Content of this Chapter

- **Fundamentals of Epitaxial Growth**
- **Self-Organized Growth of Semiconductor Quantum Dots**
- **Thin Film Growth on Flat or Vicinal Substrates**
- **Doping Engineering of Semiconductors**

Thin Film Growth on Flat or Vicinal Substrates

- **Kinetic Instabilities**
- **Homoepitaxy vs. Heteroepitaxy**
- **Critical Thicknesses in Heteroepitaxy on Flat Substrates**
- **Step Bunching and Step Suppression on Vicinal Substrates**

Current Understanding of Thin Film Growth

♦ Thin film growth is a nonequilibrium process.

♦ A specific growth mode is an interplay between thermodynamics and growth kinetics.

Thermodynamics (free energy minimization)

↕

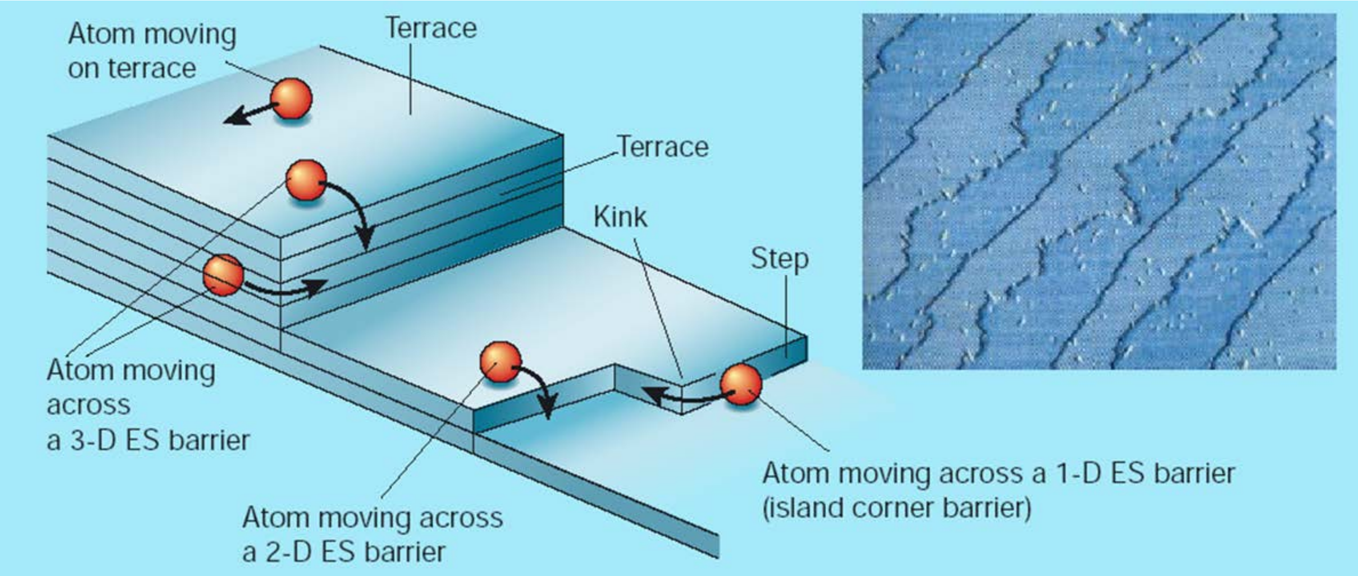
Growth kinetics (various atomic rate processes)

$$r_i = v_0 exp\{-V_i/k_B T\}.$$

Philosophy

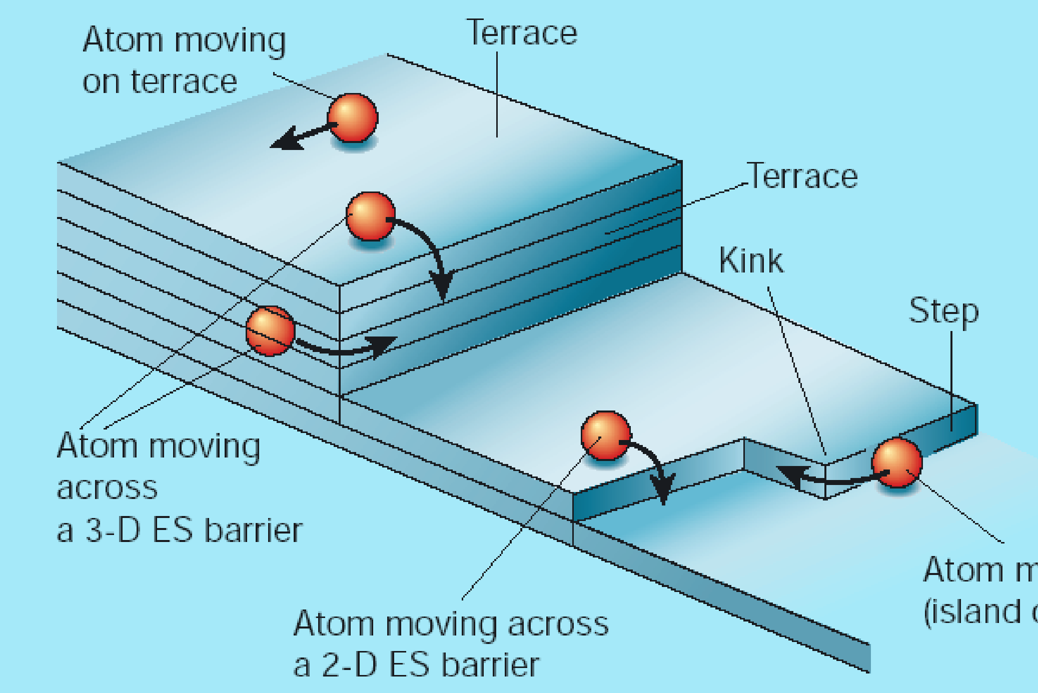
If we can establish EVERY correspondence between

Specific Atomic Rate Process ⟷ **Morphological Evolution**



then we should be able to select a preferred growth mode via precise control of the profile with various rate processes.

