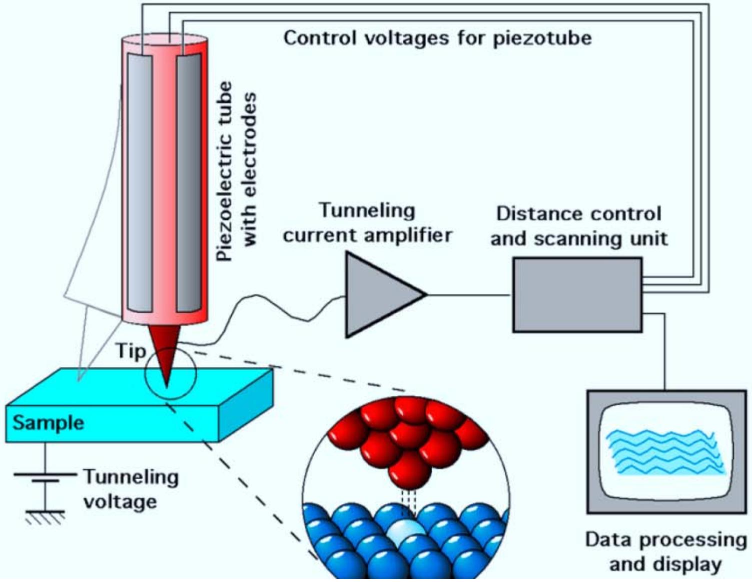
Experimental Techniques

1) Direct observation:



• <u>Field ion microscopy</u> (FIM)
→ "image-anneal-image" technique

- Limited to refractory or noble metal surfaces

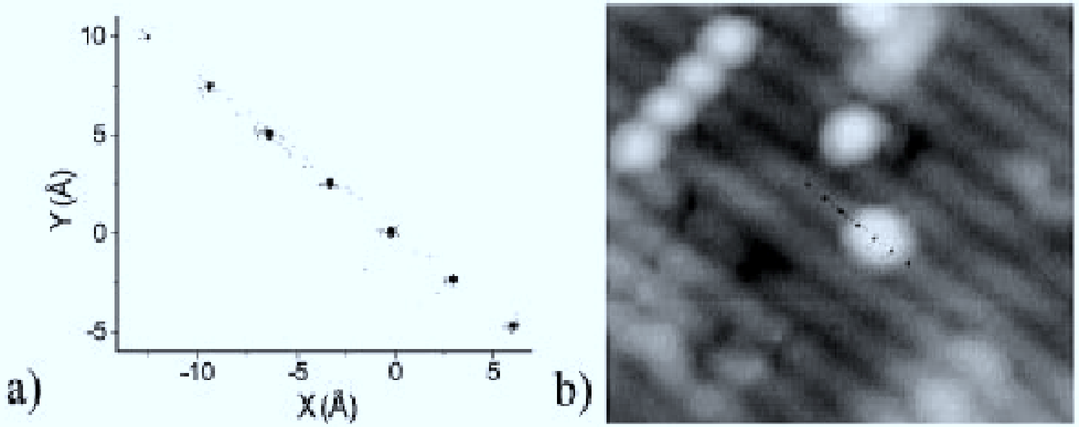


• <u>Scanning tunneling microscopy</u> (STM)
→ "image-while-hot" technique

- 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!

