

Verdampfung

H. Hertz(1882): Verdampfung von Hg
 $R_{ev} \approx p_e = p_{hydr}$

M. Knudsen (1915)

$$R_{ad} = \frac{N}{At} = \frac{p}{\sqrt{2\pi M k T}} \alpha$$

α : Verdampfungskoeffizient

Verdampfen ist ein Oberflächenprozesse:
 ⇒ Phasendiagramm dp/dT (Clausius-Clapeyron)
 ⇒ Dampfdruck (vapour pressure)

Ausgangspunkt: beide Phasen sind an der Phasengrenze im Gleichgewicht
 $\Rightarrow \mu_S = \mu_V$ bzw. $\mu_L = \mu_V$

$$R_{ads} = A \exp(-E_a / RT) \times P^x = S$$

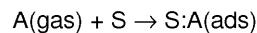
E_a : activation energy for adsorption
 A : pre-exponential (frequency) factor
 S : Sticking Coefficient

F : Flux

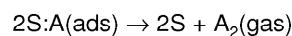
Adsorption/Desorption

Adsorption wird durch molekulare Auftreffrate R_{ad} und den „sticking Coefficient“ s bestimmt. Bei der Desorption unterscheidet man Desorption 1. Ordnung (nicht-dissoziativ) und 2. Ordnung (dissoziativ).

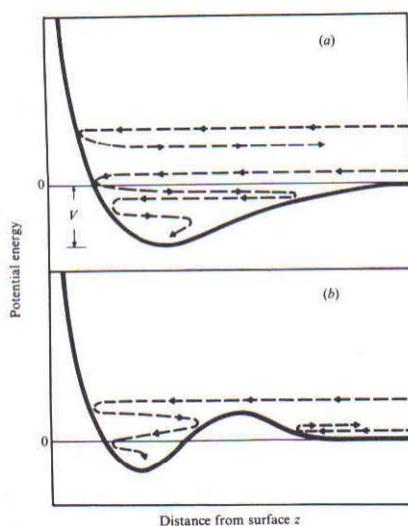
Wenn ein Gasatom oder Molekül A(gas) auf einem Substrat S gebunden wird:



Falls das Atom die Oberfläche wieder verlässt, bzw. mit einem anderen Adatom zu einem Molekül rekombiniert, dass dann in die Gasphase übergeht:



Adsorption/Desorption

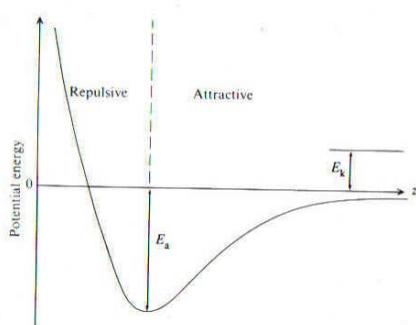


Was geschieht mit einem Atom/Molekül welches aus der Gasphase auf der Oberfläche landet?

(a) Je nach Energie:
Repulsion und Reflexion ins Vakuum
oder Umwandlung der kinetischen Energie
in Vibrations- und Rotationsfreiheitsgrade
und schliesslich Adsorption
(Physisorption oder Chemisorption)

(b) Auf gewissen Flächen können
auch niederenergetische Teilchen
reflektiert werden. Bzw. Verweilen
in einem Zwischenzustand.

Physisorption



Physisorption:
Relativ schwache Wechselwirkung
(Van der Waals Wechselwirkung)

Die kinetische Energie wird
in Phononen umgewandelt.

Um die Gleichgewichtslage wieder
zu verlassen muss die Aktivierungs-
Energie (Bindungsenergie) E_A
zugeführt werden.

Die Verweilzeit beträgt:
(residence time, stay time)

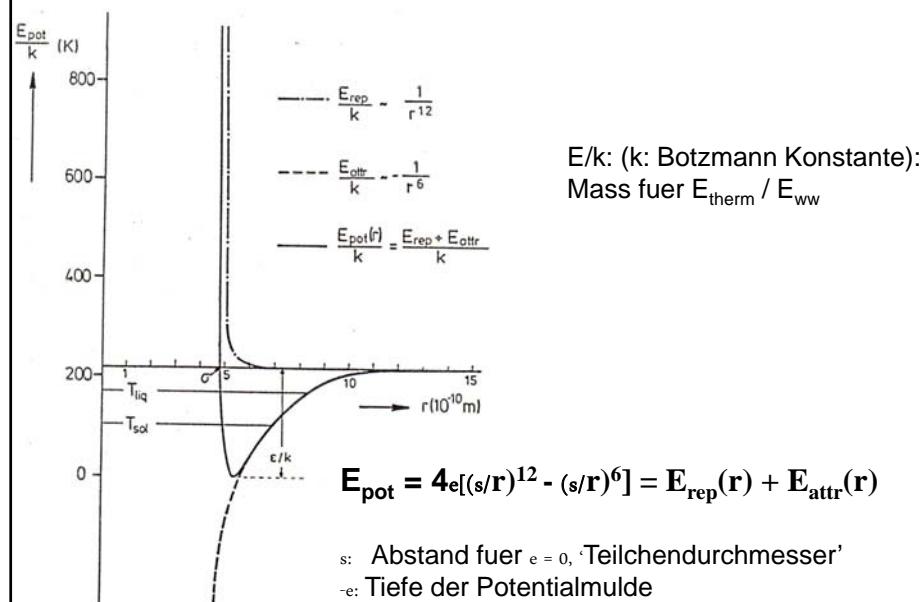
$$\tau = \tau_0 \cdot \exp\left(\frac{E_A}{k_B T}\right)$$