Multiscale Description of Crystal Growth: Important Atomic Rate Processes

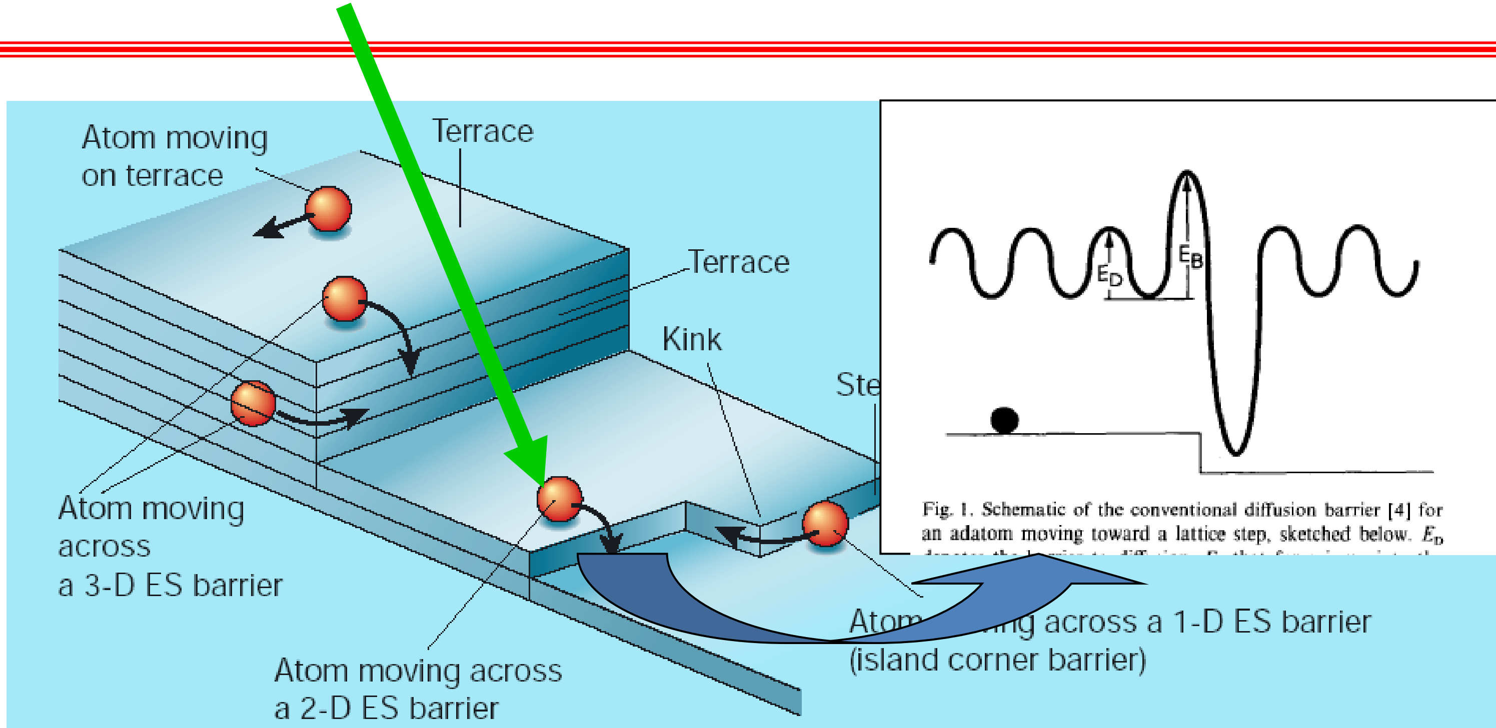


Terrace-Step-Kink (TSK) Model of Surface: Burton, Cabrera, Frank (1951)

STM confirmation: Swartzentruber, *et al*., Phys. Rev. Lett. (1989)

Important Atomic Rate Processes: Lagally & Zhang, Nature (2002)

Ehrlich-Schwoebel Barrier & Villain Instability

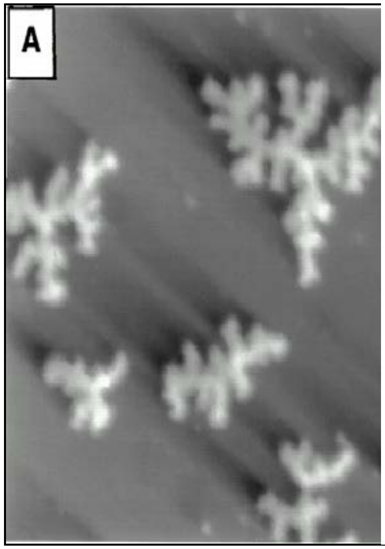


ES Barrier: An adatom descending at a step edge encounters a higher potential energy barrier than that for surface diffusion.

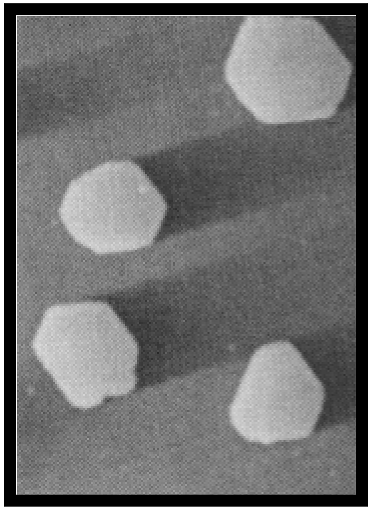
Ehrlich & Hudda (1966); Schwoebel & Shipsey (1966).

Villain Instability: Growth is unstable if there are no adatom descending events. *Villain (1991).*

Island Shape Selection in Submonolayer Epitaxy



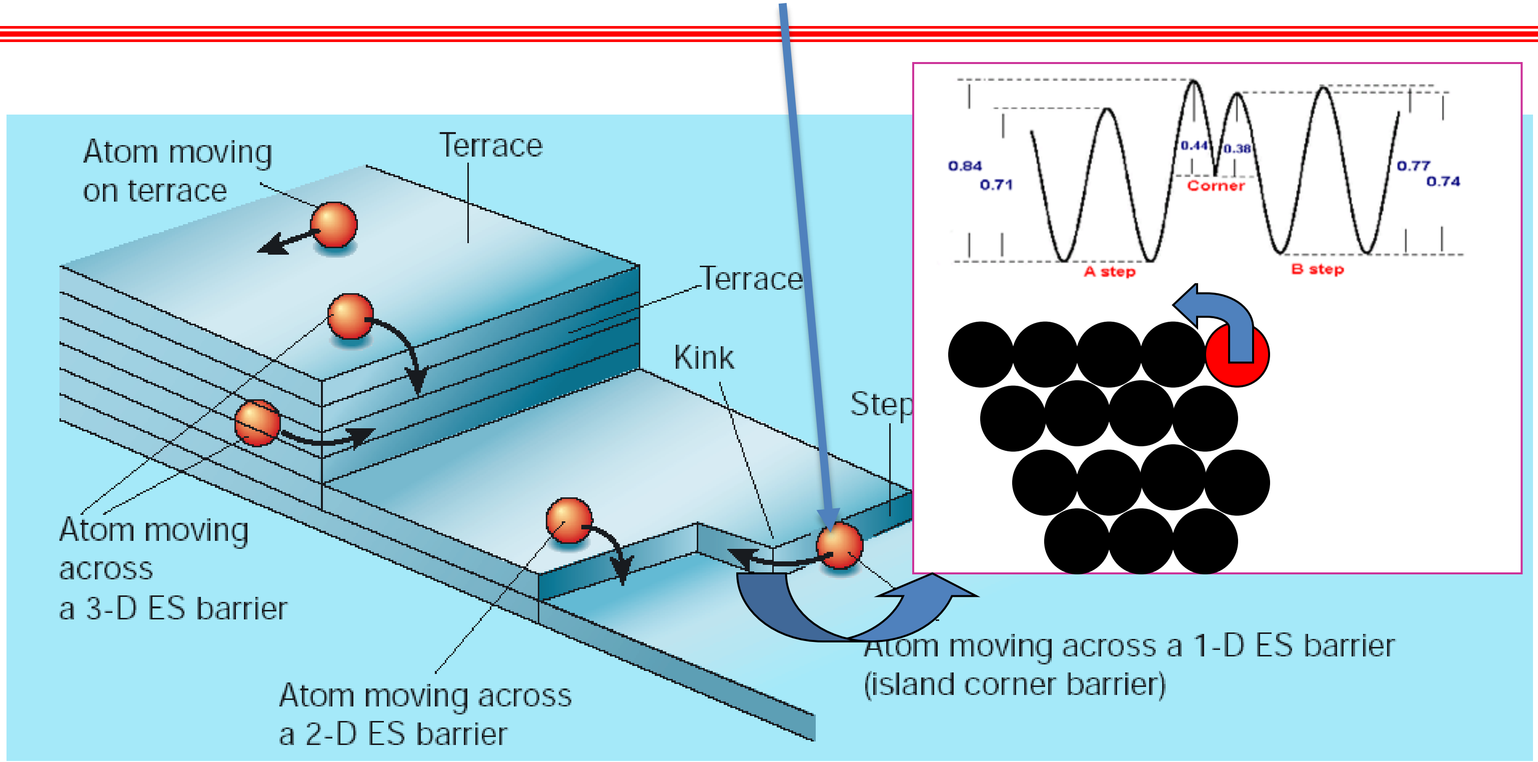
fractal/dendritic
($N \sim R^d$, d~1.7)



compact
($N \sim R^d$, d=2)

Q: What is the rate-limiting process separating the fractal from compact growth regime?

Island-Corner Barrier Effect



Without efficient adatom corner crossing, submonolayer growth will lead to the formation of fractal or dendritic islands.

