Lecture 1
Modeling and simulation for the growth of thin films

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Outline

• Epitaxial Growth
  – molecular beam epitaxy (MBE)
  – Step edges and islands
• Solid-on-Solid using kinetic Monte Carlo
  – Atomistic, stochastic
• Island dynamics model
  – Continuum in lateral directions/atomistic in growth direction
  – Level set implementation
  – Kinetic step edge model
• Conclusions
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• **Conclusions**
Molecular Beam Epitaxy (MBE) Growth and Analysis Facility

MBE Chamber

STM Chamber

Effusion Cells
STM Image of InAs

HRL whole-wafer STM surface quenched from 450° C, “low As”

20nmx20nm

250nmx250nm
1.8 V, Filled States

Barvosa-Carter, Owen, Zinck (HRL Labs)

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AlSb Growth by MBE

Barvosa-Carter and Whitman, NRL
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Basic Processes in Epitaxial Growth

(a) deposition
(b) diffusion
(c) nucleation
(d) attachment
(e) detachment

(f) edge diffusion
(g) diffusion down step
(h) nucleation on top of islands
(i) dimer diffusion
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Solid-on-Solid Model

• **Interacting particle system**
  – Stack of particles above each lattice point

• **Particles hop to neighboring points**
  – random hopping times
  – Arrhenius hopping rate $D = D_0 \exp(-E/T)$,
  – $E =$ energy barrier, depends on nearest neighbors

• **Deposition of new particles**
  – random position
  – arrival frequency from deposition rate

• **Simulation using kinetic Monte Carlo method**
  – Gilmer & Weeks (1979), Smilauer & Vvedensky, …
Pair–bond solid–on–solid model

\[ \psi = \psi_0 e^{-\beta E_N} \]

\[ \psi = \psi_0 e^{\beta E_s} \]

\[ \psi = \psi_0 e^{-2\beta E_N} \]

\( E_s \): Substrate Bond Energy

\( E_N \): Nearest Neighbor Bond Energy
Kinetic Monte Carlo

• Random hopping from site $A \rightarrow B$

• hopping rate $D_0 \exp(-E/T)$,
  - $E = E_b =$ energy barrier between sites
  - not $\delta E =$ energy difference between sites

• Transition state theory
SOS Simulation for coverage=0.2

Gyure and Ross, HRL

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SOS Simulation for coverage=10.2
SOS Simulation for coverage=30.2

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Molecular Beam Epitaxy (MBE)
Growth and Analysis Facility

MBE Chamber

RHEED

Effusion Cells

STM Chamber

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Validation of SOS Model: Comparison of Experiment and KMC Simulation
(Vvedensky & Smilauer)

Fig. 4. Island size distributions for Fe/Fe(001) from Ref. [20] (large circles) compared to pair-bond model simulation results: (a) experiment at $T = 20^\circ$C, simulation for $0.10 \leq \theta \leq 0.25$ with $E_n = 1.0$ eV and $F = 0.1$ s$^{-1}$ (open symbols) and $E_n = 0.3$ eV and $F = 0.5$ s$^{-1}$ (closed symbols); (b) experiment at $T = 133^\circ$C, simulation for $0.10 \leq \theta \leq 0.25$ with $E_n = 0.7$ eV and $F = 0.001$ s$^{-1}$ (open symbols) and $E_n = 0.3$ eV and $F = 0.2$ s$^{-1}$ (closed symbols); (c) experiment at $T = 250^\circ$C, simulation for $0.12 \leq \theta \leq 0.25$ with $E_n = 0.6$ eV and $F = 0.001$ s$^{-1}$ (open symbols) and $E_n = 0.3$ eV and $F = 0.03$ s$^{-1}$ (closed symbols); (d) experiment at $T = 350^\circ$C, simulation for $0.12 \leq \theta \leq 0.25$ with $E_n = 0.3$ eV and $F = 0.001$ s$^{-1}$.

Step Edge Density (RHEED)
Difficulties with SOS/KMC

- Difficult to analyze
- Computationally slow
  - adatom hopping rate must be resolved
  - difficult to include additional physics, e.g. strain
- Rates are empirical
  - idealized geometry of cubic SOS
  - cf. “high resolution” KMC
High Resolution KMC Simulations

- InAs
- zinc-blende lattice, dimers
- rates from ab initio computations
- computationally intensive
  - many processes
- describes dynamical info (cf. STM)
- similar work
  - Vvedensky (Imperial)
  - Kratzer (FHI)

