INFLUENCE OF EHRLICH - SCHWOEBEL BARRIER

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MECHANISM OF SURFACE DIFFUSION

HOPPING DIFFUSION

SITE-EXCHANGE DIFFUSION

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COMPARISON OF DOWN-STEP AND TERRACE DIFFUSION

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EFFECT OF EHRLICH-SCHWOEBEL BARRIER ON STEP FLOW

1. BUNCHING AND DEBUNCHING OF STEPS

1. GROWTH

back → front

2. EVAPORATION

front ← back

bunch

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BALES-ZANGWILL INSTABILITY

UNDULATION OF STEPS

\[ \nu_{total} = \nu_{up} + \nu_{down} \]

\[ \nu_{up,down} \propto D_s \left( \frac{dn_s}{dy} \right)_{up,down} \]

\[ E_{ES} = 0 \]

\[ \nu_{total,A} = \nu_{total,B} \]

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\[ E_{ES} > 0 \]
\[ v_{up,A} < v_{up,B} \]
\[ v_{down,A} > v_{down,B} \]
\[ v_{total,A} > v_{total,B} \]
THE PROTUBERANCES INCREASE THE LENGTH AND IN TURN THE TOTAL STEP ENERGY. SMOOTHING BASED ON THERMODYNAMIC THOMSON-GIBBS EFFECT TAKES PLACE:

\[ n_{se}(\rho) = n_{se} \exp \left( \frac{\kappa a^2 \gamma}{kT} \right) \]

\( \gamma \) - curvature of the bump
EHRLICH - SCHWOEBEL EFFECT ON 2D NUCLEATION

1. SECOND LAYER NUCLEATION

STM micrograph of Pt(111) surface (Krug, Politi, Michely 2000)

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CRITICAL ISLAND SIZE FOR 2nd LAYER NUCLEATION

\[ \tilde{J}_0 = J_0 l^2 \]

\( l \) - critical island size for second layer nucleation

\[ T = \frac{l}{v} \approx \frac{1}{\tilde{J}_0} = \frac{1}{J_0 l^2} \rightarrow l \approx \left( \frac{v}{J_0} \right)^{1/3} \]

\( T \) - time elapsed from nucleation of the 1st island to the nucleation event of the second island

\[ \frac{\tilde{J}_0}{v} = 1 \]

Condition for the critical size \( l \).

In integral form:

\[ \tilde{J}_0(\rho) = 2\pi \int_0^\rho J_0(r) r dr \]

\[ \frac{\int \tilde{J}_0(\rho)}{v(\rho)} d\rho = 1 \]

\[ v(\rho) = \frac{d\rho}{dt} = \frac{R}{2\pi\rho N_s N_0} \]

\[ J_0 = \alpha * D_s \frac{n_s^{i*+1}}{N_0^{i*-1}} \exp \left( \frac{E^*}{kT} \right) \]
The adatom concentration profile depends on the ES barrier:

**Diffusion problem:**

\[
\frac{d^2 n_s}{dr^2} + \frac{1}{r} \frac{dn_s}{dr} + \frac{R}{D_s} = 0
\]

\[n_s = A - \frac{R}{4D_s} r^2\]

**Boundary condition:**

\[j = j_+ - j_- = -D_s \left( \frac{dn_s}{dr} \right)_{r=\rho}\]

\[j_+ = a v n_{st} \exp\left(-\frac{E_{sd} + E_{ES}}{kT}\right)\]

\[j_- = a v n_k \exp\left(-\frac{\Delta W + E_{sd} + E_{ES}}{kT}\right)\]

\[j = a v (n_{st} - n_{se}) \exp\left(-\frac{E_{sd}}{kT}\right) \frac{1}{S}\]

\[n_{se} = n_k \exp\left(-\frac{\Delta W}{kT}\right)\]

\[S = \exp\left(-\frac{E_{ES}}{kT}\right)\]
\[ n_s = n_{se} + \frac{R}{4D_s} (\rho^2 + 2a\rho S - r^2) \]

2aS $\ll \rho$ - negligible ES barrier

\[ n_s = n_{se} + \frac{R}{4D_s} (\rho^2 - r^2) - \text{dome profile} \]

2aS $\gg \rho$ - infinitely high ES barrier

\[ n_s \approx \frac{R}{2D_s} a\rho S - \text{no dependence on } r \]

\[ \tilde{J}_0 = A[(\rho^2 + 2a\rho S)^{i^*+2} - (2a\rho S)^{i^*+2}] \]

\[ A = \frac{\pi\alpha^*}{(i^*+2)} D_s N_0^2 \exp\left(\frac{E^*}{kT}\right)\left(\frac{R}{4D_s N_0}\right)^{i^*+1} \]