Z. Y. Zhang and Max Lagally, Science, 276, 377 (1997);
Zhong, Tianjiao, Zhang, Z. Y., Lagally, PRB 63, 113403 (2001).

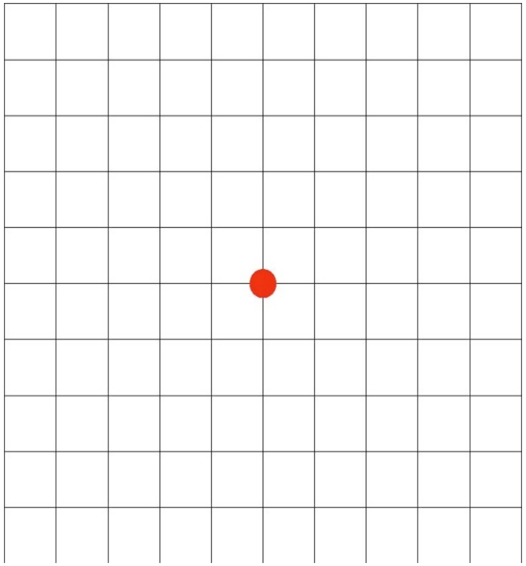
Instabilities in Homoepitaxy vs. Heteroepitaxy

Homoepitaxy: All instabilities in nonequilibrium epitaxial growth are **kinetic** in nature.

Heteroepitaxy: The growth instabilities can be **thermodynamically** driven, or **kinetically** limited, or **BOTH**, making it conceptually more demanding and challenging.

Even kinetically driven, the growth kinetics can be significantly influenced by **the mismatch-induced strain**.

Basic Atoms-to-Continuum Method



$$P(n, t+\tau) = \tfrac{1}{2}P[(n-1)a, t] + \tfrac{1}{2}P[(n+1)a, t]$$

$$P(n, t+\tau) = P(n, t) + \frac{\partial P}{\partial t}\tau + \cdots$$

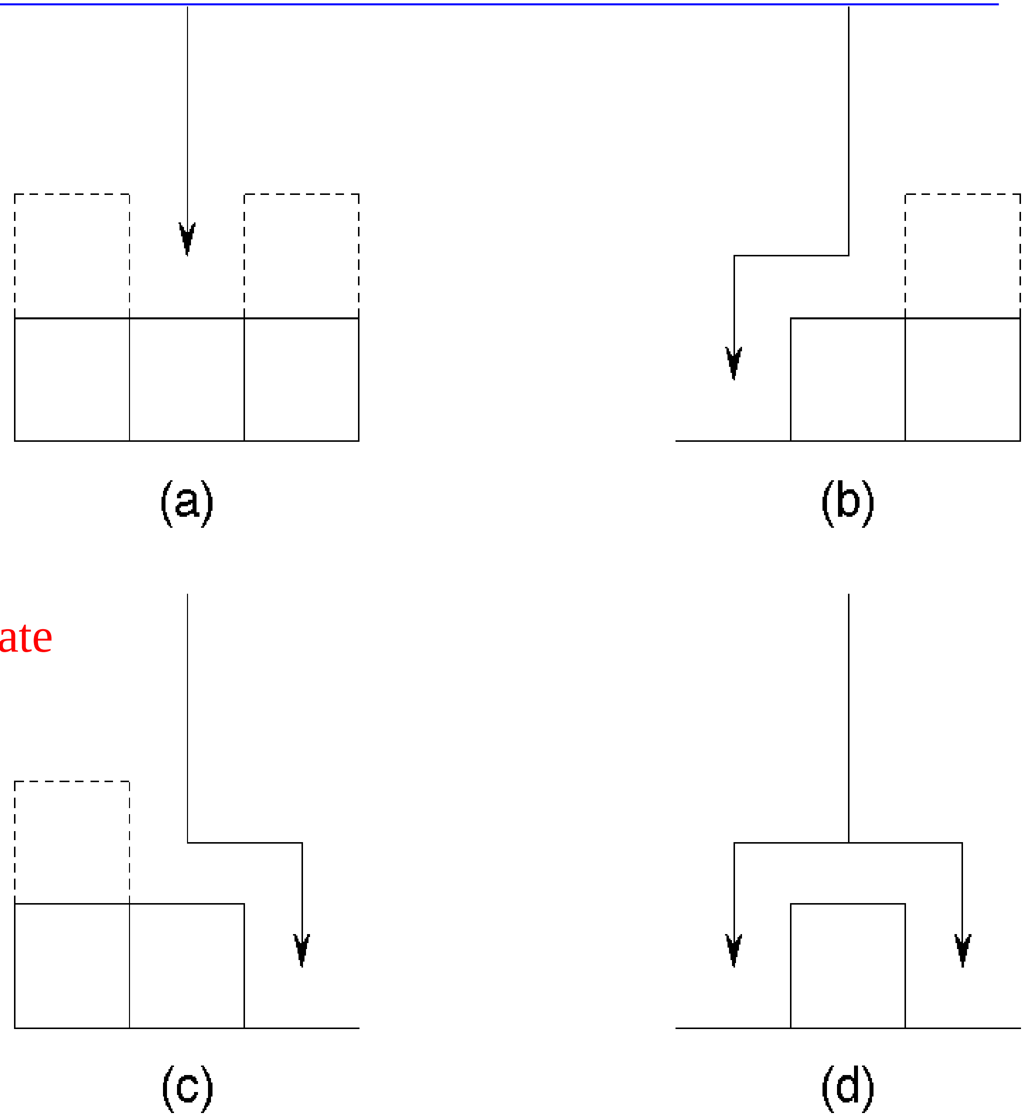
$$P[(n \pm 1)a, t] = P(n, t) \pm \frac{\partial P}{\partial x}a + \frac{1}{2}\frac{\partial^2 P}{\partial x^2}a^2 + \cdots$$

Take $a \to 0$ and $\tau \to 0$ such that a^2/τ is constant:

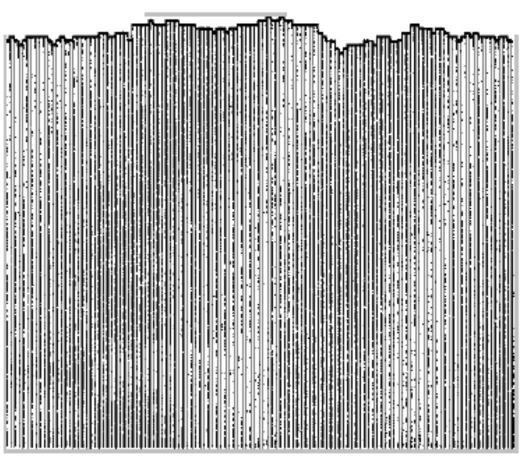
$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \qquad D = \frac{a^2}{2\tau}$$

Edwards–Wilkinson Model

A particle that arrived on top of the column at x sticks at the lowest column among the nearest neighbours, x and $x + 1$ or x-1.