High resolution KMC (left); STM images (right)
Gyure, Barvosa-Carter (HRL), Grosse (UCLA,HRL)
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Island Dynamics

\[ \frac{dN}{dt} \]
Island Dynamics

- **BCF Theory**: Burton, Cabrera, Frank (1951)
- **Epitaxial surface**
  - adatom density $\rho(x,t)$
  - Step edges = union of curves $\Gamma(t)$
  - continuum in lateral direction, atomistic in growth direction
- **Evolution of $\rho$ and $\Gamma$**
  - Adatom diffusion equation with equilibrium BC
    \[ \rho_t = D \Delta \rho + F \]
    \[ \rho = \rho_{eq} \quad \text{on} \quad \Gamma(t) \]
  - $F$= deposition rate, $D$ = diffusion coefficient
  - Step edge velocity: $\Gamma(t)$ moves at normal velocity
    \[ v = D \left[ \frac{\partial \rho}{\partial n} \right] \]
Additions to BCF Theory

- Nucleation and breakup of islands
- Step stiffness/line tension
- Strain effects (Lecture 2)
- Numerical implementation: Level set method
Nucleation (and Breakup)

• Islands nucleate due to collisions between adatoms
  – Rate = $D \sigma_1 \rho^2$
  – $\sigma_1$ = capture number for nucleation
    • accounts for correlation between random walkers: they have not collided earlier

• Modification in $\rho$ eqtn
  – Nucleation is a loss term
    $$\rho_t = D\Delta \rho + F - \frac{dN}{dt}$$
    $$\frac{dN}{dt} = \int D \sigma_1 \rho^2 \, dx$$

• Choice of nucleation time and position
  – Deterministic time, stochastic position
  – When $N$ crosses an integer, nucleate a new island
    • $N(t) \approx \#$ islands at time $t$
  – Choose position at random with probability density proportional to
    $$D \sigma_1 \rho^2$$
  – Alternatives to this choice of position were not successful
    – Ratsch et al. (2000)

• Similar method for adatom detachment and breakup of small islands
Nucleation:
Deterministic Time, Random Position

$$\frac{dN}{dt} = D \langle \rho(x,t)^2 \rangle$$

Random Seeding
independent of $\rho$

Probabilistic Seeding
weight by local $\rho^2$

Deterministic Seeding
seed at maximum $\rho^2$
Effect of Seeding Style on Scaled Island Size Distribution

Random Seeding

Probabilistic Seeding

Deterministic Seeding

Line Tension/Step Stiffness

• Gibbs-Thomson terms: boundary condition for \( \rho \) and island velocity \( v \)

\[
D \frac{\partial \rho}{\partial n} = D(\rho - \rho_*) - \tilde{\mu} \kappa
\]

\[
v = D \left[ \frac{\partial \rho}{\partial n} \right] - \tilde{\mu} \kappa_{ss}
\]

– Line tension \( \gamma \) and step stiffness \( \tilde{\gamma} \) satisfy

\[
\tilde{\gamma} = \left( \frac{T}{D \rho_*} \right) \tilde{\mu} = \text{free energy per unit length}
\]

\[
\tilde{\gamma} = \gamma + \gamma_{ss}
\]

• Asymptotic analysis of detailed step edge model for \( |\kappa| < O\left( P_{\text{edge}} \right) \ll 1 \)

– First derivation of Gibbs-Thomson from kinetics rather than energetics
   - Previous derivations use equilibrium or thermodynamic driving forces
– \( \rho_* \) from kinetic steady state RC & Li (2003)
– Anisotropy of \( \tilde{\gamma} \) RC & Margetis (2007)
Anisotropy of step stiffness \( \tilde{\gamma} \)

\[
\tilde{\gamma} = \begin{cases} 
  c \theta^{-1} & \text{for } P_E^{1/2} \ll \theta \ll 1 \\
  O(1) & \text{for } 0 < \theta \ll P_E^{1/2}
\end{cases}
\]

\[c = \bar{c} \ (f_+ + f_-) \theta\]

- \( \theta = \) angle of step edge
- \( f_+, f_- \) are flux from upper, lower terrace
- \( \theta^{-1} \) similar to results for Ising model, near-equilibrium by Einstein and Stasevich (2005)
Level Set Method

- Level set equation for description and motion of \( \mathcal{I} \)
  \[
  \mathcal{I}_n(t) = \text{boundary for islands of height } n = \{ x : \varphi(x,t) = n \}
  \]
  \[
  \varphi_t + v \cdot |\text{grad } \varphi| = 0
  \]
  \[
  v = \text{normal velocity of } \mathcal{I}
  \]
  - Nucleation of new islands performed by “manual” raising of level set function. Requires minimal size (4 atoms) for new islands

- Implementation
  - REC, Gyure, Merriman, Ratsch, Osher, Zinck (1999)
  - Chopp (2000)
  - Smereka (2000)

- Choice of grid
  - Numerical grid needed for diffusion and LS equations
  - Physical (atomistic) grid needed for nucleation and breakup
  - We use a single atomistic grid, which we consider to be a numerical grid when needed
The Levelset Method

Level Set Function $\phi$

Surface Morphology

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Simulated Growth by the Island Dynamics/Level Set Method
Multilayer Comparison Levelset - KMC

Island Densities

Surface Roughness

We choose edge diffusion in KMC as $D_{\text{edge}}/D = 0.01$.