1. 2aS $\ll \rho$ ($E_{ES} \approx 0$)

\[ \tilde{J}_0 = A\rho^{2(i^*+2)} \rightarrow N_s \propto \left(\frac{D}{F}\right)^{-\chi} \]

\[ \chi = \frac{i^*}{i^*+2} \]

2. 2aS $\gg \rho$ ($E_{ES} > 0$)

\[ (\rho^2 + 2a\rho S)^{i^*+2} \approx (2a\rho S)^{i^*+2} + (i^*+2)\rho^2 (2a\rho S)^{i^*+1} \]

\[ \tilde{J}_0 = B\rho^{i^*+3} \]

\[ B = \pi\alpha^* D_s N_0^2 \exp\left(\frac{E^*}{kT}\right)\left(\frac{RaS}{4D_s N_0}\right)^{i^*+1} \]

\[ N_s \propto \left(\frac{D}{F}\right)^{-\chi} \]

\[ \chi = \frac{2i^*}{i^*+3} \]


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CHECK OF THE THEORY

What is the number of atoms on top of the island at the moment of the 2nd layer nucleation event?

\[ n = 2\pi \int_{0}^{A} n_s (r, \Lambda) rdr \]

\[ n_s = n_{se} + \frac{R}{4D_s} (\rho^2 + 2a\rho S - r^2) \]

\[ n = \frac{\pi F}{8D} N_0^2 A^4 \left( 1 + \frac{4aS}{\Lambda} \right) \]

1. \( E_{ES} = 0 \)
   \[ \Lambda_0 \propto a \left( \frac{D}{F} \right)^{i*/2(i^*+3)} \]

2. \( E_{ES} > 0 \)
   \[ \Lambda_{ES} \propto a \left( \frac{D}{F} \right)^{i*/(i^*+5)} S^{-(i^*+1)/(i^*+5)} \]

\( F = 0.01 \text{ ML min}^{-1}, E_{sd} = 0.4 \text{ eV}, \)
\( E_{ES} = 0.2 \text{ eV}, T = 500K, i^* = 1, E^* = 0, \)

1. \( E_{ES} = 0 \)
   \[ N_s \cong 1 \times 10^{10} \text{ cm}^{-1}, \Lambda_0 \cong 20 \text{ nm} \]

2. \( E_{ES} > 0 \)
   \[ N_s \cong 1 \times 10^{12} \text{ cm}^{-1}, \Lambda_{ES} \cong 6 \text{ nm} \]
\textbf{Cu/Cu(001)} (Gerlach et al. 2001)

\[ \Lambda = 3 \times 10^{-5} \text{ cm}, T = 400 K, \]

\[ F = 0.0075 \text{ ML sec}^{-1}, \]

\[ E_{sd} = 0.4 \text{ eV}, a = 0.255 \text{ nm} \]

\[ N_0 = 1.53 \times 10^{15} \text{ cm}^{-2}. \]

\[ E_{ES} = 0.125 \text{ eV}, \]

\[ \frac{aS}{\Lambda} = 0.03 \ll 1 \]

\[ n = 70 \left( \approx 2.5 \times 10^{10} \text{ cm}^{-2} \right) \]

\textbf{Pt/Pt(111)} (Bott, Hohage, Comsa 1992)

\[ R = 5 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}, E_{sd} = 0.25 \text{ eV}, \]

\[ E_{ES} = 0.12 \div 0.44 \text{ eV}, \]

1. \( T = 425 K, \)

\[ \Theta_c = 0.3, \ N_s = 3.37 \times 10^{10} \text{ cm}^{-2}, \]

\[ \Lambda \approx 1.7 \times 10^{-6} \text{ cm}, \]

2. \( T = 628 K \)

\[ \Theta_c = 0.8, \ N_s = 3.5 \times 10^{9} \text{ cm}^{-2}, \]

\[ \Lambda \approx 8.5 \times 10^{-6} \text{ cm}, \]

\[ \frac{aS}{\Lambda} \gg 1 \]

\[ n \approx 0.01 \]

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THE LONELY ADATOM MODEL
ACCOUNTING FOR THE RANDOM CHARACTER
OF THE PROCESSES INVOLVED
KRUG, POLITI, MICHELI 2000

\[ \Delta t = \frac{1}{\pi \rho^2 R} \] - average time for atom arrival on an island of radius \( \rho \)

\[ \tau = \frac{2 \pi \rho}{\omega} \] - average time an atom resides on the island surface before rolling down and join descending step (time of departure).

\[ \omega = a \nu \exp \left( - \frac{E_{sd} + E_{ES}}{kT} \right) \] - rate of down - step diffusion

\[ \tau_{tr} = \frac{\pi \rho^2}{D_s} \] - time for an atom to visit all sites on the island surface

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\[
\frac{\tau}{\tau_{tr}} \gg 1 \quad \text{is equivalent to} \quad \frac{2aS}{\rho} \gg 1
\]

This means that if \(i^* = 1\) (stable and immobile dimers) and two atoms are simultaneously present on the island surface, their encounter is inevitable. The probability of nucleation, \(P_{\text{nuc}}\), is then equal to the probability \(P_2\), two atoms to be simultaneously present on the island surface.