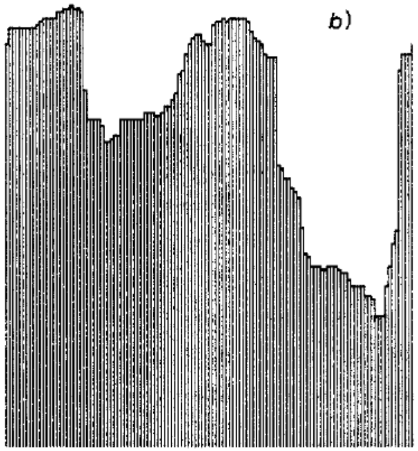
Surface configuration in the steady state

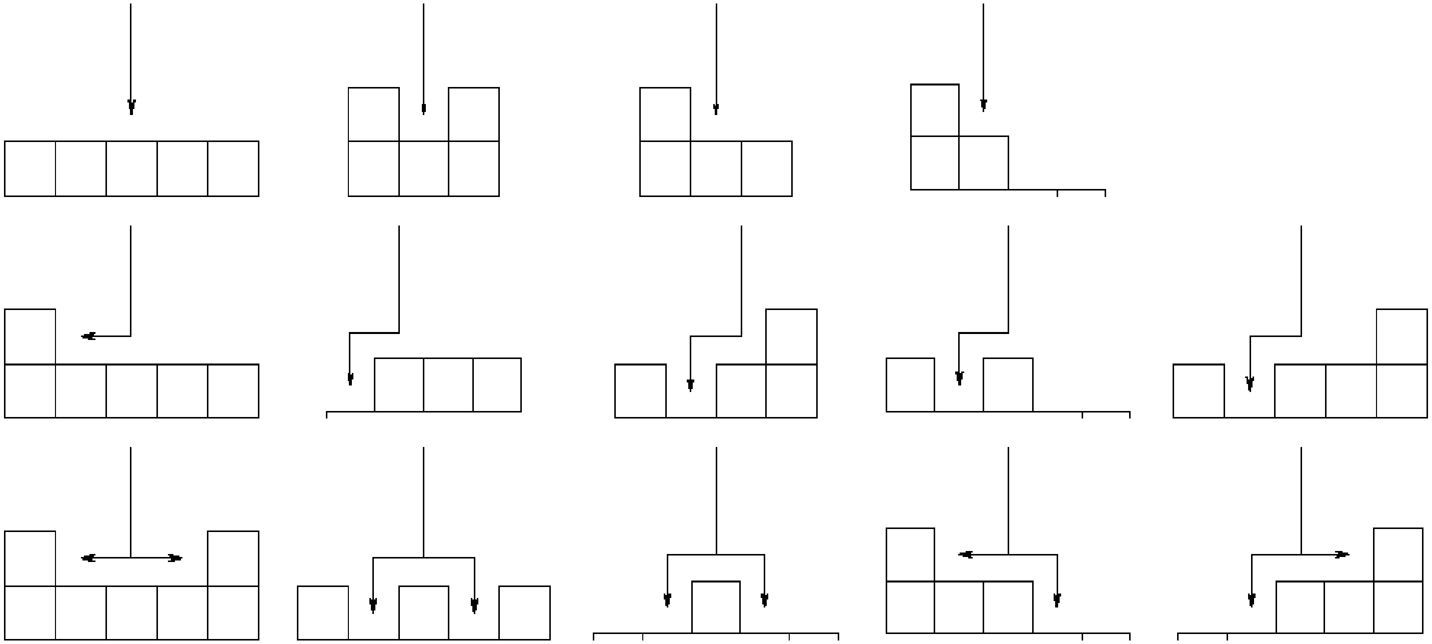


Edwards and Wilkinson, *Proc. Roy. Soc. London Ser. A* **381**, 17 (1982)

The Wolf-Villain Model

Surface configuration in the steady state





A particle that arrived chooses the column on top of which it touches the most occupied sites (*i.e*. the most occupied neighbors).
This is intended to simulate surface diffusion at not too high temperatures where the particles move only a short distance to find a favorable growth site before other particles are deposited on top of them.

Wolf and Villain, *Europhys. Lett.* **13**, 389 (1990)
Clarke and Vvedensky, *Phys. Rev. B* **37**, 6559 (1988)

Main Focus of Those Statistical Modeling

Gives Scaling Properties & Universality (but minimal touch with real systems)

Thin Film Growth on Flat or Vicinal Substrates

Dynamics of Strained Film Growth on Vicinal Substrates

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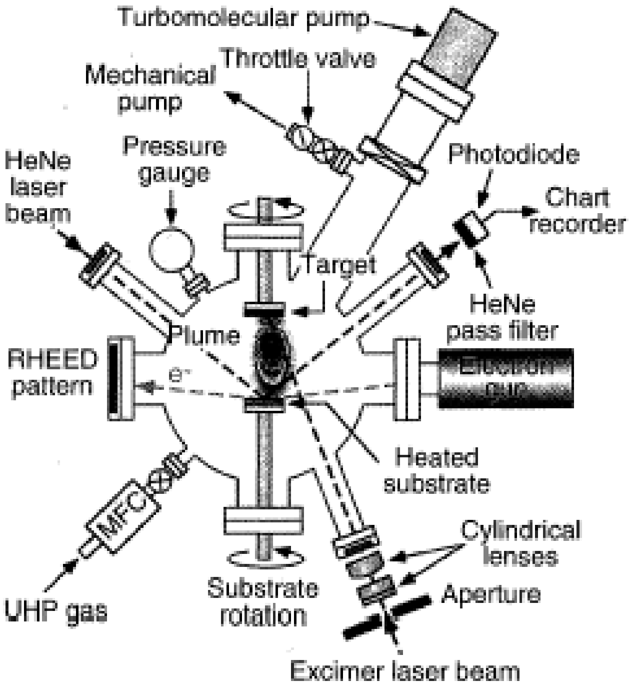
In Collaboration with

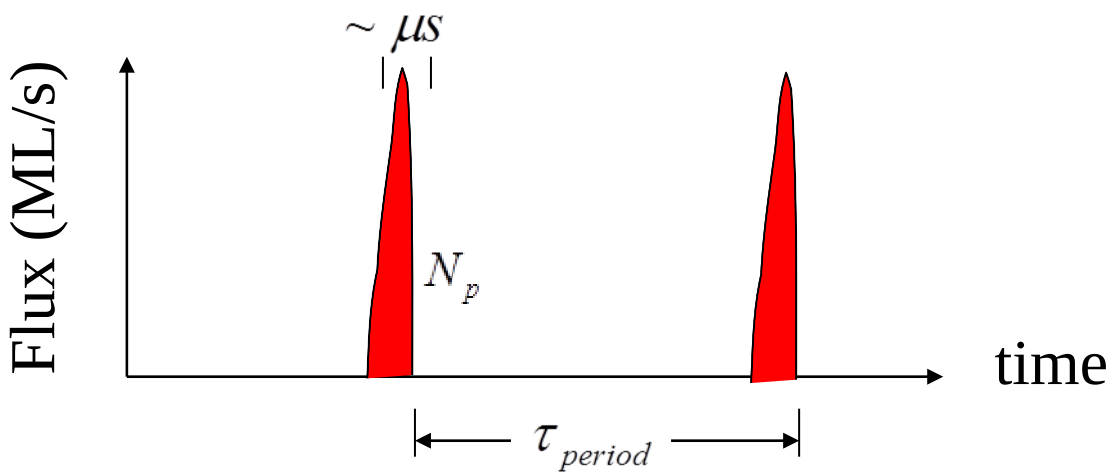
Experiment: Ho Nyung Lee, Hans Christen (*ORNL*)

Theory: Wei Hong, Zhigang Suo (*Harvard*), Zhenyu Zhang (*ORNL,UT*)

Pulse Laser Deposition (PLD)



Lowndes *et al*., Science **273**, 898 (1996)

