diffusion, growth and nucleation at surfaces
Pt atoms are evaporated on a Rh tip. Between subsequent images the tip is briefly annealed to induce thermal diffusion (cook and look method). Similar studies can be performed with STM but then it is more difficult to come back to the same spot on the crystal after heating due to thermal drifts.
Diffusion by exchange is often more efficient than by hopping since less bonds are broken. It works however only for homo diffusion. Which mechanisms is active depends on the details of the bonds between adatom and substrate atoms.

Fig. 10.3. Illustration of two different transport mechanisms that take an adatom from one site to the next equivalent site: (a) the hopping process and (b) the exchange process where the adatom dives into the surface and pushes the atom in the surface layer upwards into the adjacent site. Note that the transport is in different directions in the two cases.
Hopping vs exchange

As a rule of thumb diffusion energy barriers are typically from 1/5 to 1/3 of the cohesive energy for homo-diffusion or of the adsorption energy for adsorbates. Diffusion is therefore activated for substrate temperatures above such factor.

Table 10.1. Activation energies for self-diffusion on some fcc(100) surfaces; "hop" stands for adatom hopping, "ex" for exchange of adatoms, and "vac" for vacancy diffusion. The activation energies are approximate insofar as different values have been calculated from experimental data as well as from different theoretical approaches (see e.g. [10.12]).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Rh(100) a</th>
<th>Ir(100) b</th>
<th>Pt(100) c</th>
<th>Cu(100) d</th>
<th>Cu(100) f</th>
<th>Au(100) g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism</td>
<td>hop</td>
<td>ex.</td>
<td>ex.</td>
<td>vac.</td>
<td>hop</td>
<td>hop</td>
</tr>
<tr>
<td>$E_a / \text{eV}$</td>
<td>0.88</td>
<td>0.93</td>
<td>0.47</td>
<td>0.42</td>
<td>0.44</td>
<td>0.50</td>
</tr>
</tbody>
</table>

(a: [10.6], b: [10.7], c: [10.8], d: [10.9], f: [10.10], g: [10.11])
Single jumps ($w_1$) vs double jumps ($w_2$) for one dimensional diffusion

**Fig. 10.5.** Diffusion of W and Pd atoms on W(211) (after Senft et al. [10.13]). Panel (a) shows a ball picture of the W(211) surface. Diffusion is solely along the [111] direction in the temperature range of interest here (white arrow). For W atoms, the probability $w_2$ of long jumps with twice the nearest neighbor distance is small (b). The distribution calculated with $w_2/w_1 = 0.015$ is compatible with the data as well as the distribution with $w_2 = w_3 = 0$. For Pd on the other hand the experimental result can only be fitted to a distribution calculated with significant contributions from long jumps (c).
Energy barriers and diffusion: absolute rate theory

The jump rate $v(T)$ is given by a prefactor (depending on $T$ in a power law form) and by an exponential term

$$
v(T) = v_0(T) e^{-\frac{E_{\text{act}}}{k_B T}}
$$

Let’s introduce a reaction coordinate $q$, corresponding to the minimum path length to move between two potential energy minima. $G$ has a maximum at the *transition state*. Hopping diffusion may involve also the motion of the substrate atoms so that the vibrational spectrum enters the problem. For $G=G\{q, p\}$ with $\{q\}$ and $\{p\}$ the coordinates and the momenta of the ensemble of the particles involved in the motion.

The probability that a particle reaches the transition state is

$$
w(q_r, p_r) dq_r dp_r = e^{-\frac{G(q^+)}{k_B T}} e^{-\frac{p_r^2}{2\mu k_B T}} \frac{dq_r dp_r}{h}
$$
Contribution to G of the momentum along the reaction coordinate

The transition rate is then given by the integral of the probability to reach the transition state times the velocity along the reaction path:

\[

w(q_r, p_r) \, dq_r \, dp_r = e^{-\frac{G(q^+)}{k_B T}} \frac{d^2 q_r}{2 \mu k_B T} \frac{d^2 p_r}{\hbar} e^{-\frac{G_i}{k_B T}} \frac{\Delta G}{\hbar e^{\frac{k_B T}{k_B T}}}

\]

If G contains only energetic terms (i.e. no entropic terms) then the prefactor \( v_0 \) has noting to do with an attempt frequency.

