Growth as a non equilibrium phenomenon

Epitaxial thin film growth is a non-equilibrium kinetic phenomena.

In thermodynamic equilibrium all atomic processes proceed in opposite directions at equal rates, i.e. there is hence no net growth and average macroscopic quantities such as surface coverage or roughness stay constant.

**a 2D laboratory: single crystal surfaces**

Each process $i$ has an energy barrier $E_i$ and a rate $v$

$$v = v_0 \exp\left(-\frac{E_i}{kT}\right)$$

**diffusion processes:**

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

$a \rightarrow$ lattice constant, $t \rightarrow$ time

Growth as a non-equilibrium phenomenon

Aim: controlling

• mean size
  (size distribution)
• density
• shape
• composition

Control parameters:

• substrate temperature $T$
• deposition flux $F$
• surface coverage $\Theta$
• substrate/overlayer material
  (strain, mixing, etc.)
• substrate symmetry or
  patterning
Statistical growth: $T \rightarrow 0$ K

- thermally-activated diffusion is frozen
  \[ \nu = \nu_0 \exp(-E_i / kT) \rightarrow 0 \]

- coverage determines mean island size $n$

- large size distribution

Co/Pt(111)

0.03 ML, $T = 50$ K: \[ n = 1.2 \]
0.10 ML, $T = 50$ K: \[ n = 2.9 \]

$n = \text{mean island size} = \text{coverage/island density}$
Cluster diffusion: Co/Pt(111)

Sequential activation of cluster diffusion results in size selection

\[ T < 60 \text{ K}: \text{monomers} \]

\[ 60 \text{ K} < T < 90 \text{ K}: \text{dimers and trimers} \]

\[ 100 \text{ K} < T < 130 \text{ K}: \text{tetramers and pentamers} \]

S. Rusponi et al. unpublished
Rate equations: $i = 1$

Assumption: adatom can diffuse with a rate $D$
but
dimer is stable, i.e. when two atoms meet, they can not detach
Critical size (nucleus) $i=1$

\[
\frac{dn_1}{dt} = F - 2\sigma_1 Dn_1^2 - \sigma_x Dn_1 n_x - k_x F(Ft - n_1) - 2k_1Fn_1
\]

\[
\frac{dn_x}{dt} = \sigma_1 Dn_1^2 + k_1 Fn_1
\]

\[
D = D_0 \exp(-E_m / kT)
\]

Rate equations give the formation rate for adatom and stable islands
Rate equations: \( i > 1 \)

- Capture and decay processes \( \rightarrow \) cluster size

![Diagram showing capture and decay processes]

- Rate equations:

\[
\begin{align*}
\frac{dn_1}{dt} &= R \frac{n_1}{\tau_{ads}} - \frac{n_1}{2} \left( 2\delta_2 n_2 + \sum_{j=3}^{i} \delta_j n_j - 2\sigma_1 Dn_1^2 - n_1 \sum_{j=2}^{i} \sigma_j Dn_j \right) - n_1 \sigma_x Dn_x \\
\frac{dn_j}{dt} &= n_1 \sigma_{j-1} Dn_{j-1} - \delta_j n_j + \delta_{j+1} n_{j+1} - n_1 \sigma_j Dn_j \\
\frac{dn_x}{dt} &= n_1 \sigma_i Dn_i
\end{align*}
\]

(adatom density) (subcritical clusters) (deposition rate) (metastable clusters) (stable clusters)
Island density

\[ n_x = \eta(\theta, i) \left( \frac{D}{F} \right)^{-\chi} \exp \left( \frac{E_i}{(i + 2)kT} \right) \]
\[ \chi = \frac{i}{i + 2} \]

\[ i = 1 \rightarrow E_i = 0 \rightarrow n_x = \eta(\theta, i) \left( \frac{D}{F} \right)^{-1/3} = n_x = \eta(\theta, i) \left( \frac{D_0}{F} \right)^{-1/3} \exp \left( \frac{E_m}{3kT} \right) \]

The slope gives \( E_m \)

Comparison of experimental island densities for Ag/Pt(111) with self-consistent calculations from mean-field nucleation theory. (a) Arrhenius plot of saturation island densities ((cov. = 0.12 ML) for the regime where dimers are stable nuclei. (b) Island density vs. coverage at 75 K).
Nucleation and coalescence regime depend on growth conditions (F and T) and island shape.

