SURFACE DIFFUSION NUCLEATION AND GROWTH



Adsorption and diffusion of atoms



Once adsorbed on a surface, the adatom diffuses by overcoming an activation barrier E_d i.e. the saddle point between two dsorption sites.

The Einstein formula

The Einstein relation describes well the movement of atoms on a substrate:

$$\left< \Delta x^2 \right> = Dt$$

 $\left< \Delta x^2 \right>$: root mean square

- Diffusivity: $D = D_0 \exp(-E_d/kT)$
- D_0 is the preexponential factor:



 Δx

 V_0 can be interpreted as the attempt frequency of the system to overcome the potential barrier E_d i.e. typical frequencies of the lattice vibrations:

$$v_0 \approx 10^{12} - 10^{13} Hz$$
 For $l = 0.3 nm \longrightarrow D_0 \approx 10^{-3} \frac{cm^2}{s}$

Surface diffusion and island density









Density of islands $N \propto (R \vartheta / D_0)^{1/3} e^{\frac{E_d}{3kT}}$



1/T

Island densities and shapes





A simple case study:

Ag on Pt(111) as a function of substrate temperature

Coverage 0.1 ML



Two points:

Island density decreases with T Island size increases with T

H. Roeder, H. Brune, J.P. Bucher, and K. Kern, Surf. Sci. 298, 121 (1993).

Density of islands from STM images

Saturation density of islands:

 $\eta(\theta)$: slowly varying function of θ i : size of the critical nucleus E_i : binding energy of critical nucleus

$$N = \eta(\vartheta) \left(\frac{R}{\nu_0}\right)^{\frac{i}{i+2}} \exp \frac{E_i + iE_d}{kT(i+2)}$$

Venables et al. Rep. Prog. Phys. 47, 399 (1984)

The density of islands can be established by considering an adatom diffusing by Λ_d on the average during its life time τ :

The density of adatoms « n » is the product of the deposition rate R by the lifetime:

The rate of dimer formation can then be determined and thus for i=1, the average density of islands N defined by the Voronoi polygons of capture area Λ_d^2 (see course).

Generalization to 1D, 2D and 3D systems: A. Pimpinelli et al. Phys. Rev. Lett. 69, 985 (1992).



 $n = \frac{R\Lambda_d^2}{D}$

Diffusion barriers from STM images



For i=1 we retrieve the simple expression for N with the exponent 1/3

$$N \propto (R \vartheta / D_0)^{1/3} \exp \frac{E_d}{3kT}$$

Arrhenius plot of N as a function of 1/T for T \leq 110K, i = 1 and R = 1.1 × 10⁻³ ML/s

 \rightarrow E_d= 157 ±10 meV

Assuming $\eta(\theta) \approx 1 \rightarrow 1 \times 10^{13} \le v_0 \le 4 \times 10^{14}$ Hz The dimer (i=2) becomes the critical nucleus for T>120K

Island shapes



Low temperature (130 K) grown Ag islands on Pt(111)



Itteration of Koch's snow flake

Such structures are called self-similar

H. Roeder, E. Hahn, H. Brune, J.P. Bucher, and K. Kern, Nature, 366, 141 (1993).

Fractal growth

Le volume d'un objet arbitraire peut être mesuré en le remplissant avec des balles de dimension I et de volume l^d il nous faut N(I) balles pour le remplir:

$$V = N(l) l^d$$

On s'attend à ce que : $N(l) \propto l^{-d}$ puisque le volume d'un objet ne change pas si on change l'unité de mesure l. $d = \lim_{l \to 0} \frac{\ln N(l)}{\ln(1/l)}$ Normalement, d=1, 2, 3, ... Si l'objet est fractal, d ne sera pas entier Exemple: k=1 k=2 k=3 k=4 $N(l) = 3^k$ triangles de taille linéaire $l = (1/2)^k$; $d = \frac{\ln 3}{\ln 2} = 1.585$

Co islands grown on Ag(111) at low temperature



T=110 K R=1.6 10⁻⁵ ML/s θ = 0.12 ML

Fractal analysis

Original stage of growth

STM images of small Ag_N clusters grown on Pt(111) at 80 K



Average cluster size N=13 60 nm x 47 nm

Average cluster size N=2 60 nm x 19 nm



Two possible Y-shaped clusters

Why three branch dendrites?





Growth scenari of dendrites in the A-direction for frozen corner diffusion towards B-steps

Total energy calculation of Ag adatom diffusing around a Ag_7 cluster on Pt(111)

3.0

x,y-Position (nm)

4.0

5.0

1.0

2.0

J. Norskov et al. Surf. Sci. 349, L115 (1996).

Island shape: compact islands

Pt islands shapes on Pt(111) after deposition at various substrate temperature :



T. Michely et al. Phys. Rev. Lett. 70, 3943 (1993).

Article de vulgarisation: « Fabriquer des objets à l'échelle atomique » Pablo Jensen, La Recherche N°283, Janvier 1996.