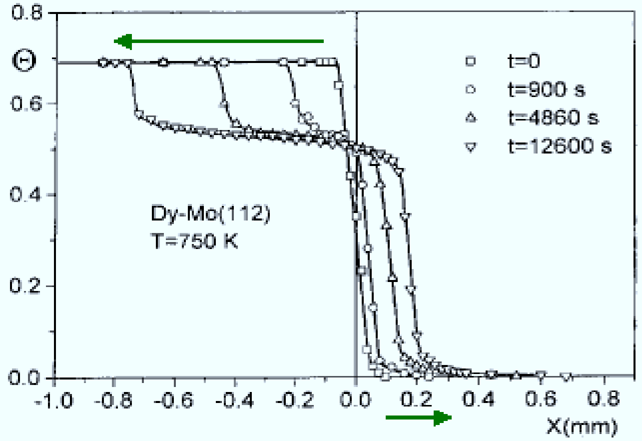
Experimental Techniques

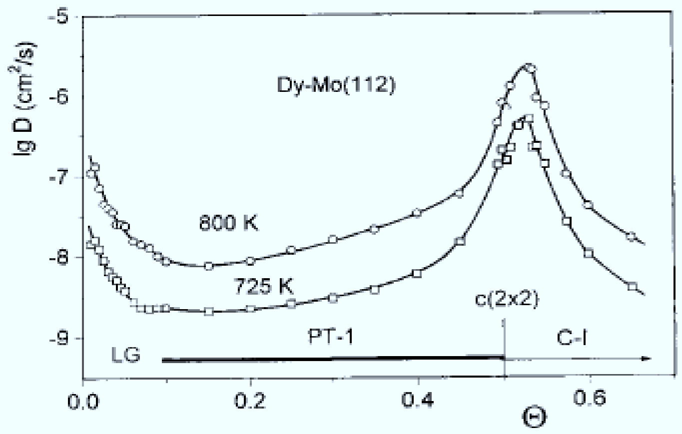
2) Profile evolution method:

- 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:

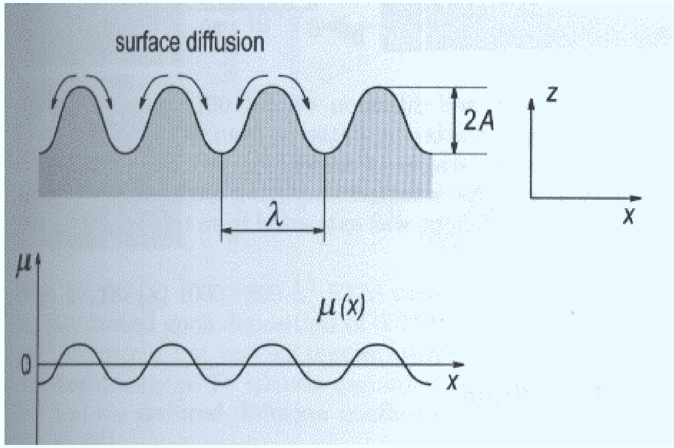
- A surface is perturbed from its lowest energy configuration...