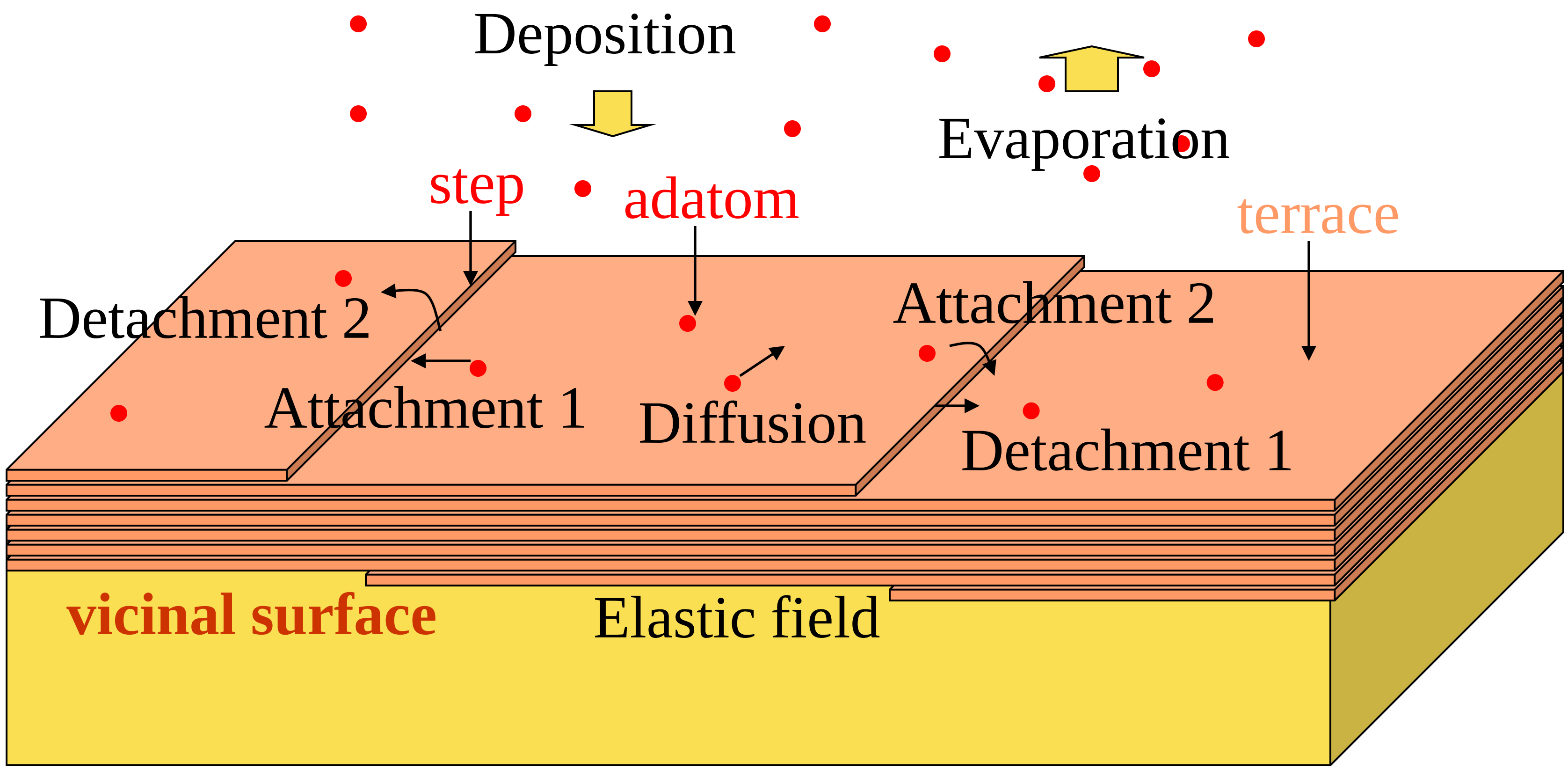


# of monolayers per pulse $N_p = 0.006\,\mathrm{ML}$

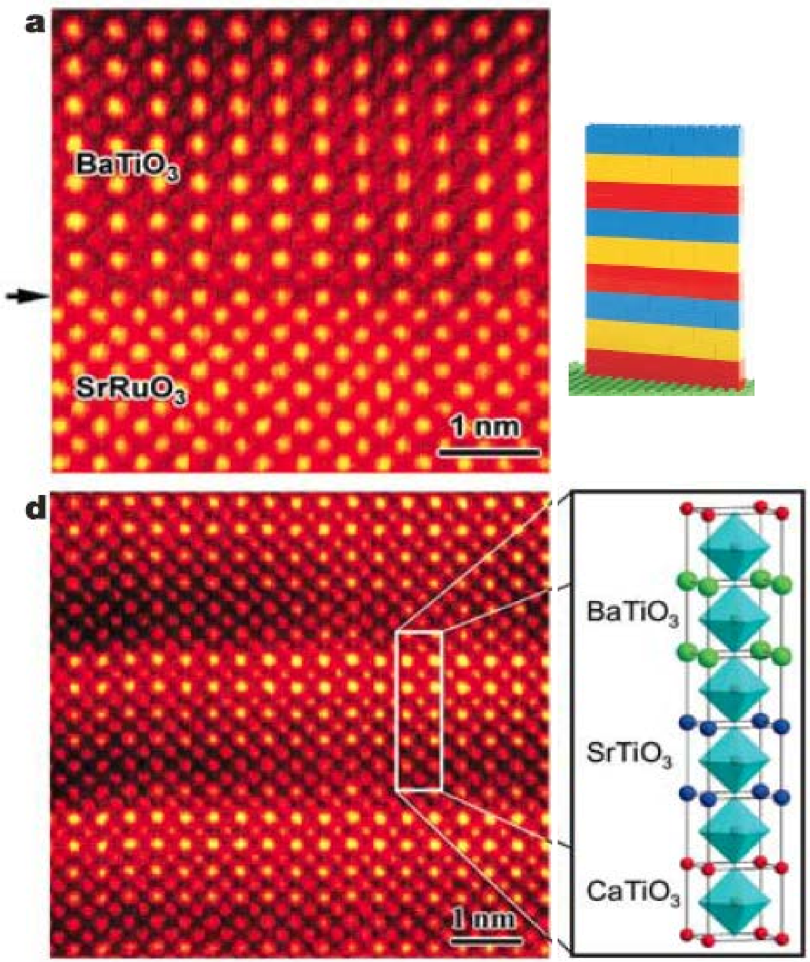
Time between two pulses $\tau_{period} = 0.1s$

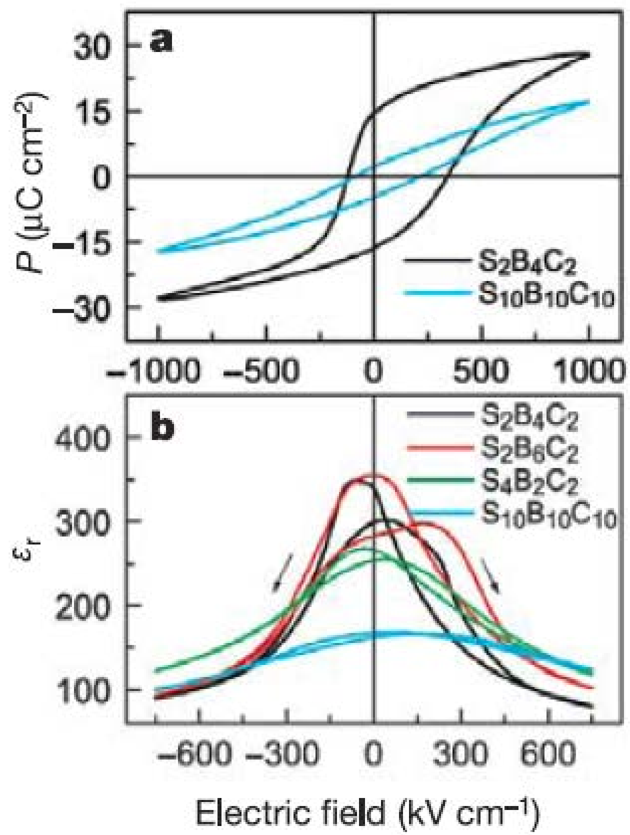
Average flux $F = \dfrac{N_p}{\tau_{period}}$ (ML/s)