Island shape: wires

How do we make a 1D system out of a 2D system ?



For example : use a fcc(110) surface



Cu wires grown on Pd(110)



320 K

350 K

J.P. Bucher et al. Europhys. Lett. 27, 473 (1994)

GROWTH AND STRAIN

Growth modes

Frank-van der Merve Stranski-Krastanov Volmer-Weber (FM) growth (SK) growth (VW) growth 0.5 ML $\Delta \gamma = \gamma_{film} + \gamma_{int} - \gamma_{sub}$ 1 ML γ_{film} = surf. free energy of the film γ_{sub} = surf. free energy of substrate 1.5 ML γ_{int} = interface energy $\gamma_{int} \approx 0$ if substrate & film similar 2 ML $\gamma_{int} \neq 0$ if there is strain

- $\Delta \gamma > 0$ 3D (VW) growth
- $\Delta \gamma \leq 0$ for every additionnal layer \rightarrow 2D growth (FM)
- $\Delta \gamma \leq 0$ for a limited number of layers \rightarrow 2D growth followed by 3D islands growth

Case study: Ag on Pt(111)

$$\gamma_{Ag(111)} = 1280 \, mJ \,/\, m^2$$

 $\gamma_{Pt(111)} = 2550 \, mJ \,/\, m^2$
 $\Delta \gamma \le 0 \quad \rightarrow \text{ wetting: layer by layer}$



Molecular beam epitaxy





Growth and RHEED signal

Layer by layer growth of the Frank-van der Merve type and corresponding RHEED signal



Molecular dynamics



Snapshots of the molecular dynamics calculation of a melting crystal

Molecular dynamics



 c_{ab} : equilibrium distance; ε_{ff} : depth of the film-film potential ; ε_{ss} : depth of the substrate-substrate potential

The potential Φ is acting between type "a" atom and type "b" atom through a distance r_{ij} . The potentials are troncated for $r_{ij} \ge 2.5 c_{ab}$

Relative strength of the f-s potential: $W = \varepsilon_{fs} / \varepsilon_{ff}$

Misfit: $\eta = (c_{\rm ff} / c_{\rm ss}) - 1$

Molecular dynamics

Grabow and Gilmer, Surf. Sci. 194, 333 (1988)



Plotted quantity :

(F_N - N μ_B)/ N₀ versus N / N₀

 F_N change of free energy on adding N atoms to the film

 μ_B chemical potential of the bulk

 N_0 number of available substrate sites

$$\mu = \partial F / \partial N$$

Strain and growth modes

- When the interaction f-s<f-f \rightarrow Volmer-Weber is favorable
- A strong f-s interaction is not sufficient to guarantee a Frank van der Merve growth in the presence of strain
- There is a third possibility in which one to a few monolayers (ML) grow layer-by-layer, followed by a cluster growth (Stranski-Krastanov growth).

Molecular dynamics predicts that a uniform film with a thickness exceeding of a few ML cannot be an equilibrium state for any finite misfit η >0

In the previous example, $\mu > \mu_B$ after the first two MLs implies that a uniform film does not lead to an absolute equilibrium state. The system can lower its chemical potential by forming 3D clusters \rightarrow SK mode

Strain and growth modes



• FvdM or layer by layer is only stable for η =0 and W>1

• It is the strain in the film which provides the driving force ΔF for the cluster nucleation. It is the difference between the energy per atom of an additional ML and that of the bulk :

$\Delta F = F(N_{n+1}) - F(N_n) - \mu_B [N_{n+1} - N_n]$

this is nothing but the difference between two successive minima in the figure (molecular dynamics). Estimate based on the elasticity theory:

$$\Delta F = \frac{2\mu(1+\nu)}{(1-\nu)}e^2$$

- μ shear modulus
- v Poisson's ratio
- e deformation // to the film plane $|e_{//}| = \eta$

INCOMMENSURATE PHASES

Nucleation on a network of discommensuration line

STM images of the domain wall network obtained after annealing a Ag-bilayer deposited on Pt(111)





Ag island nucleation at 110K. Each superstructure unit cell contains one Ag island.

Incommensurate modulated layer



- Soliton solution of the 1D Frenkel-Kontorova model. The ground state ٠ satisfies the static sine Gordon equation:
- $d^2 \varphi / d n^2 = pA \sin(p\varphi)$ $x_n \rightarrow \text{ continuous function } \varphi(n)$ •

We consider a chain of atoms connected by springs of constant k subjected to a harmonic potential of amplitude V and period b. The total energy of this model is given by :

$$H = \sum_{n} \frac{k}{2} (x_{n+1} - x_n - a)^2 + \sum_{n} V \left[1 - \cos\left(\frac{2\pi}{b} x_n\right) \right]$$

 x_n is the position of the n'th atom

a, is the distance of nearest neighbour atoms of the chain in the absence of substrate potential, with $a \neq b$.