Physisorption:
Typ. : 50meV-0.25eV

Bsp.: He, Ne, CH₄ auf diversen Oberflächen

Lennard – Jones Potential

vereinfachtes 'workhorse' Potential, attraktiv (vdW) und repulsiv (Pauli Kontakt)



Wiederholung II

- Ionenstreuung → Rekonstruktionen und Relaxationen
- Dampfdruck / Verdampfung (Quelle und Vakuumproblem)
- Adsorption / Desorption
 - a) Physisorption – VdW / Lennart Jones
 - b) Chemisorption



Wiederholung

- Photoemission: Grundlagen (XAS, XPS, UPS etc.)
- Photonenquellen
- ESCA / XPS chemische Information: Spin Bahn Aufspaltung / Chemical Shift / Depth Profiling
- Electronic Interaction in XPS
- Beam Damage, Imagig XPS
- UPS / Molekuele Wechselwirkung von Elektronenzustaenden und Chemische Reaktionen / Porphyrinen



**24346-01+Vorlesung mit Übungen: Oberflächenphysik 4 KP
Di, 10.00-12.00 wöchentlich verlegbar**

.....
Di, 21.02.2012 Fixing Dates, Intro to Vacuum Technology, Laboratory visit Basel (Toni Ivas, Sylwia Nowakowska, Roland Steiner)

Di, 28.02.2012 Fasnacht

- Di, 06.03.2012 Introduction, Concepts Samples and Structure (Thomas Jung)
- Di, 13.03.2012 Adsorption / Desorption (Thomas Jung)
- Di, 20.03.2012 Electronic Properties and Surface Electron Spectroscopies: XPS/UPS, Auger, ARPES (Andriy Romanuk)
- Di, 27.03.2012 Diffusion and Growth (Thomas Jung)
- Di, 03.04.2012 Electron Diffraction Methods, in particular RHEED, LEED (Bert Müller)
- Di, 10.04.2012 Local Probes and Experiments I, STM, Inelastic tunneling and STS (Thomas Jung)
- Di, 17.04.2012 X-ray Absorption Spectroscopy (Frithjof Nolting)
- Di, 24.04.2012 Surface Magnetism XMCD / PEEM (Frithjof Nolting)
- Di, 01.05.2012 Surface Optics, Kelvin Probe (Thilo Glatzel)
- Di, 08.05.2012 Local Probes and Experiments II, AFM FIM (Thomas Jung)
- Di, 15.05.2012 Applications of Surface Science in Industry (M. de Wild)
- Di, 22.05.2012 Schlussprüfung (Jan Girovsky, Thomas Jung)
- Di, 29.05.2012 Excursion (Thomas Jung)



Surface Physics 2010

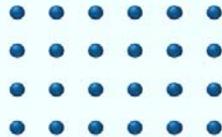
Surface Diffusion



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 :

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

a = jump distance; v = hopping frequency

(Note that vt = number of hops!)

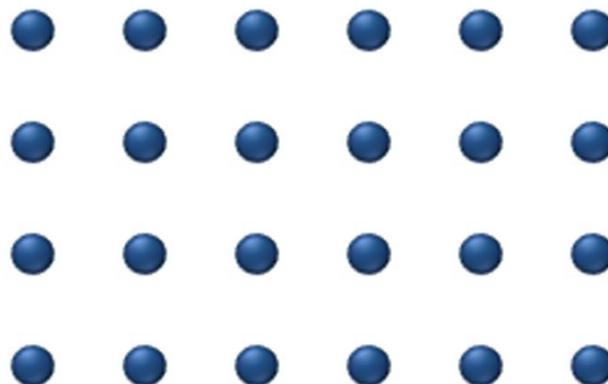
$$\langle \Delta^2 r(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle [R_i(t) - R_i(0)]^2 \rangle$$

- Diffusion coefficient:

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

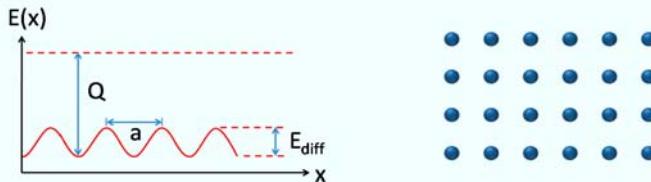
z = number of first neighbors = $\begin{cases} 2 \text{ in 1D diffusion} \\ 4 \text{ on a square lattice} \\ 6 \text{ on a hexagonal lattice} \end{cases}$

Diffusion



Random-Walk Motion

- Hopping → surmounting a potential barrier



- Arrhenius law:

$$v = v_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)$$

v_0 = oscillation frequency of the atom in the well;
 E_{diff} = barrier height

Typically $E_{diff} \sim 5\text{-}20\%$ of Q (heat of desorption)

- For chemisorbed species: $E_{diff} \gg k_B T$
- 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):

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

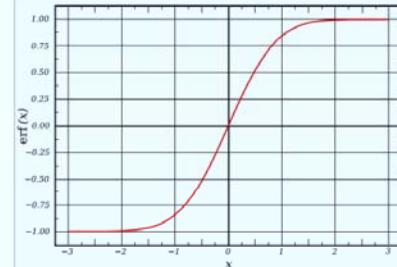
← from equation of continuity

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

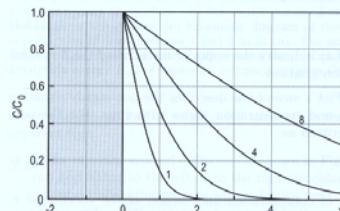
Analytical Solutions of Fick's Laws

- We introduce the **error function**

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



- Source of constant concentration:



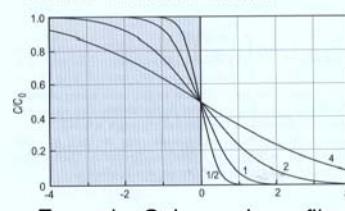
$$c(x, t) = c_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

$2\sqrt{Dt}$: diffusion length

Example: Submonolayer film with 2D islands supplying mobile adatoms

Analytical Solutions of Fick's Laws

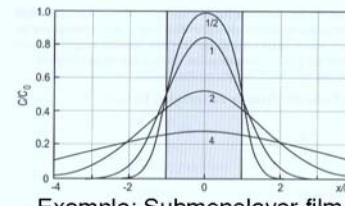
- Source of infinite extent:



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

- Example: Submonolayer film

- Source of limited extent:



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

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

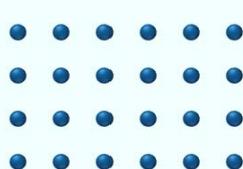
Diffusion Mechanisms

- 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

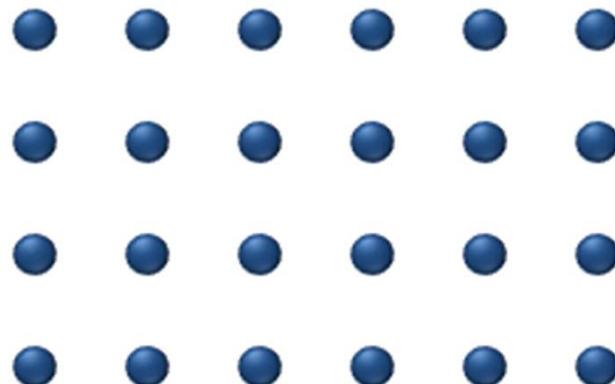
- Fick's first law can be generalized:

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

chem. diff. coefficient coverage

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

'Chemical Diffusion'



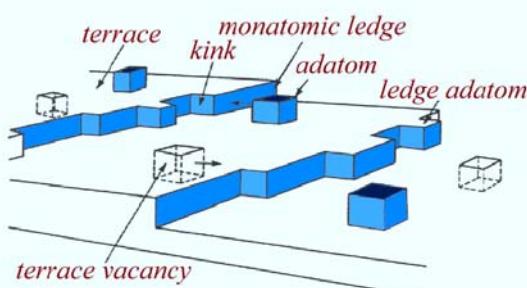
Diffusion Mechanisms

- 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 \rightarrow Spatial limit ~ 100 nm
- In practice: no strong distinction from tracer diffusion



Mass Transfer Diffusion

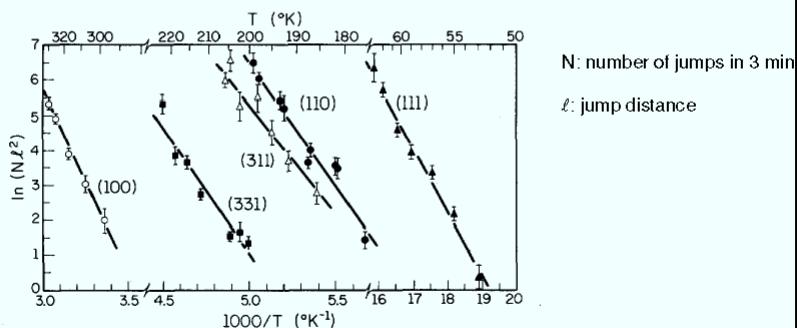
- Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)
- If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent
- If adatoms and substrate are the same chemical species:

$$D = \frac{v_0 a^2}{z} \exp\left(-\frac{\Delta G + E_{diff}}{k_B T}\right) \quad \Delta G = \text{energy of adatom formation}$$

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

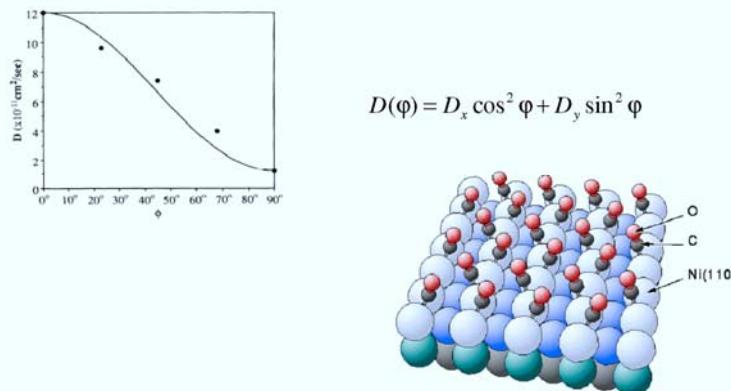
- **Orientational Anisotropy:** the diffusion coefficient depends on the orientation of the surface
- Example: Rh surfaces at different T (Ayrault & Ehrlich, JCP 1974)



- 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 \rightarrow directional anisotropy (Xiao et al., PRL 1991)

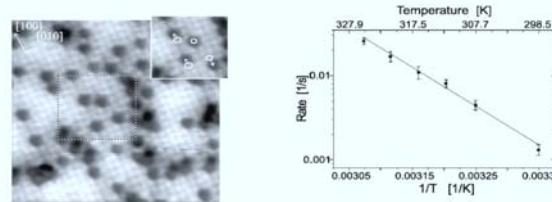


Atomistic Mechanisms

1) Hopping mechanism:



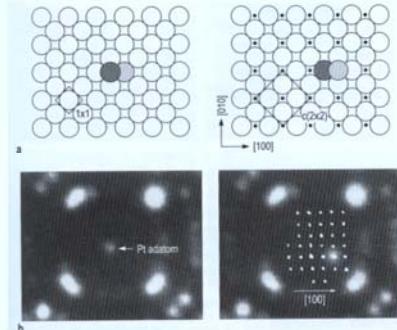
- Example: N adatoms on $\text{Fe}(100)$ (Pedersen et al., PRL 2000)



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

Atomistic Mechanisms

2) Atomic exchange mechanism:



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

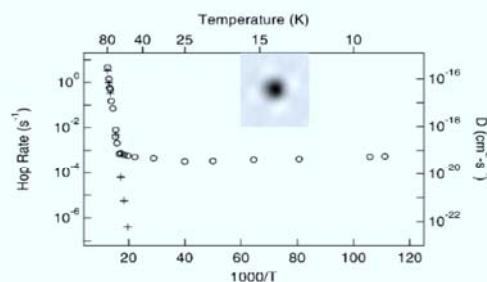
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

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

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



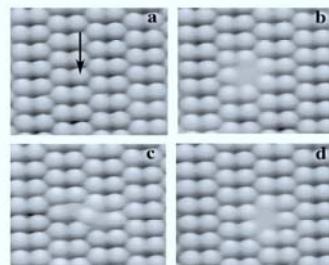
- Above 60 K: Arrhenius law with $v \sim 10^{13} \text{ s}^{-1}$, $E_{diff} = 0.20 \text{ eV}$
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



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

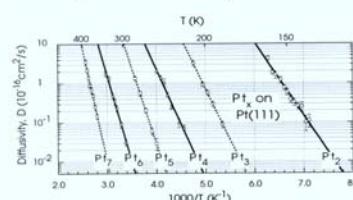


-Vacancy created with the STM tip
- T-activated hopping of neighboring atoms

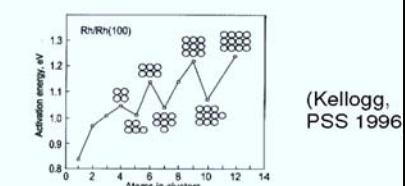
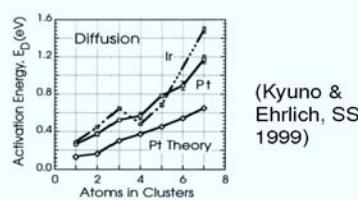
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

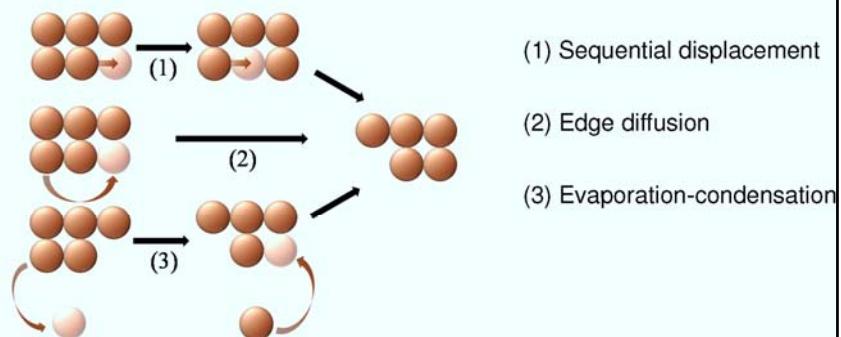


- Activation energy increases with cluster size:



Cluster Diffusion

Individual mechanisms:



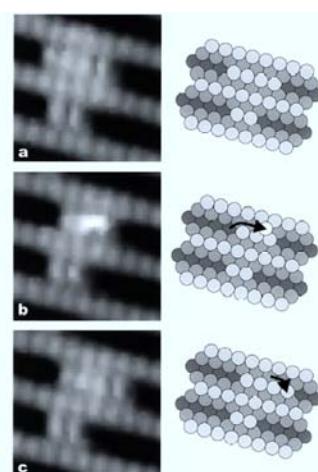
Cluster Diffusion

Individual mechanisms:

(4) "Leapfrog" mechanism:



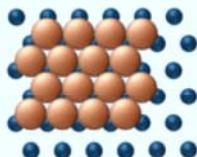
- Example: Pt(110)2x1
(Linderoth et al., PRL 1999)



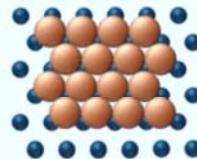
Cluster Diffusion

Concerted mechanisms:

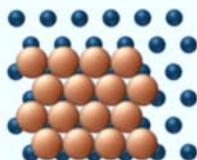
(1) Glide:



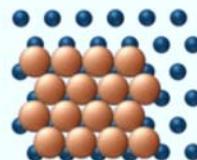
(2) Shear:



(3) Reptation:

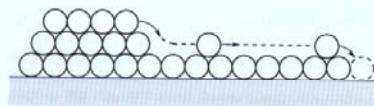


(4) Dislocation:



Phase Formation

- Coverage $\Theta \sim 0.1\text{-}1 \text{ ML}$ → formation of surface phases
- First layer atoms are usually immobile → “unrolling carpet” mechanism



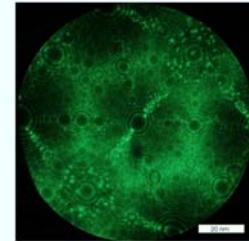
Surface Electromigration

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

Experimental Techniques

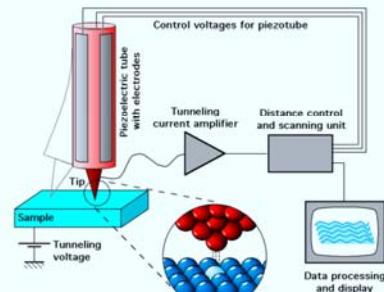
1) Direct observation:

- Field ion microscopy (FIM)
→ "image-anneal-image" technique
 - Limited to refractory or noble metal surfaces



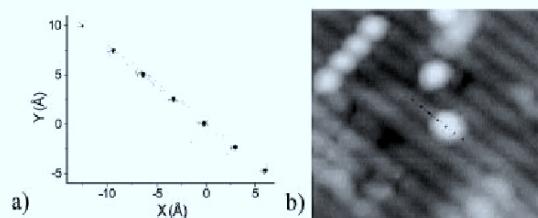
- Scanning tunneling microscopy (STM)
→ "image-while-hot" technique

- 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)

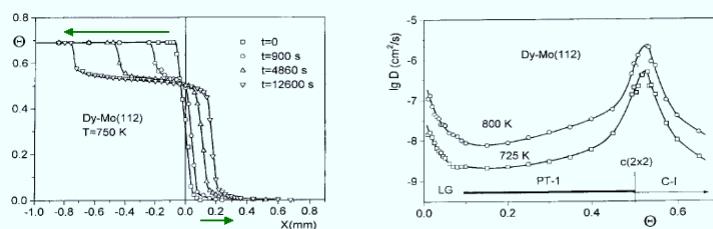


- Electric fields from the STM tip influence surface diffusion!

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...
 - $D(\Theta)$ can be evaluated
- Example: Dy on Mo(112) (Loburets et al., SS 1998)

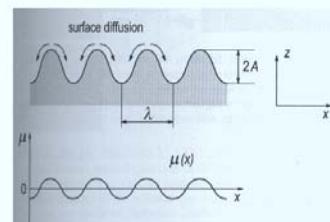


Experimental Techniques

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):

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

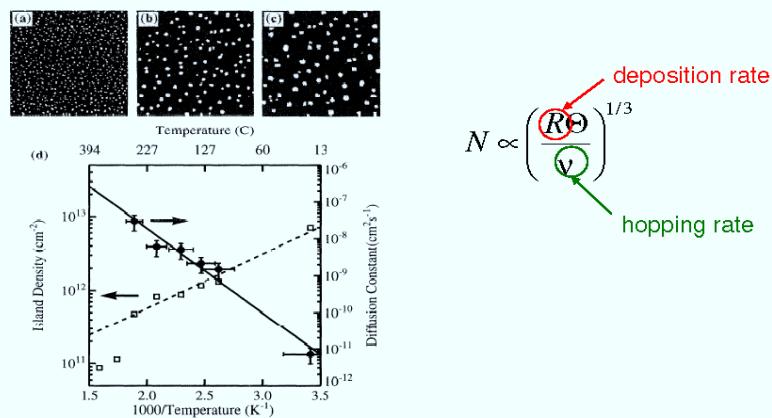


γ = surface tension; V = atomic volume; n_0 = surface density

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)



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

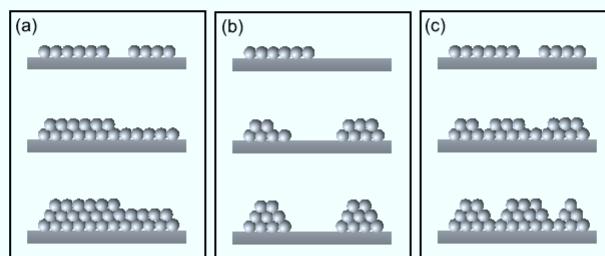
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Growth of Thin Films



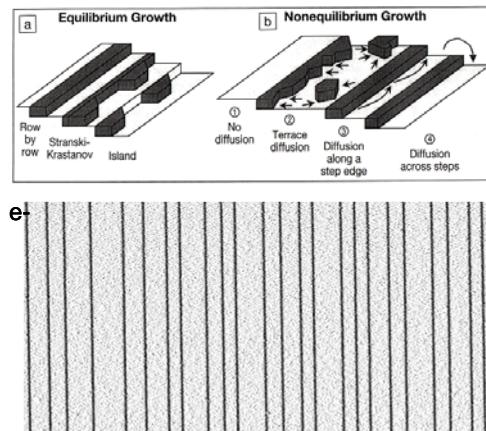
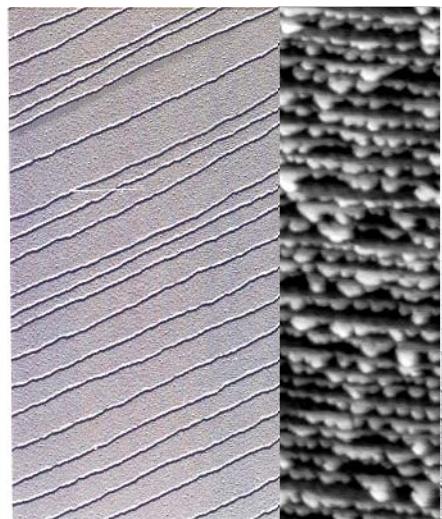
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Growth Modes