Epitaxy on a Vicinal Surface



Superlattice of Ferroelectric Oxides

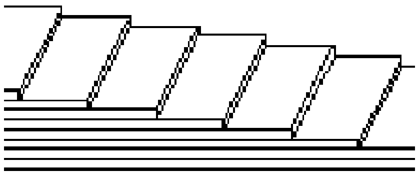


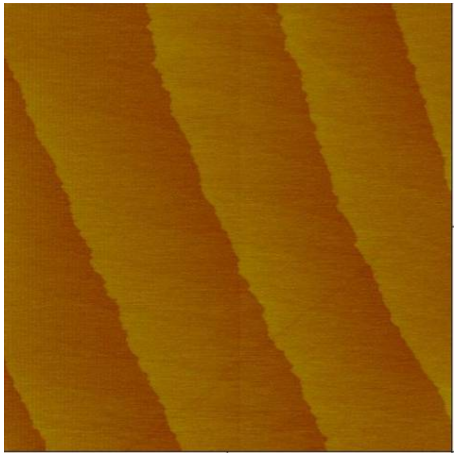


Lee *et al*., Nature **433**, 395 (2005)

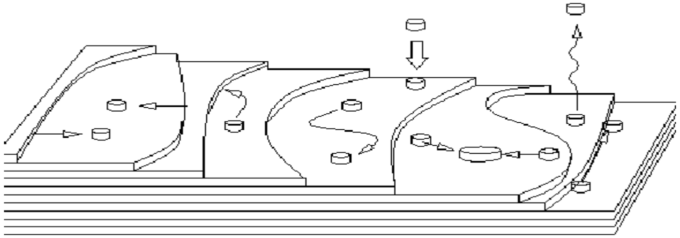
Growth Modes

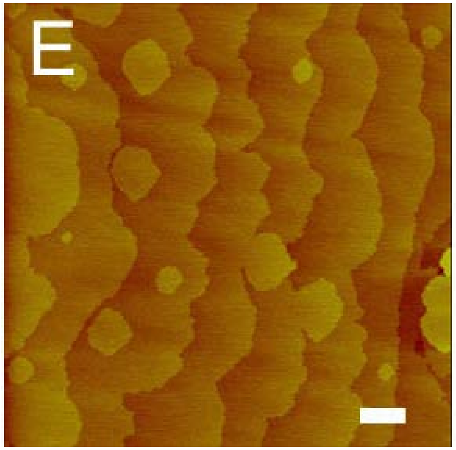
Step Flow



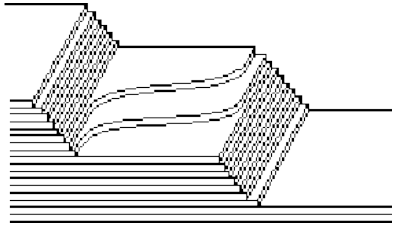


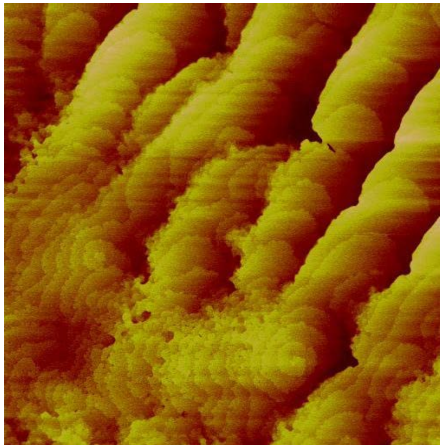
Island Formation





Step Bunching

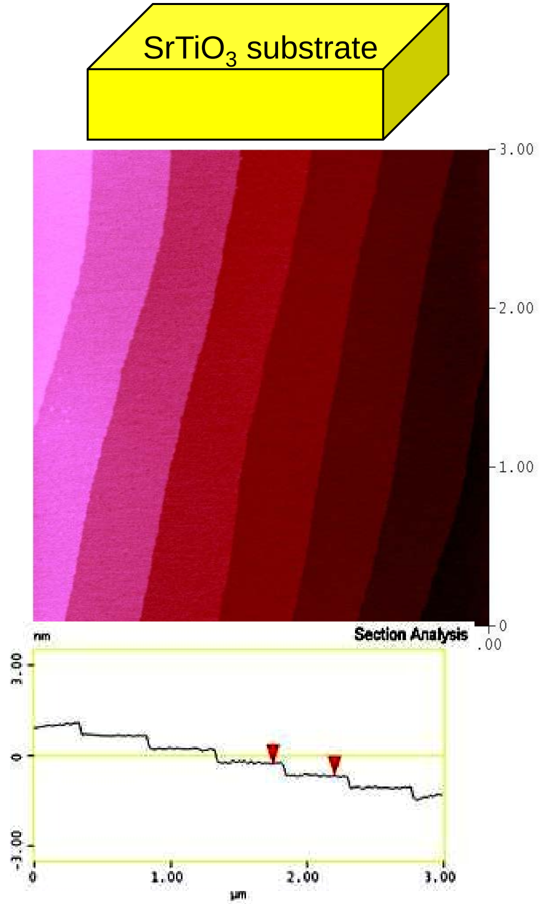


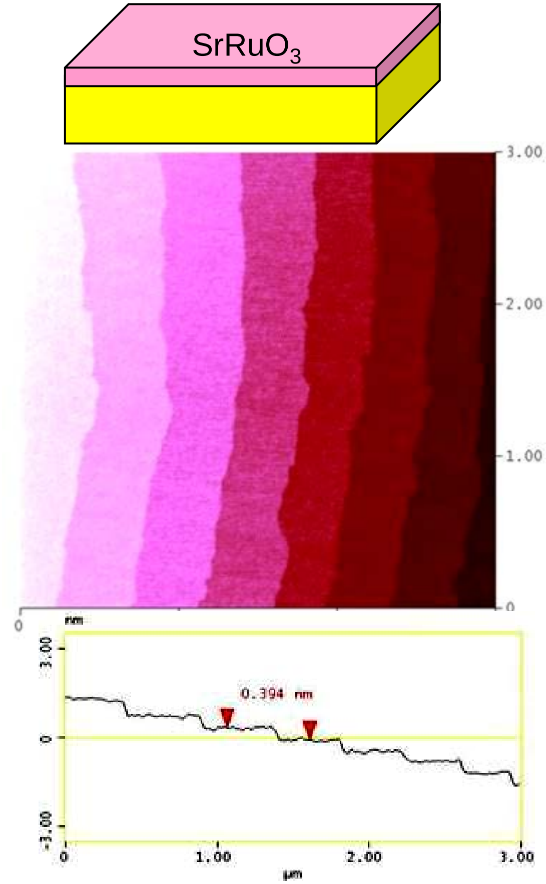


Step flow is preferred **But how to achieve step flow?**

for applications that require defect-free, atomically smooth films.

Experiments: $SrRuO_3$ on $SrTiO_3$ Growth by PLD





$a_{STO} = 0.391nm$

$\varepsilon_m = 0.6\%$ $\quad a_{SRO} = 0.393nm$

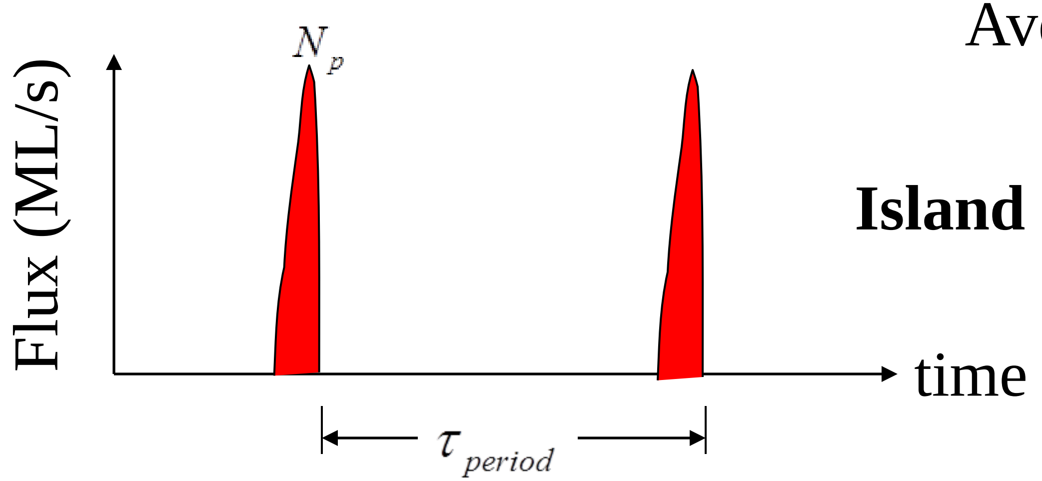
Experiments: H. Lee et al.