At 300 K it has, however, \( v_0 = 6 \times 10^{12} \text{ sec}^{-1} \)

Terahertz range very close to phonon frequencies!
Diffusion along a 1 Dim potential

Vibrational energy levels in the harmonic approximation

\[ \omega = 2\pi \sqrt{(E^+ - E_g) / 2a_{nn}^2 M} \]

Gibbs free enthalpy, calculating the entropy from the harmonic vibrational eigenstates

\[ \Delta G = E^+ - E_g + k_B T \ln \sum_n \exp(-\hbar \omega(n + 1/2) / k_B T) \]

\[ = E^+ - (E_g + \frac{1}{2} \hbar \omega + k_B T \ln(1 - e^{-\hbar \omega / k_B T})) \]

In the limit \( k_B T \ll \hbar \omega \), the prefactor remains \( k_B T / \hbar \) and the "attempt frequency" \( \omega \) does not enter the prefactor at all. In the reverse case \( k_B T \gg \hbar \omega \), the prefactor becomes temperature independent and equal to the "attempt frequency"

\[ \nu_0 = \omega / 2\pi = \sqrt{(E^+ - E_g) / 2a_{nn}^2 M} \]

The same discussion holds true also for the prefactor in thermal desorption. In that case the vibrational frequency is generally higher so that one is often closer to the low rather than to the high temperature limit.
Table 10.2. Activation energies for diffusion $E_{\text{act}}$ in eV and prefactors $\nu_{\text{0,th}}$ in $10^{12}$ s$^{-1}$ for the low index surfaces of Cu and Ni according to Ulrike Kürpick [10.10] together with the values for $\nu_{\text{0,mod}}$ calculated from (10.15). The work of Kürpick quotes prefactors for the diffusion coefficient which are converted into the prefactors $\nu_{\text{0}}$ according (10.6) and (10.7).

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{\text{act}}$(Cu)</th>
<th>$\nu_{\text{0,th}}$(Cu)</th>
<th>$\nu_{\text{0,mod}}$(Cu)</th>
<th>$E_{\text{act}}$(Ni)</th>
<th>$\nu_{\text{0,th}}$(Ni)</th>
<th>$\nu_{\text{0,mod}}$(Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.44</td>
<td>3.8</td>
<td>2.3</td>
<td>0.68</td>
<td>5.9</td>
<td>3.0</td>
</tr>
<tr>
<td>(110)</td>
<td>0.25</td>
<td>1.7</td>
<td>1.7</td>
<td>0.39</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>(111)</td>
<td>0.042</td>
<td>0.74</td>
<td>1.2</td>
<td>0.063</td>
<td>1.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Concerted motion: lowering of the diffusion barrier

Motion of dimers

Fig. 10.9. Diffusion mechanisms of dimers on (100) surfaces. Dimer shearing (a) has a lower activation energy than single atom hopping on Cu(100) [10.15]. The same holds for exchange diffusion (b) on Pt(100) [10.16].
Concerted motion: lowering of the diffusion barrier

Collective motion of larger clusters: tetrameres

**Fig. 10.10.** Diffusion of a tetramer by shearing. The two atoms in the ellipse move together in a concerted motion. The activation energy for this cluster diffusion process is significantly lower than for diffusion by evaporation of an atom (after Zhu-Pei Shi et al. [10.15]).

**Fig. 10.11.** Island diffusion by generation and motion of a partial dislocation. The mechanism is effective for large islands, in particular when the island is elastically compressed because of a misfit between the lattice constant of the island and the substrate.
Diffusion across steps and the Ehrlich – Schwoebel barrier

Fig. 10.18. Microscopic view on an undulated surface. Profile decay requires *intralayer* as well as *interlayer* mass transport across step edges (arrow). Interlayer mass transport requires to overcome an activation barrier which is often larger than the activation barrier for intralayer transport. The additional activation energy is called ES-barrier.
Diffusion across steps and the Ehrlich – Schwoebel barrier