... and allowed to relax via diffusion

- Relaxation rate → Coefficient of diffusion

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

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

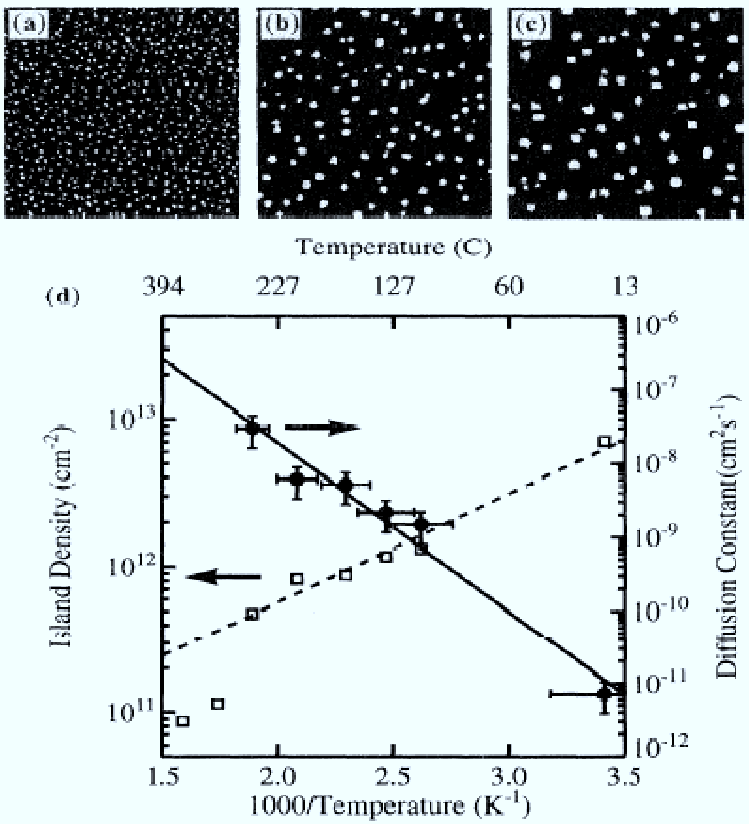


γ = surface tension; V = atomic volume; n_0 = surface density

Experimental Techniques

4) Island growth techniques:

- <u>Number density of islands</u> after submonolayer deposition <u>is monitored</u>
- 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

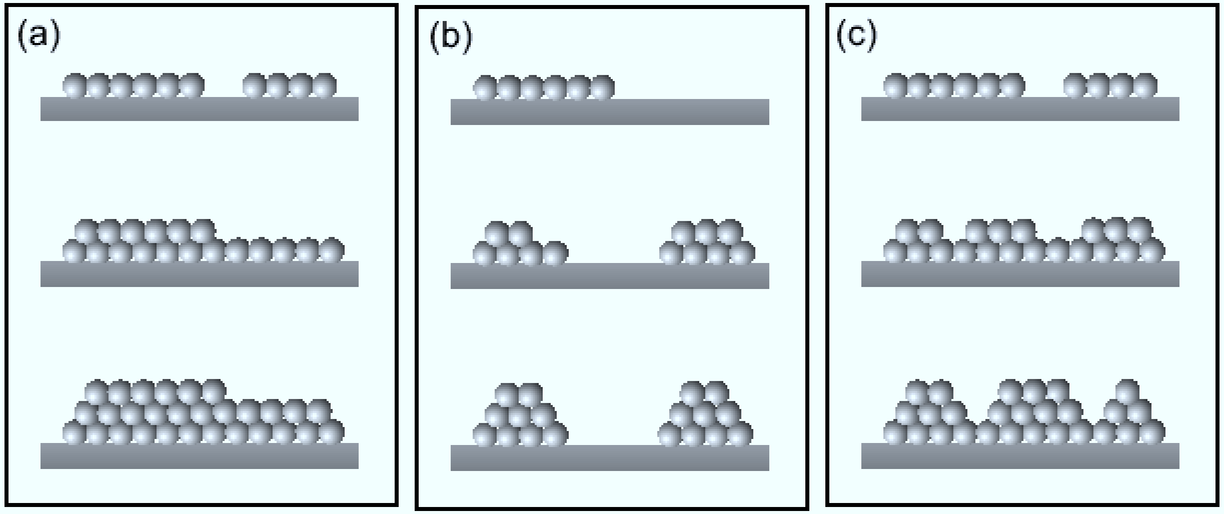
- K. Oura et al., Surface Science, Springer 2003, chapter 13
- A.G. Naumovets & Yu.S. Vedula, Surf. Sci. Rep. 4 (1985) 365
- R. Gomer, Rep. Prog. Phys. 53 (1990) 917
- G.L. Kellogg, Surf. Sci. Rep. 21 (1994) 1

Surface Physics 2010

Growth of Thin Films

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 preparation.