X-ray diffraction:

SRO films were fully strained to match the STO substrates.

Island Formation in PLD

- Temperature is high. In each deposition pulse, islands may (or may not) form, but they are unstable.
- Time to evacuate adatoms from a terrace $\tau_{life} = L^2 / 2D$
- Islands will form when $\tau_{life} > \tau_{period}$



Average flux $F = \dfrac{N_p}{\tau_{period}}$

Island Formation Condition

$$\boldsymbol{F > 2N_p D / L^2}$$

- **Kinetic effect**
  - Asymmetric attachment promotes step flow.

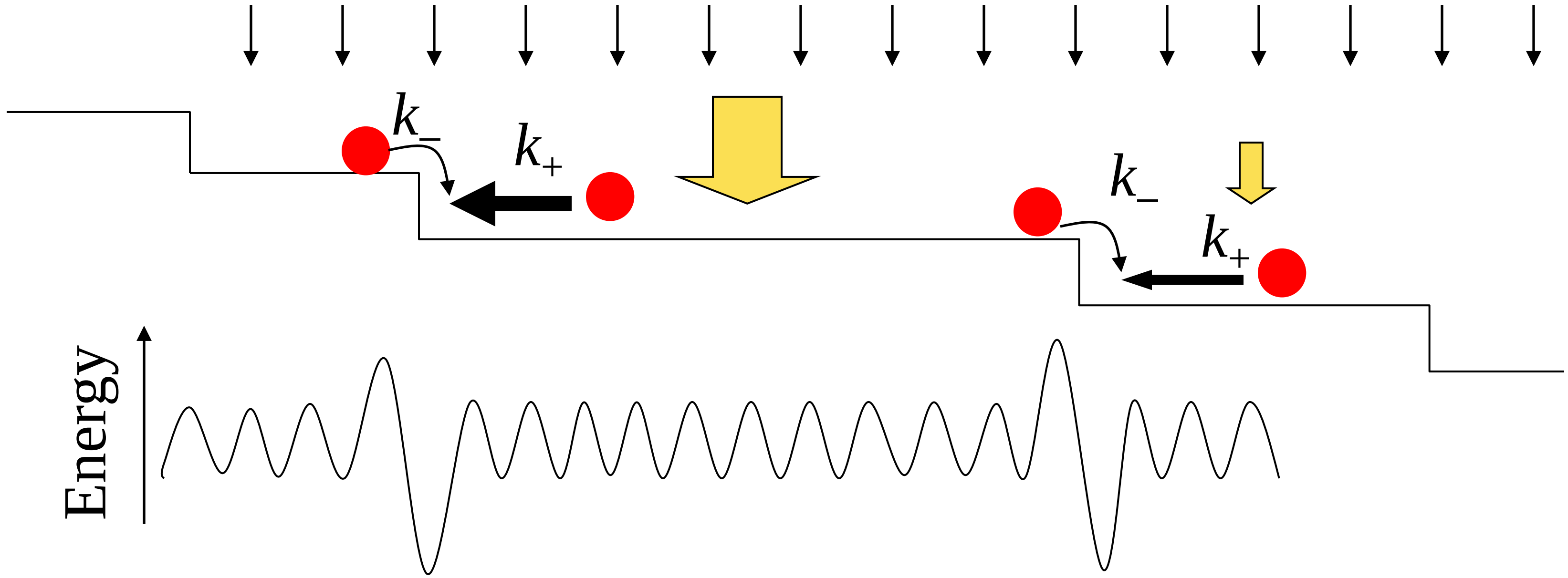
Schwoebel, J. Appl. Phys. **40**, 614 (1969)

- **Energetic effect**
  - Elastic energy promotes step bunching.

Tersoff et al, PRL **75**, 2730 (1995)

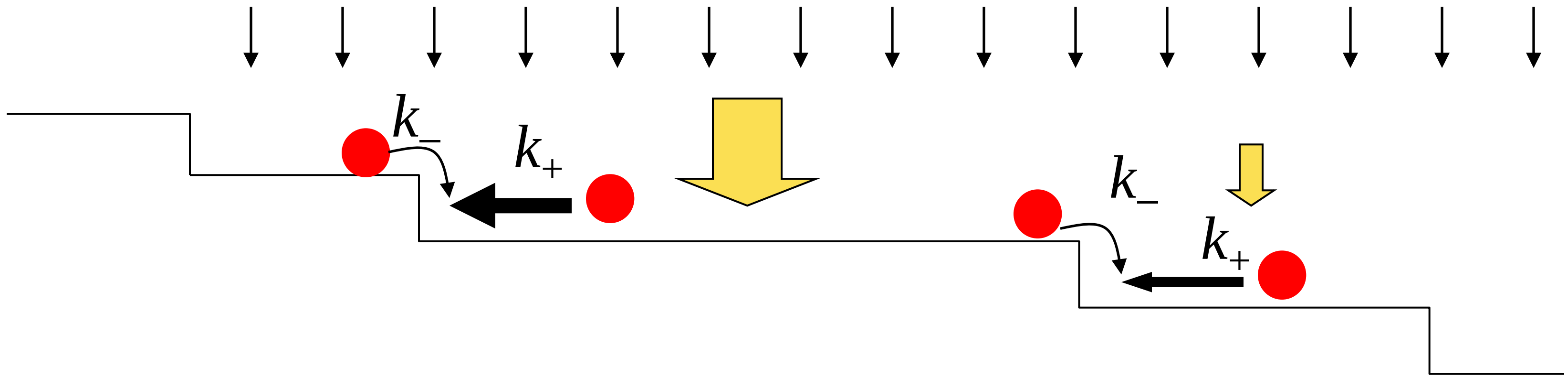
Step flow prevails when deposition flux is high enough.

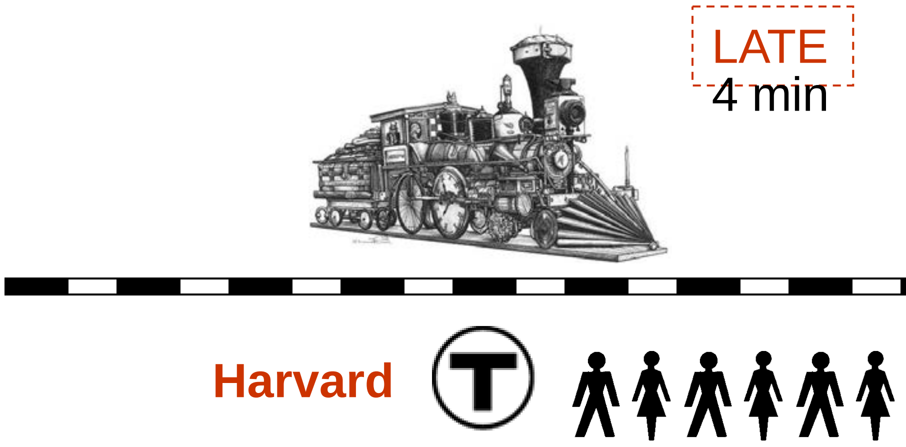
Asymmetric attachment promotes step-flow



- Ehrlich-Schwoebel barrier Schwoebel, J. Appl. Phys. **40**, 614 (1969)
- Asymmetric attachment: $k_+ >> k_-$
- Schwoebel effect: during deposition, a large terrace becomes small, and a small terrace becomes large.