Frank and van der Merve solved this model analytically by replacing the index "n" by a continuous variable and x_n by a continuous function ϕ_n the phase shift of an atom of the chain with respect of the potential minimum :

with
$$\varphi(n) = (2\pi x/b) - 2\pi n \rightarrow \frac{k}{2} (x_{n+1} - x_n - a)^2 = \frac{kb^2}{8\pi^2} (\varphi_{n+1} - \varphi_n - 2\pi \frac{a}{b} + 2\pi)^2$$

In the continuum approximation, the energy can be written :

$$H = \int \left[\frac{kb^2}{8\pi^2} \left(\frac{d\varphi}{dn} - 2\pi\delta \right)^2 + V(1 - \cos(p\varphi)) \right] dn$$

Where δ =(a-b)/b is the lattice mismatch and p is the commensurability. The hamiltonian can be minimized exactly. The ground state satisfies the time-independent sine Gordon equation:

$$\frac{\partial^2 \varphi}{\partial n^2} = \frac{p(2\pi)^2}{b^2} \frac{V}{k} \sin(p\varphi)$$

This equation has the form :

$$\frac{\partial^2 \varphi}{\partial n^2} = pA \sin(p \varphi)$$

One solution of this equation is the solitary lattice distortion, the so-called soliton :

$$\varphi(n) = \frac{4}{p} \arctan\left[\exp\left(pn\sqrt{A}\right)\right]$$
 with $A = \left(\frac{2\pi}{b}\right)^2 \frac{V}{k}$

For slightly differing lattice parameters of chain and substrate potential, the lowest energy state of the system consists of large commensurate domains separated by **regularly spaced domain walls** (discommensurations). The soliton solution is shown in the figure below for the domain wall located at n=0



On a surface (2D), the domain walls become domain **lines** that form a regular network of lines that may cross each others as shown in the next example.

Nucleation on surface reconstructions



Zigzag reconstruction of Au(111)

S. Padovani, I. Chado, F. Scheurer, and J.P. Bucher, Phys. Rev. B 59, 11887 (1999).

Nitrogen induced reconstructions

Periodic arrays of islands consisting of atomic nitrogen (0.2 ML) induced reconstruction of the Cu(100) surface obtained after annealing



120 nm × 120 nm



60 nm × 60 nm

0.2 ML of Fe grown on the free Cu surface in between the N-islands

T.M. Parker, L.K. Wilson, N.G. Condon, F.M. Leibsle, Phys. Rev. B 56, 6458 (1997).

Reconstruction et commensurabilité

La maille élémentaire d'une structure reconstruite est différente de la maille "idéale" obtenue par la projection de la maille volumique à la surface.

Décrivons mathématiquement les relations possibles entre maille de la structure reconstruite et maille "idéale".

Soit
$$\vec{a}_{S1} = (a_{S11}, a_{S12})$$
; $\vec{a}_{S2} = (a_{S21}, a_{S22})$

Les vecteurs de base du réseau superficiel,

et
$$\vec{a}_{V1} = (a_{V11}, a_{V12})$$
; $\vec{a}_{V2} = (a_{V21}, a_{V22})$

ceux du réseau du substrat.

La relation entre ces deux vecteurs s'écrit:

$$\vec{a}_{S1} = m_{11}\vec{a}_{V1} + m_{12}\vec{a}_{V2}$$

$$\vec{a}_{S2} = m_{21}\vec{a}_{V1} + m_{22}\vec{a}_{V2}$$

Sous forme matricielle:

$$\begin{pmatrix} \vec{a}_{S1} \\ \vec{a}_{S2} \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} \vec{a}_{V1} \\ \vec{a}_{V2} \end{pmatrix}$$

$$a_{S} = Ma_{V}$$

Reconstruction et commensurabilité

Les aires élémentaires sont:

$$A_{S} = \left| \vec{a}_{S1} \wedge \vec{a}_{S2} \right| \quad A_{V} = \left| \vec{a}_{V1} \wedge \vec{a}_{V2} \right| \quad \text{Avec} \qquad A_{S} = \left| M \right| A_{V}$$

$$\det M = |M| = M_{11}M_{22} - M_{12}M_{21}$$

Les structures superficielles peuvent être classifiées selon la valeur de det M.

1) det M= entier

La structure superficielle possède la classe de symétrie du substrat. *La maille superficielle coïncide avec les points du réseau du substrat*. La supersructure est **commensurable**.