Island shape


Temperature scale of Al(111) homoepitaxy

Ag/Pt(111) T=110K:
Adatom stick at the island edge and stop diffusing

Co/Pt(111) T=270K:
Adatom edge diffusion is activated
Schematic of the energy landscape seen by an adatom approaching a step edge

Inter-layer diffusion depends on the island size and shape

Self-organized growth of nanostructure arrays on strain-relief patterns

Island confinement

Nucleation of an island superlattice on a reconstruction network. (a) STM image of the domain wall network formed by the second Ag monolayer on Pt(111). (b) Ag nucleation on this network at $T = 110K$ ($\theta = 0.10$ ML). (c) Almost monodispersed size distributions are associated with the periodic island spacing. (d) Detail showing that islands form exclusively on the fcc stacking areas.

Self-assembled nanostructure arrays

Self-organized growth of nanostructure arrays on moiré patterns: Graphene/Ir(111)

A moiré is a superposition of two lattices generating a third one.

\[ \mathbf{k}_{\text{moiré}} = \frac{\mathbf{k}_2 - \mathbf{k}_1}{2} \]

- \( a_{Ir} = 0.27 \text{ nm} \)
- \( a_c = 0.245 \text{ nm} \)

Supercell with (10x10) C atoms on (9x9) Ir substrate atoms

Self-assembled nanostructure arrays

Self-organized growth of nanostructure arrays on moiré patterns: Graphene/Ir(111)

Graphene/Ir(111)+Ir
Ir deposition:
I=10.5 A, V=4.90 volts  T=375 K

Graphene/Ir(111)+Ir+Co
Ir dep.: I=10.5 A, V=4.90 volts  T=375 K
Co dep.: 1 ML tdep=8 min  T=300 K

Epitaxial growth of two-dimensional alloys

\[ v = v_0 \exp\left(-\frac{E_i}{kT}\right) \]
Epitaxial growth of two-dimensional alloys

\[ \nu = \nu_0 \exp(-E_i / kT) \]

Fe: \( T_{\text{dep}} = 140 \text{ K} \)
\( \Theta = 0.25 \text{ ML} \)

Co: \( T_{\text{dep}} = 140 \text{ K} \)
\( \Theta = 0.25 \text{ ML} \)

Island size = 90 atoms/isl

Island size = 390 atoms/isl

Alloy (Fe\(_x\)Co\(_{1-x}\)) growth by co-deposition:
the island size (density) depends on the relative percentage of the two elements!!!!

Nanostructured surface
Epitaxial growth of two-dimensional alloys

Pre-defined nucleation sites to define the island density

Growth of the alloyed nanostructures on the template substrate
Epitaxial growth of two-dimensional alloys

Pt
\[ T_{\text{dep}} = 200\text{K} \]
\[ \Theta = 0.2 \text{ ML} \]

Annealing to 800 K

Co\textsubscript{x}Fe\textsubscript{1-x} decoration
\[ T_{\text{dep}} = 250\text{K} \]
\[ \Theta = 0.2 \text{ ML} \]
At the Fermi energy ($E_F$) the local density of states (LDOS) oscillates around the impurity with a wavelength of $\lambda_F = 2\pi/k_F$, where $\lambda_F$ is the Fermi wavelength and $k_F$ the Fermi wave vector. This variation of the LDOS at $E_F$ due to standing-wave formation modifies the adsorption energy of the adsorbates.