Fig. 10.19. Schematic drawing of the potential for an atom near a step edge with an ES-barrier $E_{ES}$. $E_A$ is the binding energy to a step site and $E_D$ the activation energy for terrace diffusion. The dashed lines represent a potential with an attachment barrier and with a higher or lower binding energies at the last binding site at the upper step edge. All three alternatives may exist independently. An ES-barrier may exist also for vacancy diffusion.
E-S barriers for the different paths (eV): note the negative value for KX

Fig. 10.20. A basic set of possibilities for adatoms to traverse densely packed steps on (a) fcc(100) and (b) fcc(111) surfaces. "H" stands for hopping, "X" for exchange, and "KX" for exchange at a kink site. On the (111) surface the type of step (A or B) is added to the notation.
Ostwald ripening

Particles of different size have different chemical potential. The equilibration process takes place via 2D evaporation/condensation and diffusion of the atoms. The particle density decreases with time, while the average size increases.

Fig. 10.21. A series of STM images of about 60 nm × 60 nm of a Cu(111) surface showing an adatom island inside a vacancy island at different times t. The temperature was 303 K. Vacancy islands and adatom islands were produced by sputtering and subsequent evaporation of Cu. The images are excerpts from a movie of a larger area from which these particular frames were selected for quantitative analysis (after Schulze Icking-Konert).
Fig. 10.22. Excerpts from STM images of a Cu(100) surface taken at 343 K and the rate as function of time. The inset shows the potential for vacancy migration and incorporation into an ascending step. The constancy of the rate is indicative of detachment/attachment limited decay. The fact that islands C and B decay with the
Increasing CO pressure

How Sensitive is Epitaxial Growth to Adsorbates?

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Fig. 1. Five STM topographs are compared corresponding to deposition of 0.15 ML Pt at 400 K at a rate of $5 \times 10^{-3}$ ML/s with different CO partial pressures. The CO pressure was set 100 s before deposition started and maintained during the 30 s deposition time. The Pt islands resulting from clean deposition in Fig. 1a are triangular consisting of $\{110\}/\{111\}$ steps ($\{111\}$-microfaceted steps oriented along $\langle 110 \rangle$, briefly $B$ steps) with a certain number of kinks. One triangle vertex of each island points to the right. A CO partial pressure of $1.0 \times 10^{-10}$ mbar causes drastic changes in the island shapes (Fig. 1b). The islands are more compact and contain also segments of $\{110\}/\{100\}$—or $A$ steps. In Fig. 1c at a CO pressure of $4.7 \times 10^{-10}$ mbar the island edges are already dominated by $A$ steps and start to develop a triangular shape, now with one triangle vertex pointing to the left. At CO pressures of $9.5 \times 10^{-10}$ mbar (Fig. 1d) and $1.9 \times 10^{-9}$ mbar (Fig. 1e) fully triangular islands consisting almost exclusively of $A$ steps result from growth. Most of the islands in Figs. 1d and 1e already support a second-layer island, in contrast to those grown at lower CO pressures.

![STM topographs](image)

FIG. 1. STM topographs after deposition of 0.15 ML Pt on Pt(111) at 400 K with a deposition rate of $5 \times 10^{-3}$ ML/s and with different CO partial pressures during growth. (a) $p_{\text{CO}} < 5 \times 10^{-17}$ mbar ("clean"); (b) $p_{\text{CO}} = 1 \times 10^{-10}$ mbar; (c) $p_{\text{CO}} = 4.7 \times 10^{-10}$ mbar; (d) $p_{\text{CO}} = 9.5 \times 10^{-10}$ mbar; (e) $p_{\text{CO}} = 1.9 \times 10^{-9}$ mbar. CO was admitted 100 s prior deposition. Scan size $1700 \times 2500$ Å.
Influence of adsorbates on diffusion and E-S barrier height

FIG. 2. Critical diameter \( d_c \) for nucleation on top of an island (left axis and full circles) and associated step edge barrier height according to Ref. [5] (right axis and full squares). Lines are to guide the eye.