- (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

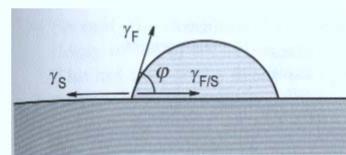


F. Himpel, Th. Jung et al.
MRS Bulletin 24, 20-24 (1999).



Growth Modes

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

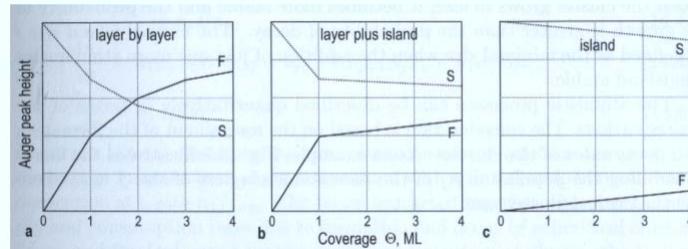


$$\gamma_s = \gamma_{sf} + \gamma_f \cos \varphi$$

- Island growth: $\varphi > 0 \rightarrow \gamma_s < \gamma_{sf} + \gamma_f$
- Layer-by-layer growth: $\varphi = 0 \rightarrow \gamma_s \geq \gamma_{sf} + \gamma_f$

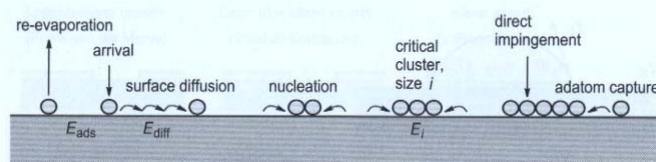
Growth Modes

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



Island Number Density

- Nucleation and growth on surfaces:



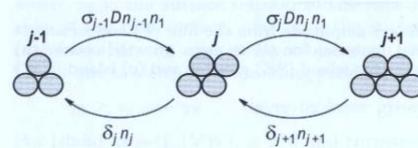
- Diffusion coefficient:
$$D = \frac{v}{4n_0} \exp\left(-\frac{E_{diff}}{k_B T}\right)$$

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

- **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:

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

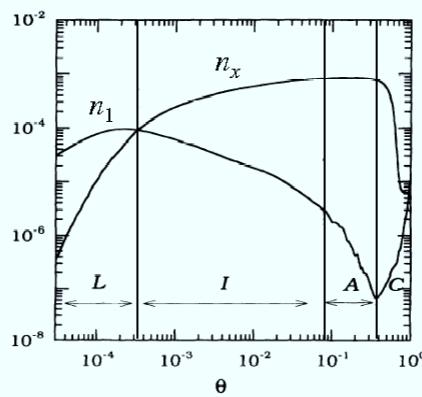
adatom density subcritical clusters stable clusters

$\frac{dn_j}{dt} = n_1 \sigma_{j-1} Dn_{j-1} - \delta_j n_j + \delta_{j+1} n_{j+1} - n_1 \sigma_j Dn_j$ 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: $n_l \gg n_x$

- In such case:

$$n_l \propto \Theta \quad n_x \propto \Theta^3$$

When $n_x \sim n_l \rightarrow$ (2) Intermediate-coverage regime

- In such case:

$$n_l \propto \Theta^{-1/3} \quad n_x \propto \Theta^{1/3}$$

When mean island separation \sim mean free path of adatoms

\rightarrow (3) Aggregation regime ($\Theta \sim 0.1\text{-}0.4$ ML)

When the island join together

\rightarrow (4) Coalescence and percolation regime

Island Number Density

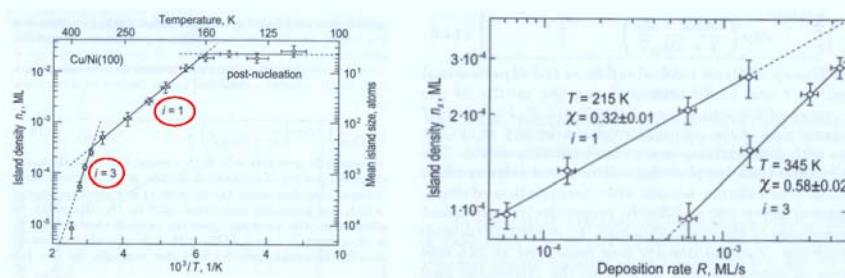
• Saturation density (Venables et al., 1984):

$$n_x = n_0 \eta(\Theta, i) \left(\frac{4R}{v_0 n_0} \right)^{\frac{i}{i+2}} \exp\left(\frac{iE_{diff} + E_b}{(i+2)k_B T} \right)$$

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

i binding energy
E_b of critical cluster

• 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):

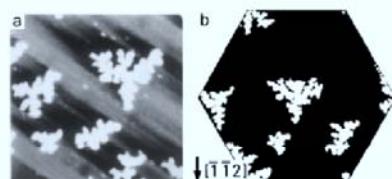


- Adatoms stick at islands
- Fractal shape
- Branch thickness ~ 1 atom
- No influence of lattice geometry

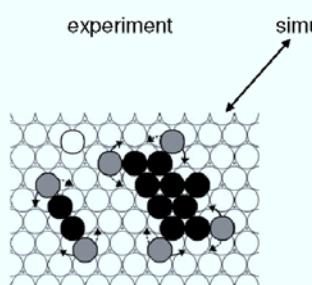
- In real growth (STM experiments):
 - Fractal shape
 - Branch thickness > 1 atom
 - Influence of lattice geometry

Island Shape

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



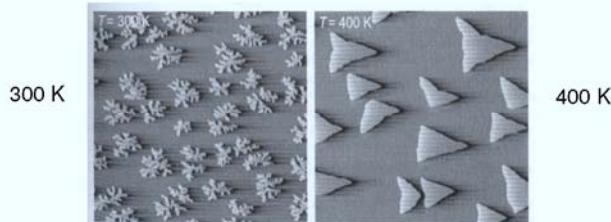
- Branch thickness ~ 4 atoms
- Trigonal symmetry