2) det M=p/q, fraction rationnelle (p,q entiers)

La superstructure est commensurable mais *seule une fraction des atomes superficiels est localisées dans des sites à haute symétrie*. Il existe un **réseau de coïncidence**.

3) det M= nombre irrationnel

Il n' y a pas de réseau de coïncidence, le superréseau est incommensurable

Reactions at surfaces: from atoms to complexity

By Gerhard Ertl, Nobel Lecture, December 8, 2007



The structure of the Pt(110) surface a) The 1x2structure of the clean surface, b) the 1x1-structure representing termination of the bulk structure

Spiral waves during CO-oxidation on Pt(110)



PEEM images with 500 μm diameter, steady-state conditions: p_{02} = 4 x 10^{-6} mbar, p_{c0} = 4.3 x 10^{-5} mbar, T = 448 K

Target patterns in catalytic oxidation of CO on a Pt(110) surface as imaged by photoemission electron microscopy (PEEM)

Missing row: Instead of the termination by the corresponding bulk crystal plane (1x1 structure), every second row along the [1-10] direction is missing, giving rise to as 1x2-structure. In this way small facets with (111)-orientation are exposed, leading to a lower energy than with the 1x1-phase.

The two phases differ also with respect to their adsorption properties: Chemisorption of CO is accompanied by a higher adsorption energy on the 1x1-phase than on the 1x2-structure, so that local $1x2 \rightarrow 1x1$ transformation takes place as soon as the CO coverage exceeds a value of 0.2 ML. On the other hand, the sticking coefficient for dissociative oxygen coverage on the 1x1-phase exceeds that on the 1x2-phase by about 50%.

Oscillatory kinetics in catalytic oxidation of CO on Pt(110)



The occurrence of temporal oscillations in the rate of CO_2 can now be rationalized as follows: If a clean Pt(110) surface (1x2) is exposed to a proper mixture of $CO+O_2$, adsorption of CO will suffice to cause local $1x2 \rightarrow 1x1$ transformation. On the newly created 1x1-patches, the oxygen sticking coefficient will be higher, so that a higher O coverage will be built up, giving rise to an enhanced production of CO_2 . By this latter process the excess CO will be consumed so that the surface structure transforms back from $1x1 \rightarrow 1x2$, and one cycle is completed.

Mathematical modeling requires in this case three variables, the coverages of O and CO, and the fraction of the surface being present as 1x1-phase. Solution of the resulting 3 coupled nonlinear differential equations for properly chosen parameters is shown above and reproduces the experimental findings.

EVOLUTION WITH TEMPERATURE

The roughening transition (two level system)

• Suppose a surface with N available sites that are occupied by N_1 atoms ($N_1 < N$). Burton, Cabrera and Frank were the first to realize that such a two level problem is analogous to the 2D Ising model of ferromagnetism.

- such a system shows a critical behavior since above a given temperature T_c, the spins are oriented randomly
- analogy with the 2D Ising model:

i,j

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Occupied site : spin \uparrow
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Vacant site : spin \downarrow
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 ΔE between a disordered 2D Ising system at finite T and a ferromagnetic one at T=0 is:

$$\Delta E = -J \sum_{i,j} (S_i S_j - 1/4)$$

nearest neighbors and $S_i = +1/2$: spin \uparrow
 $S_i = -1/2$: spin \downarrow

The probablity p_i of occupation of site "i" is:

$$p_i = S_i + 1/2 \implies p_i = 0 \text{ or } 1$$

The roughening transition (cont)

$$\Delta E = -J\sum_{i,j} (p_i p_j - \sum_{i,j} p_i) = -J\sum_{i,j} (p_i p_j - z\sum_i p_i)$$

z is the coordination number of the 2D network. In this model the energy difference between the disordered surface and the smooth surface is given by:

$$\Delta E = -\varepsilon (\sum_{i,j} p_i p_j - z N_1)$$

 $p_i = 1$ occupied $p_i = 0$ vacant

$$N_1 = \sum_i$$

ε: energy involved inthe formation of onebond between n.n.

Approximate solution (effective field). In this approximation the atoms are distributed randomly and are not correlated. We get:

 p_i

$$\Delta E = -\varepsilon \left(\sum_{i,j} \left\langle p_i \right\rangle \left\langle p_j \right\rangle - z N_1\right)$$

 $\left< p_i \right>$ is the average occupation of site i $\left< p_i \right> = \frac{N_1}{N} = \Theta$ Θ is the coverage

The roughening transition (effective field)



For α >2 the surface is disordered and rough. The roughening temperature is

$$T_{R} = \frac{z\varepsilon}{2k_{B}} \quad T_{R} = \frac{\varepsilon}{k_{B}\ln(1+\sqrt{2})}, \text{ is Onsager's}$$