MISCUT ANGLE α → STEP SPACING

Adsorbate deposition

1/4th MONOLAYER ⇝ WIDTH OF WIRES

Annealing $T<T_s$

DIFFUSION ⟷

Annealing $T>T_s$

DIFFUSION ⟷ ↕

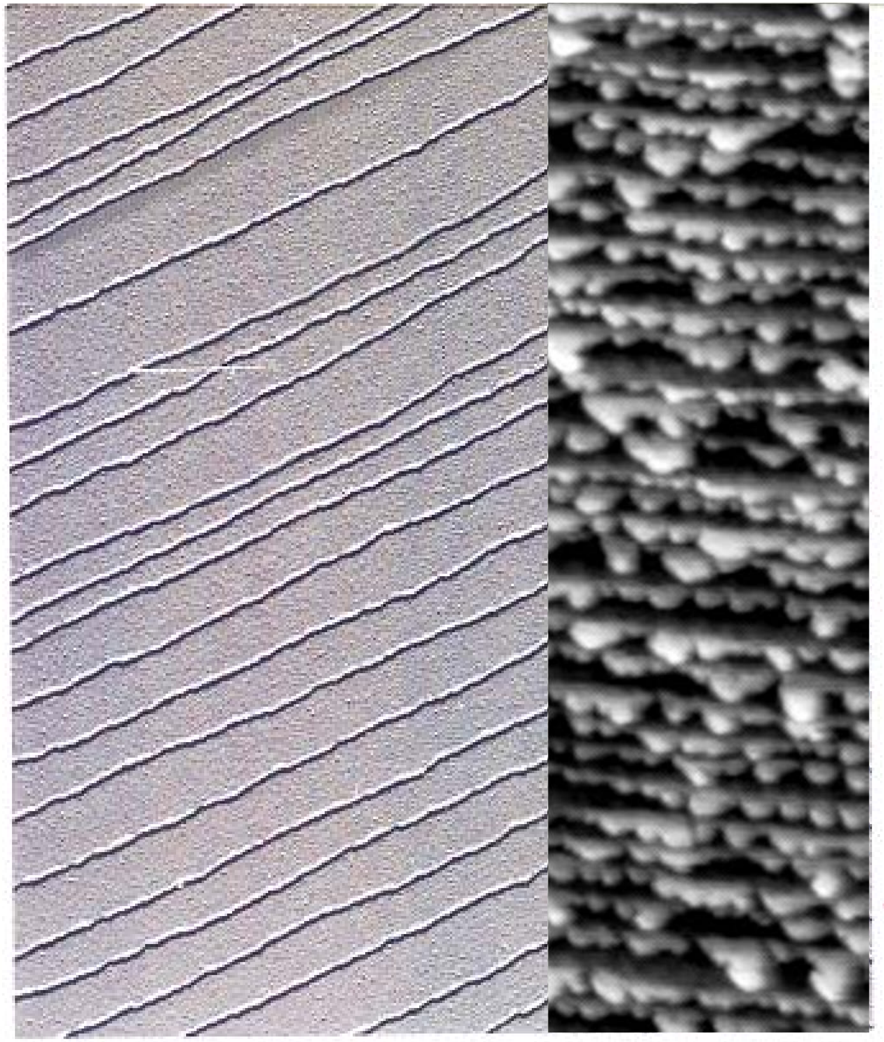
CONTROLLING GROWTH KINETICS:

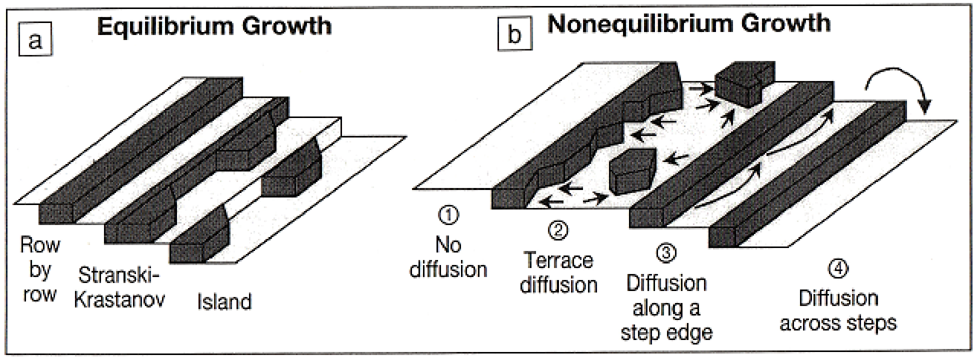
Diffusion Anisotropy

⇝ Preferential Growth in certain Direction

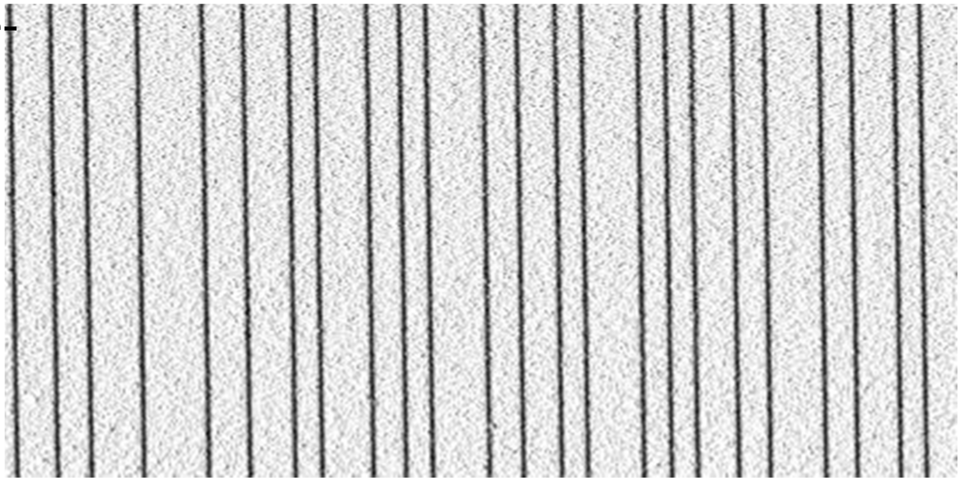
⇝ Special Shapes of Grown Islands

‘Physical’ Self Assembly of e.g. Nanowires



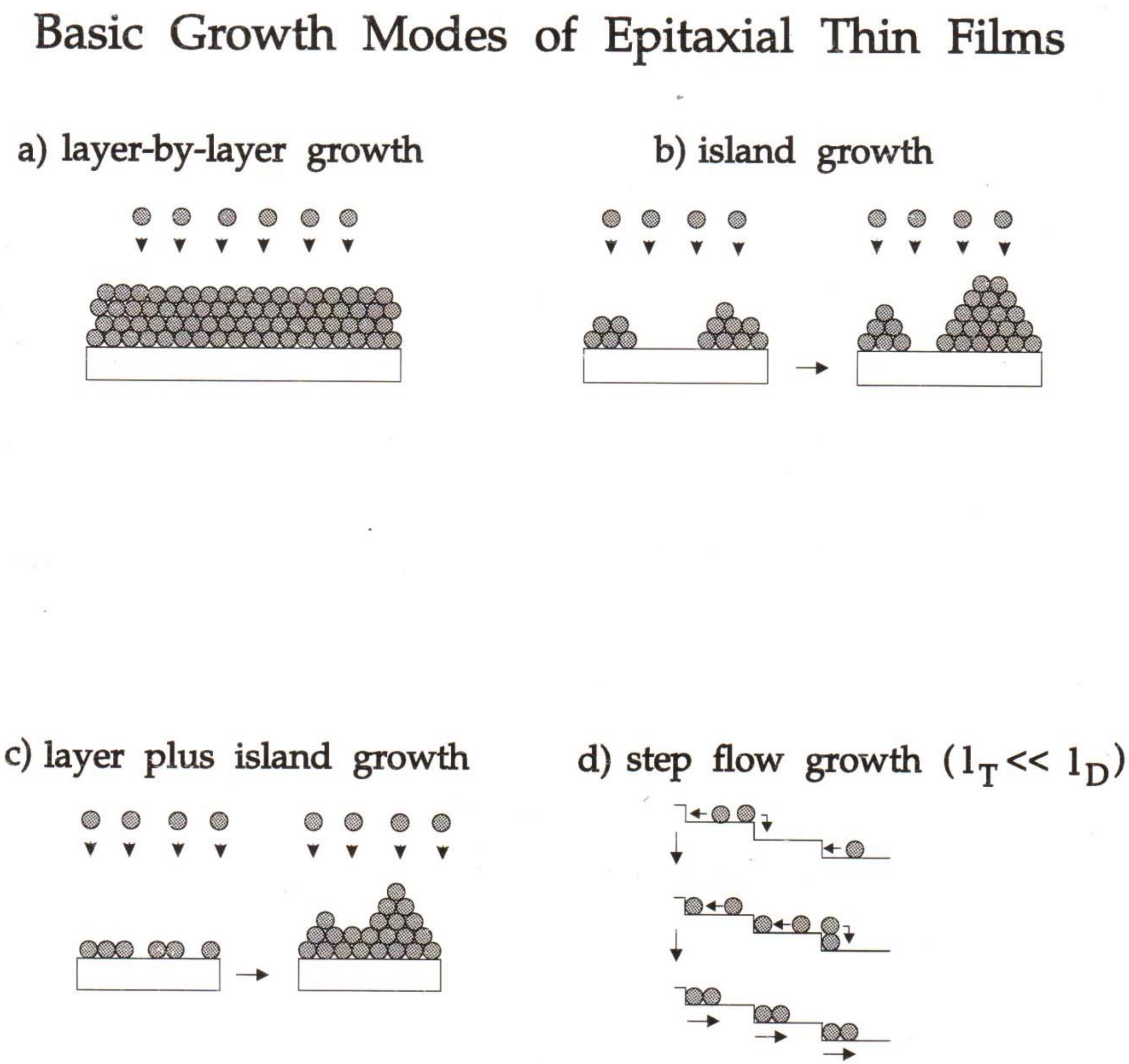