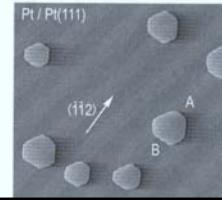
- Higher coordination is preferred

Island Shape

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

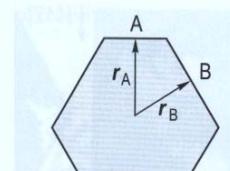


- The equilibrium shape is hexagonal:
(deposition at 425 K + annealing at 700 K)



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

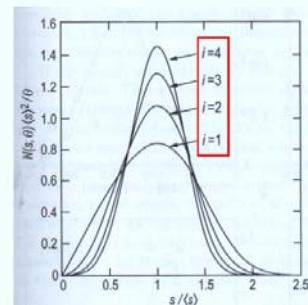
- Island size distribution depends on:

- Critical island size
- Coverage
- Substrate structure
- “Coarsening” (at high Θ)

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

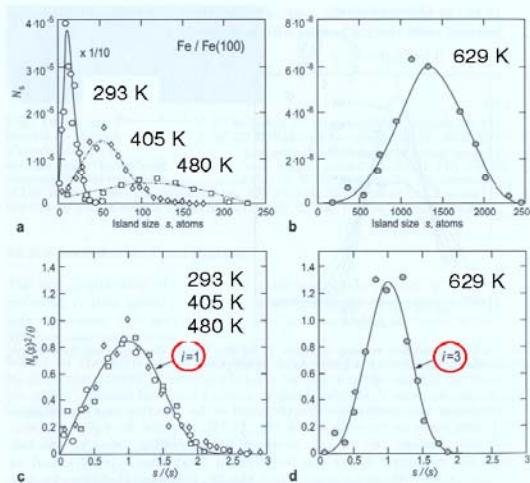
$$N_s = \frac{\Theta}{\langle s \rangle^2} f_i \left(\frac{s}{\langle s \rangle} \right)$$

- Comparing with experimental results
→ critical island size



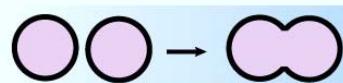
Island Size Distribution

- Example: Fe on Fe(100) (Stroscio et al., PRL 1993, Amar et al., PRB 1994)



Coarsening Phenomena

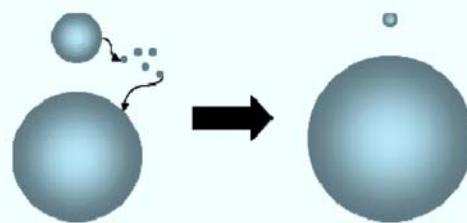
1) Coalescence:



- 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:



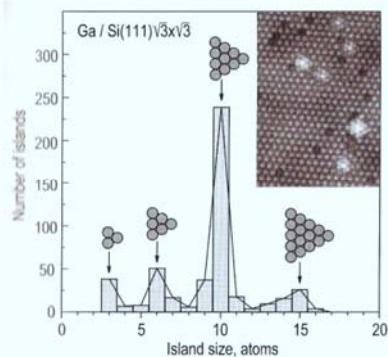
- Chemical potential of a circular island:

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

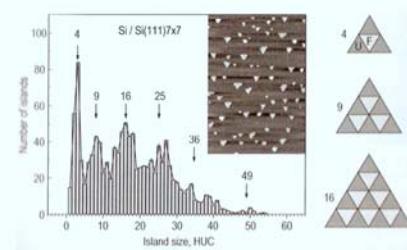
Reducing free energy → net flow from smaller to larger islands!

Magic Islands

- Ga on Si(111) $\sqrt{3}\times\sqrt{3}$ (Lai & Wang, PRL 1998):



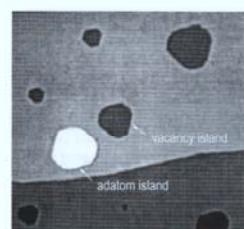
- Si on Si(111)7x7 (Voigtländer et al., PRL 1999):



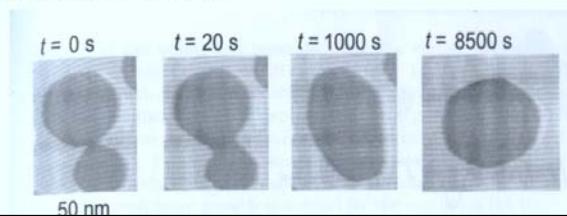
Formation of a new row → high energy cost!

Vacancy Islands

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

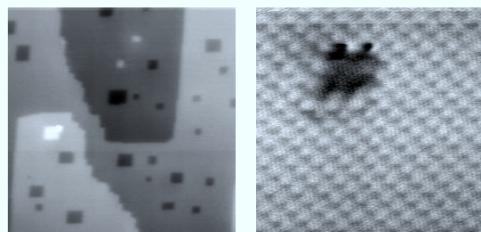


- Analogies with adatom islands



Vacancy Islands

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

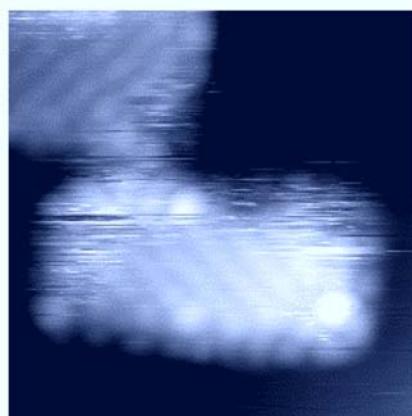


KBr(100)

- Irradiation with 1 keV electrons at 130 °C
- Rectangular pits with area of 1x1 nm² up to 30x30 nm²
- 1 ML deep (0.33 nm)