The necessary and sufficient condition two atoms to meet each other and give rise to a stable cluster is thus \(\tau \gg \tau_{tr}\).

Two atoms will be simultaneously present on the island surface if the time of arrival, \(t_2\), of the second atom is shorter than the time of departure, \(t_1\), of the first atom. Assuming \(t_1\) and \(t_2\) are randomly distributed around the average values \(\tau\) and \(\Delta t\)

\[
P_{\text{nuc}} = \frac{1}{\tau \Delta t} \int_0^\infty dt_1 \exp\left(-\frac{t_1}{\tau}\right) \int_0^{t_1} dt_2 \exp\left(-\frac{t_2}{\Delta t}\right)
\]

\[
P_{\text{nuc}} = \frac{\tau}{\tau + \Delta t}
\]

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LIMITING CASES:

1. $\tau \gg \Delta t \rightarrow p_{nuc} = 1$
   The time of departure of the 1st atom is always much longer than the time of arrival of the 2nd atom. The ES barrier is effectively infinite.

2. $\tau << \Delta t \rightarrow p_{nuc} = \frac{\tau}{\Delta t} << 1$
   The time of departure of the atoms is shorter than the time of arrival. Most of the time the island is empty. Sometimes it is visited by an atom and very rarely due to a fluctuation by a second atom. In average this gives a constant number much less than unity.

$$\tilde{J}_0(\text{random}) = \pi \rho^2 R p_{nuc} \propto \frac{a \rho^5 R^2 S}{D_s}$$

The mean field approximation

$$\tilde{J}_0 = B \rho^{i^*+3}, \quad B = \pi \alpha * D_s N_0^2 \exp \left( \frac{E^*}{kT} \right) \left( \frac{RaS}{4D_s N_0} \right)^{i^*+1} \text{ with } i^* = 1 \text{ gives}$$

$$\tilde{J}_0(\text{mean field}) \propto \frac{a^2 \rho^4 R^2 S^2}{D_s}$$

$$\frac{\tilde{J}_0(\text{mean field})}{\tilde{J}_0(\text{random})} = \frac{aS}{\rho} \gg 1$$

The reason for this discrepancy is that in the mean field approach there is always an atom on top of the island although it is smaller than unity. The constant number assumes an infinitively high ES barrier.

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2. STEP KINETICS

**Diffusion problem:**
\[
\frac{d^2 n_s}{dr^2} + \frac{1}{r} \frac{dn_s}{dr} + \frac{R}{D_s} = 0
\]

**Boundary conditions:**
\[
j_i = \pm D_s \left( \frac{dn_s}{dr} \right)_{r=\rho_i} \quad (i = 1, 2)
\]

\[
\frac{d\Theta_1}{d\tau} = 1 - F(\Theta_1, \Theta_2)
\]
\[
\frac{d\Theta_n}{d\tau} = F(\Theta_{n-1}, \Theta_n) - F(\Theta_{n}, \Theta_{n+1})
\]
\[
\frac{d\Theta_N}{d\tau} = F(\Theta_{N-1}, \Theta_N)
\]

\[
F(\Theta_n, \Theta_{n+1}) = \frac{\Theta_n - \Theta_{n+1} + qS\sqrt{\Theta_n}}{\ln\left(\frac{\Theta_n}{\Theta_{n+1}}\right) + \frac{qS}{\sqrt{\Theta_n}}}
\]
\[ F(\rho_n, \rho_{n+1}) = \pi N_s \left( \frac{\rho_n^2 - \rho_{n+1}^2}{\ln \left( \frac{\rho_n^2}{\rho_{n+1}^2} \right)} + \frac{aS}{\rho_n} \right) \]

1. \( \frac{aS}{\rho_n} \ll 1 \rightarrow F(\Theta_n, \Theta_{n+1}) = \frac{\Theta_n - \Theta_{n+1}}{\ln \left( \frac{\Theta_n}{\Theta_{n+1}} \right)} \).