FIG. 3. Surface morphology after deposition of 5 ML with a rate of \( 5 \times 10^{-3} \) ML/s at 300 K for (a), (b) and at 400 K for (c), (d). CO partial pressures during growth were \( p_{CO} < 5 \times 10^{-12} \) mbar (clean) in (a), (c) and \( p_{CO} = 9.5 \times 10^{-10} \) mbar in (b), (d). Scan sizes are \( 1070 \times 1070 \) Å in (a), (b) and \( 2130 \times 2130 \) Å in (c), (d).

FIG. 4. Island density versus CO pressure for the experiments illustrated in Fig. 1.
In conclusion, we have demonstrated that all aspects of homoepitaxial growth on Pt(111) are influenced by minute amounts of adsorbed CO. The sensitivity to adsorbates is due to the preferential adsorption of CO on step atoms, i.e., at those places where growth proceeds. In clean growth on Pt(111) only one triangular growth shape is present, which is bounded by $B$ steps. The presence of $A$ steps at temperatures below 470 K always indicates the presence of CO. The consequences of this finding are in agreement with recent ab initio calculations [14], which predict a negligible edge barrier at $A$ steps in clean growth on Pt(111). The experiments presented indicate also that in order to obtain results representative for a clean growth system, deposit atom to impurity atom impingement rates of $10^{-4}$ or below may be necessary. This is substantially less than previously anticipated.
Nucleation and growth

Crystal Growth is important for the production of electronic devices which need atomically flat interfaces. Deposited clusters are the base for nanodots and Q-bits.

Whenever a material is deposited onto a flat surface, it has to aggregate into stable nuclei, a phenomenon which requires supersaturation of adparticles. One talks of epitaxial growth when the deposited layer assumes the same lattice configuration of the substrate, the Greek word epitaxy meaning positioning or lining up.

Homoepitaxy: growth of the same material as the substrate,
Heteroepitaxy different chemical species.

In UHV epitaxial growth can be achieved by Molecular Beam Epitaxy (MBE).
In MBE the flux of the particles is accurately controlled and kept constant using molecular beams directed to the surface.
Otherwise the material can be provided from the gas or from the liquid phase and reacted on the surface. In this case one speaks of Chemical vapor deposition (CVD) or of Liquid Phase Epitaxy (LPE). In the latter case the supersaturation is controlled by external parameters as e.g. the electrode potential in an electrochemical cell.
Growth modes in surface epitaxy

Fig. 16.6. Schematic view of the three topologically distinct epitaxial growth modes (Kern, Le Lay & Metois, 1979).
Growth modes in surface epitaxy

FIGURE 2.27. Equilibrium growth modes in epitaxy: (a) layer-by-layer (Frank-van der Merwe); (b) layer plus island (Stranski-Krastanov); (c) island growth (Volmer-Weber).
Monitoring crystal growth

Fig. 16.8. Time dependence of Mo and Cu Auger peak intensities as Cu grows epitaxially on Mo(100). See text for discussion (Soria & Poppa, 1980).

**Cu exposure in monolayers**

<table>
<thead>
<tr>
<th>Cu/Mo(100)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal layer by layer growth</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Auger amplitude (arbitrary units)**

- Mo: 300 K, 965 K, 573 K
- Cu: deposition rate: $3.8 \times 10^{12}$ atoms cm$^2$ s$^{-1}$

**Deposition time (s)**

0 150 300 450 600 750 900 1050 1200

**RHEED intensity**

Ga shutter open

Ga shutter closed

**FV growth**

**SK growth**

θ = 0
θ = 0.25
θ = 0.5
θ = 0.75
θ = 1
Monitoring crystal growth

The growth can be monitored also by recording He atom scattering in anti-phase conditions.

Fig. 11.10. Calculated intensities for a beam of He-atoms reflected in anti-phase condition from a growing surface.
Nucleation and growth

Let’s consider a constant flux of atoms and let’s neglect re-evaporation. Agglomeration leads to clusters form which become stable beyond a critical size. The process proceeds more rapidly at higher temperature.

![Fig. 11.1. 190 nm x 190 nm STM images of Ag(111) after deposition of a few monolayers of Ag at different temperatures with the same flux. The lower density of islands at higher temperatures is due to the faster diffusion (courtesy of Margret Giesen, unpublished).](image)
Critical size of the clusters

The size of the stable cluster depends on surface and adatom species (on fcc(100) e.g. square configurations are the most stable).