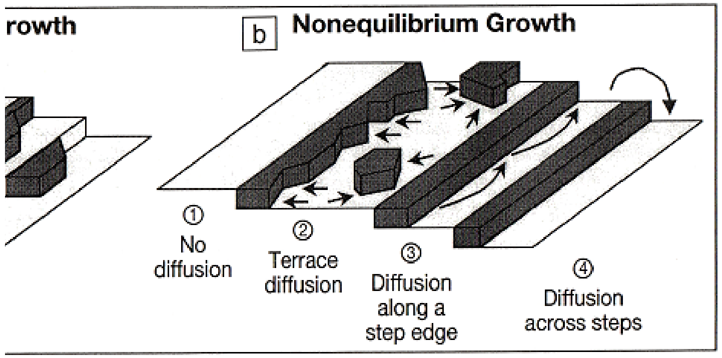
e-

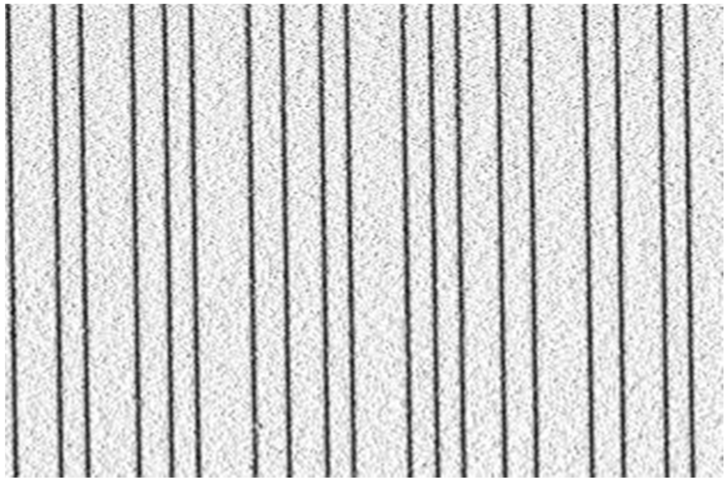


F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

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







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