2. \( \frac{aS}{\rho_n} \gg 1 \rightarrow F(\Theta_n, \Theta_{n+1}) = \Theta_n \)

\[
\frac{d\Theta_1}{d\tau} = 1 - \Theta_1
\]

\[
\frac{d\Theta_n}{d\tau} = \Theta_{n-1} - \Theta_n
\]

\[
\frac{d\Theta_N}{d\tau} = \Theta_{N-1}
\]

Analytical solution \((\tau = 0, \Theta_n = 0)\):

\[
\Theta_1 = 1 - e^{-\tau}
\]

\[
\Theta_2 = 1 - (1 + \tau)e^{-\tau}
\]

\[
\Theta_3 = 1 - (1 + \tau + \frac{1}{2} \tau^2)e^{-\tau}
\]

\[
\Theta_3 = 1 - (1 + \tau + \frac{1}{2} \tau^2 + \frac{1}{6} \tau^3)e^{-\tau}
\]
EPITAXIAL GROWTH

επι (epi) - ON
ταξις (taxis) - IN ORDER
Royer 1928

Cu/Ag(111)

\[ a_{Cu} = 0.255 \text{ nm} \]
\[ a_{Ag} = 0.289 \text{ nm} \]

\[ f = \frac{a_{Cu} - a_{Ag}}{a_{Ag}} \]

\[ f = -11.8\% \]
THERMODYNAMIC DEFINITIONS

\( (T = 0) \) \( \mu_\infty = -\varphi_{1/2} \)
\( \mu'_\infty = -\varphi'_{1/2} \)
\( \mu'_\infty = \mu_\infty + (\psi - \psi') \)
\( \psi = \psi' \to \text{crystal growth} \)
\( \psi \neq \psi' \to \text{epitaxial growth} \)
\( \varepsilon_m = -\text{misfit energy per atom} \)

1. HETEROEPITAXY
\( \psi - \psi' \gg \varepsilon_m \)
\( \text{In}_{x}\text{Ga}_{1-x}\text{As}/\text{InP}(001) \)
\( x = 0.43, f = 0, \varepsilon_m = 0 \)

2. HOMOEPITAXY
\( \psi - \psi' \ll \varepsilon_m \)
\( \text{Si(B)/Si(P)}, \psi \cong \psi' \)

\( \varphi'_{1/2} = \varphi_{1/2} - (\psi - \psi') \)
\( \varphi'_{1/2} - \text{separation work from a kink position} \)
on a foreign substrate
\( \varphi_{1/2} - \text{separation work from a kink position} \)
on the same crystal
\( \psi - \text{work to separate two like atoms} \)
\( \psi' - \text{work to separate two unlike atoms} \)

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MAIN PROBLEMS IN EPITAXY

1. STRUCTURE OF EPITAXIAL INTERFACE
   (i) misfit dislocations (type, density, origin, energy)
   (ii) residual strain
   (iii) distribution of strain in small coherent crystals
   (iv) relaxation of misfit strain
   (v) effect of alloying

2. MECHANISM OF GROWTH - 2D OR 3D
   (i) dependence on interatomic forces, temperature, misfit, crystallographic orientation, surfactants
   (ii) instabilities of growth due to the misfit strain
   (iii) mechanism of 2D - 3D transformation
STRUCTURE AND ENERGY OF EPITAXIAL INTERFACE
MODELS OF EPITAXIAL INTERFACE

1. COINCIDENCE LATTICE MODEL

(i) both lattices are assumed rigid
(ii) interatomic forces are non-directional

\[ \text{substrate atoms} \quad \text{deposit atoms} \]

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2. BALL-AND-WIRE MODEL
Hornstra (1958) dislocations in diamond
Holt (1966) dislocations in heterojunctions
3. VOLTERRA DISLOCATION MODEL
BROOKS 1952, MATTHEWS 1972

\[ E_{strain} = \frac{Gb^2}{4\pi(1-\nu)} \ln \left( \frac{R}{r_0} \right) \]

- \( G \) – shear modulus
- \( b \) – Burger's vector
- \( \nu \) – Poisson ratio

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4. DISLOCATION MODEL OF FRANK AND VAN DER MERWE

(i) rigid substrate
(ii) elastically strained deposit
MODES OF MISFIT ACCOMMODATION
1. Misfit dislocations
2. Pseudomorphism
3. Roughening (Asaro-Tiller-Grinfeld instability)
4. 3D islanding
5. Formation of cracks
6. Alloying

\[
\begin{align*}
AB & \ll^{a} AA \ (BB) \\
BB & \ll^{c} AA \\
\text{ma} & \approx nb \ (m = n \pm 1) \\
AA & \approx BB \approx AB
\end{align*}
\]