Islands smaller than the critical size dissolve spontaneously.
Fig. 11.4. STM Image (195 nm×195 nm) of a vicinal Cu(111) surface on which the width of one terrace has accidentally exceeded the nucleation length (courtesy of Margret Giesen, unpublished). Nucleation occurs on that terrace, followed by nucleation of further islands on top of each other as the growth proceeds because of the Ehrlich-Schwoebel barrier on Cu(111) surfaces (Sect. 10.3).
Low temperature growth - growth without diffusion

The atoms stay where they hit the surface

Fig. 11.5. Schematic side view of a cold-deposited film. The atoms stay in the sites where they have arrived. The checkerboard-patterned squares symbolize single atoms.
Growth with hindered interlayer transportation of matter

Fig. 11.8. (a) STM image of a Pt(111) surface after deposition of 40 ML of platinum at 440 K in the presence of $1.9 \times 10^{-9}$ mbar CO which increases the Ehrlich-Schwoebel barrier (after M. Kalff et al. [11.4]). (b) Top view on hexagonal symmetric pyramids as calculated from (11.22) for an infinitely high Ehrlich-Schwoebel barrier. The solid lines mark the steps. (c) Cross section through the calculated shape.
Growth with facile interlayer transport

Fig. 11.9. Growth with unhindered interlayer transport and moderately rapid diffusion ($\nu/F = 10^5$). (a) Coverage in layers 1-5 vs. the total coverage, (b) fraction of open area in layers 0-4, (c) rms-roughness and step density.
Homoepitaxy of Pt on Pt(111)

Layer by layer growth: $kT > E_{\text{Schwoebel}}$

Blocked interlayer transport: $kT < E_{\text{Schwoebel}}$

Re-entrant layer by layer growth:
The islands have a ramified structure and the atoms of the upper terraces have a high chance of reaching the step edge and kink sites due to the long perimeter of the islands.

Fig. 11.11. Experimental data for deposition of Pt on Pt(111) after Kunkel et al. [11.7]. The deposition rate was between 1/40 and 1/36 monolayers per second. (a) Layer-by-layer growth, (b) growth with blocked interlayer transport, (c) reentrant layer-by-layer growth at low temperatures.
Nucleation and growth in strained systems

Because of the large lattice mismatch Ni grows pseudomorphic only in the submonolayer regime. After its completion additional Ni atoms are incorporated in the first layer until the Ni contracts to its bulk lattice constant causing a corrugation pattern to appear. Nucleation density is highest on monolayer films. The white dashed lines indicate steps on the Ru substrate. They induce a corrugation which enhances Ni nucleation.

**Fig. 11.22.** STM-image (courtesy of R. J. Behm) of an annealed Ni-film on a Ru(0001) substrate onto which an additional amount of 0.05 monolayers of Ni was deposited at 300 K. Image size is 400 nm × 400 nm. The numbers indicate the thickness of the Ni-film in monolayers. The dashed lines mark some of the steps on the underlying ruthenium substrate, ascending from left to right. The higher nucleation density on thinner films is indicative of a smaller diffusion coefficient (after Meyer et al. [11.24]).
Diffusion barrier and total energy for a strained surface

Fig. 11.23. Top panel: Total energy of silver atoms in the fcc-sites and bridge-sites of an Ag(111) film as function of the surface lattice constant. Bottom panel: Differences in the energies of bridge and fcc-sites, the activation energy for diffusion (after C. Ratsch et al.)
Dendritic growth on strained layers

Fig. 11.24. (a) Dislocation network of a two-monolayer Ag-film on Pt(111). Within the distorted hexagons, the Ag atoms reside in fcc-sites. (b) Nucleation of the next silver layer follows the dislocation pattern; nucleation occurs in the center of the fcc-areas (courtesy of Harald Brune [11.27]).
Ordered Clusters at surfaces

Fig. 11.25. (a) Hut cluster of Ge formed on a pseudomorphic Ge-layer on Si(100). The facets display \{105\}-orientation. (b) A multifaceted dome cluster (courtesy of Bert Voigtländer, see also [11.28]).