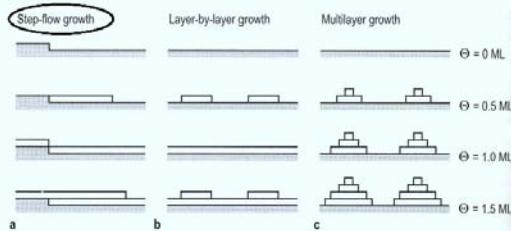
Vacancy Islands

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

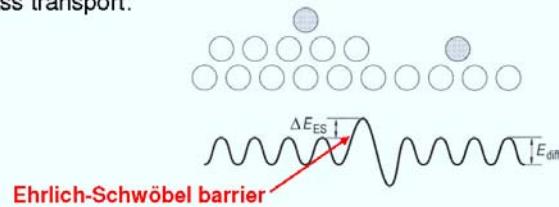


Kinetic Effects in Homoepitaxy

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

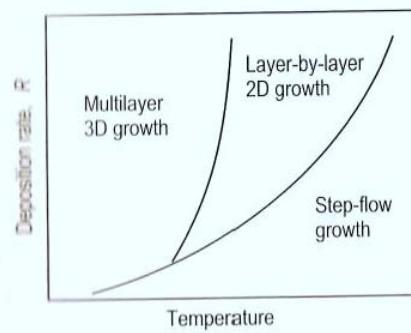


- Interlayer mass transport:



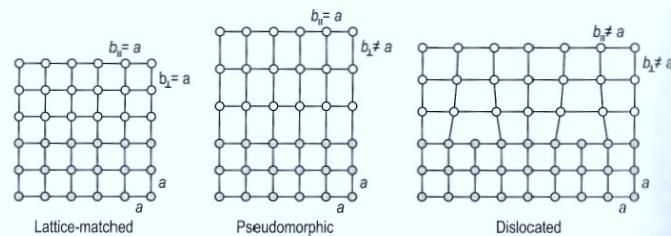
Kinetic Effects in Homoepitaxy

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



Strain Effects in Heteroepitaxy

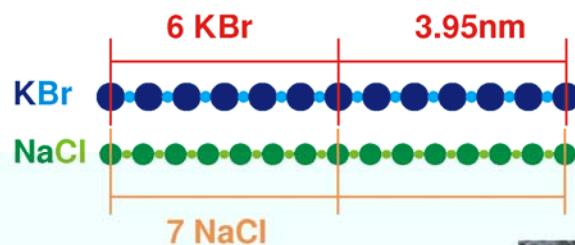
- Heteroepitaxy growth modes:



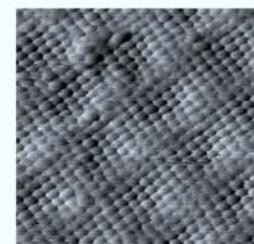
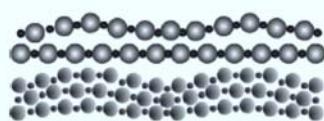
- Lattice **misfit** \rightarrow elastic strain and dislocations
- Pseudomorphic growth below critical misfit and film thickness

Strain Effects in Heteroepitaxy

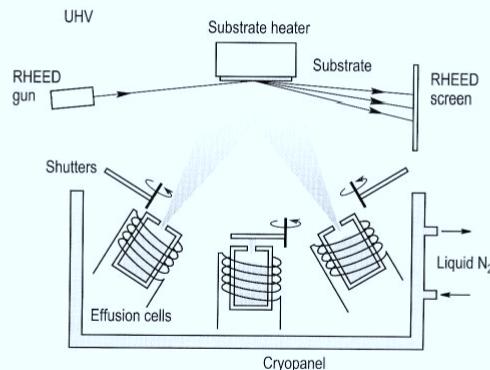
- Heteropitaxy on insulating surfaces (Maier et al., PRB 2007):



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



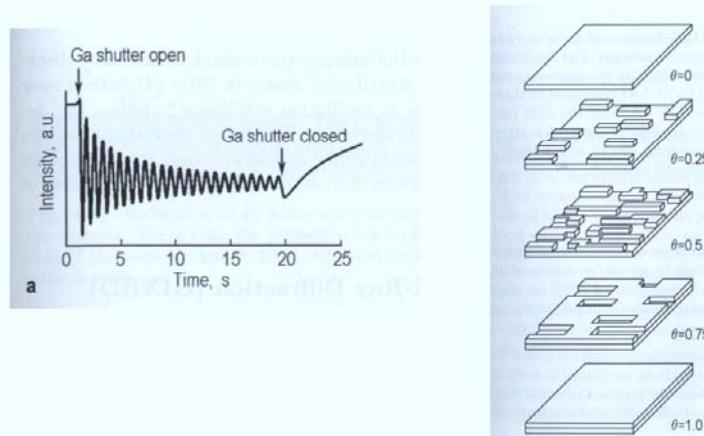
Molecular Beam Epitaxy



- Used both in research and in semiconductor device fabrications

Molecular Beam Epitaxy

- The growth process can be monitored by RHEED:



Solid Phase Epitaxy

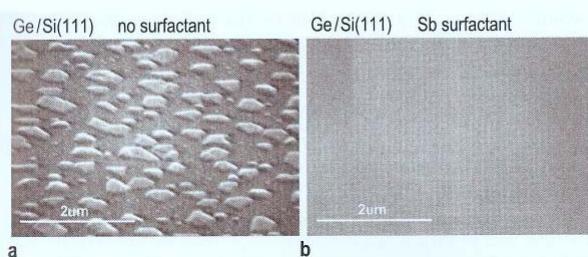
- Amorphous film deposited at low T and then crystallized upon heating at high T
- Lower crystallinity than MBE
- Used in semiconductor industry

Chemical Beam Epitaxy

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

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