LS = level set implementation of island dynamics
Island size distributions

Experimental Data for Fe/Fe(001), Stroscio and Pierce, Phys. Rev. B 49 (1994)

D = detachment rate

Stochastic nucleation and breakup of islands

Petersen, Ratsch, REC, Zangwill (2001)
Computational Speed: Level Set vs. KMC

• LS ≈ KMC for nucleation dominated growth
  – Diffusion computation on atomistic lattice is slow
• LS >> KMC for attachment/detachment dominated
  – Frequent attachment/detachment events represented by single effective detachment
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Kinetic Theory for Step Edge Dynamics

- Theory for structure and evolution of a step edge
  - Mean-field assumption for edge atoms and kinks
  - Dynamics of corners are neglected
- Equilibrium solution (BCF)
  - Gibbs distribution $e^{-E/kT}$ for kinks and edge atoms
  - Detailed balance at edge between each process and the reverse process
- Kinetic steady state
  - Based on balance between unrelated processes
- Applications of detailed model
  - Estimate of roughness of step edge, which contributes to detachment rate
  - Starting point for kinetic derivation of Gibbs-Thomson
- References
  - REC, E, Gyure, Merriman & Ratsch (1999)
  - Related models by Evans & collaborators
Step Edge Model

- adatom density $\rho$
- edge atom density $\phi$
- kink density (left, right) $k$
- terraces (upper and lower)

Evolution equations for $\phi$, $\rho$, $k$
\[
\begin{align*}
\partial_t \rho - D_T \Delta \rho &= F \quad \text{on terrace} \\
\partial_t \phi - D_E \partial_s^2 \phi &= f_+ + f_- - f_0 \quad \text{on edge} \\
\partial_t k - \partial_s (w (k_r - k_\ell)) &= 2 (g - h) \quad \text{on edge}
\end{align*}
\]

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Equilibrium from Detailed Balance

edge atom ↔ terrace adatom:
\[ D_E \varphi = D_T \rho \]

kink ↔ edge atom:
\[ D_K k = D_E k \varphi \]

kink pair ("island")
↔ edge atom pair:
\[ D_K (1/4) k^2 = D_E \varphi^2 \]

kink pair ("hole") + edge atom
↔ straight step:
\[ D_S = D_E (1/4) k^2 \varphi \]
Equilibrium from Detailed Balance

edge atom ↔ terrace adatom:
\[ D_E \varphi = D_T \rho \]

kink ↔ edge atom:
\[ D_K k = D_E k \varphi \]
kink pair ("island")

↔ edge atom pair:
\[ f = D_K (1/4) k^2 = D_E \varphi^2 \]
kink pair ("hole") + edge atom

↔ straight step:
\[ D_S = D_E (1/4) k^2 \varphi \]

\[ f = \text{net flux to step edge} \]
Equilibrium Solution

\[ \rho = \left( \frac{D_E}{D_T} \right) \varphi \]
\[ \varphi = \frac{k^2}{4} \]
\[ k = 2\sqrt{\frac{D_K}{D_E}} \]

- Solution for \( F=0 \) (no growth)
- Derived from detailed balance
- \( D_T, D_E, D_K \) are diffusion coefficients (hopping rates) on Terrace, Edge, Kink in SOS model

Comparison of results from theory(−) and KMC/SOS (●)

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Kinetic steady state

\[
\rho_{\pm} = \left( \frac{D_E}{D_T} \right) \varphi
\]

\[
\varphi = \frac{k^2}{4}
\]

\[
k = \left( \frac{16}{15} P_{\text{edge}} \right)^{1/3}
\]

• Solution for \(F>0\)
• Derived from kinetic balance, not detailed balance
• \(k > k_{\text{eq}}\)
• \(P_{\text{edge}} = f/D_E\) “edge Peclet #”

Comparison of scaled results from steady state (-), BCF(- - -), and KMC/SOS (● □ △) for \(L=25,50,100\), with \(F=1, D_T=10^{12}\)

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Hybrid and Accelerated Methods: Island Dynamics and KMC

- Schulze (2004)
- DeVita, Sander, Smereka (2006)
- Sun, Engquist, REC, Ratsch (2007)
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Summary

• Island dynamics method for epitaxial growth
  – Coarse-graining of KMC
  – Stochastic nucleation

• Kinetic model for step edge
  – kinetic steady state ≠ BCF equilibrium
  – validated by comparison to SOS/KMC

• Next lectures
  – Inclusion of strain in epitaxial systems
  – Strain leads to geometric structure (e.g. quantum dots) and alloy segregation