Schwoebel effect





Questions to be addressed

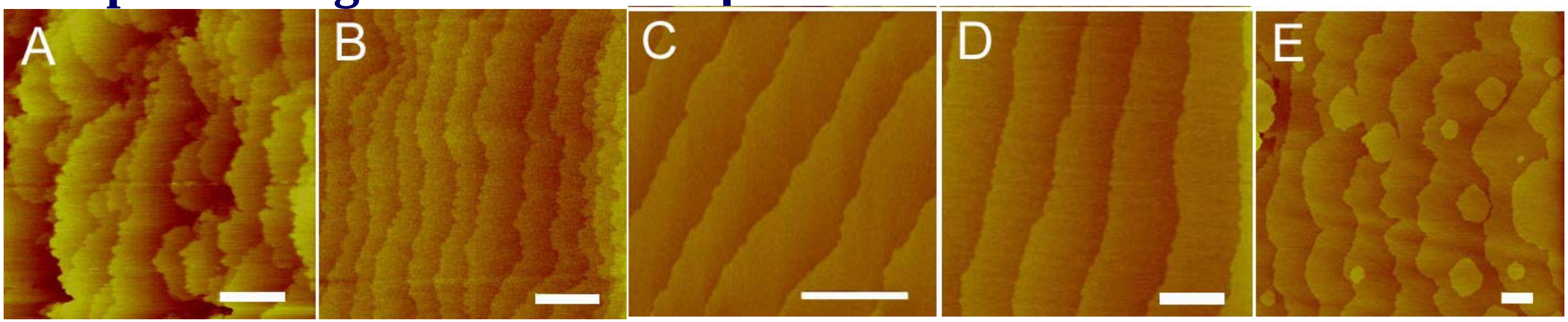
- How to stabilize step flow?

- Can we determine the stability of step flow in the early stage before step bunching occurs?

- Is there any thickness dependence in the step flow?

How to Stabilize Step Flow?

Step bunching **Step flow** **Island formation**



AFM images of $SrRuO_3/SrTiO_3$

Images from [W. Hong et al., Phys. Rev. Lett. 95, 095501 (2005)]

Thus, in order to achieve step flow:

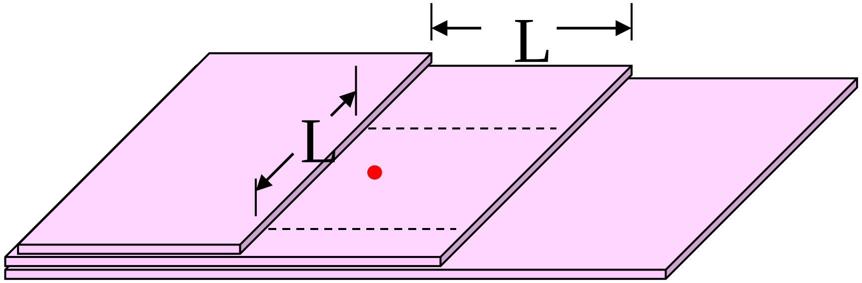
- **Avert island formation**
- **Avert step bunching**

Avert Island Formation
In Molecular Beam Epitaxy (MBE) condition

Homogeneous deposition of adatoms

Temperature is Low

Once an island forms, it is **stable**



Life time of adatoms (time for an adatom reach a step): $\tau_{life} = L^2 / 2D$

Landing time (time between two consecutive incident adatoms to land in an area of L^2):

$$\tau_{land} = \left(\frac{a}{L}\right)^2 \frac{1}{F}$$

To avert island formation: $\tau_{life} < \tau_{land}$

D: diffusitivity,
F: flux
a: lattice constant

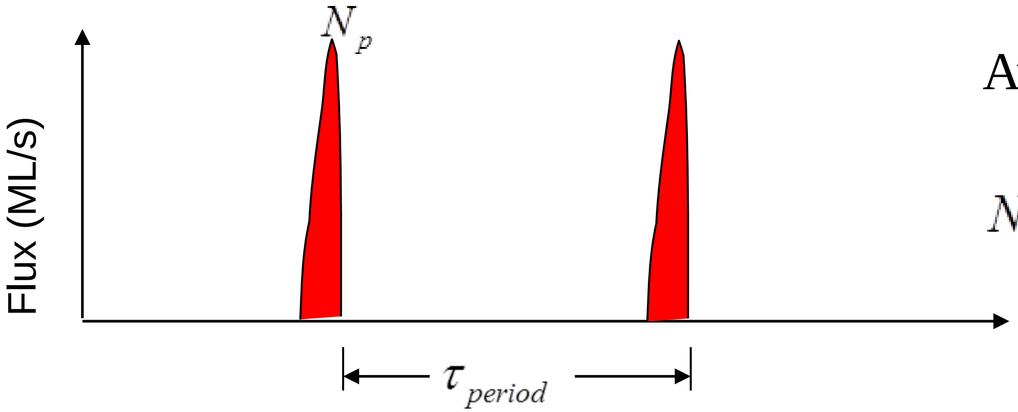
$$\Rightarrow \quad F < 2Da^2 / L^4$$

Avert Island Formation in Pulsed Laser Deposition Condition

Each pulse deposits a large number of atoms

Temperature is high

In each deposition pulse, islands may form, but they are **unstable**



Average flux $F = \frac{N_p}{\tau_{period}}$

$N_p = 0.006\text{ML}$ $\tau_{period} = 0.1s$

Life time of adatoms (time for an adatom reach a step): $\tau_{life} = L^2 / 2D'$

Landing time (period between pulses): $\tau_{period} = \frac{N_p}{F}$

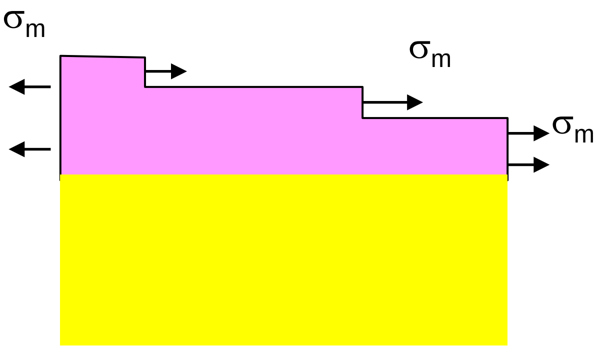
To avert island formation: $\tau_{life} < \tau_{period}$

$$\Rightarrow F < 2N_p D / L^2$$

D': effective diffusivity

Avert Step Bunching

❖ Heteroepitaxy: Elastic Energy



- **Energetics effect:**

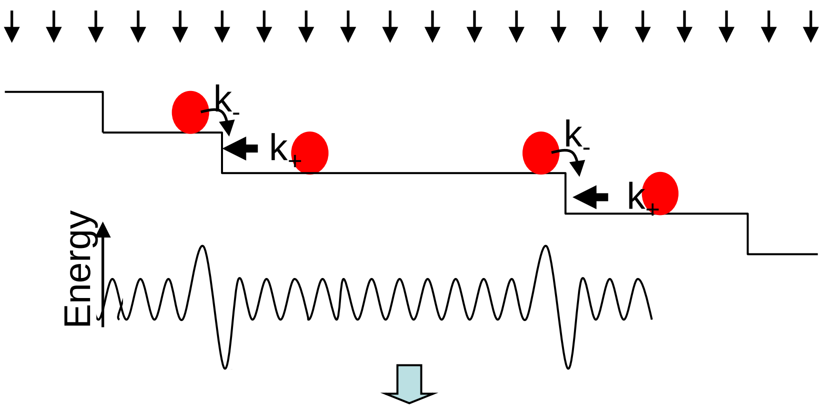
On a strained surface, steps **attract** each other

[Marchenko, JEPT 54, 605 (1981)]

[Tersoff et al., PRL (1995)75, 2730]

step bunching

❖ On a vicinal substrate: Ehrlich-Schwoebel barrier



step flow

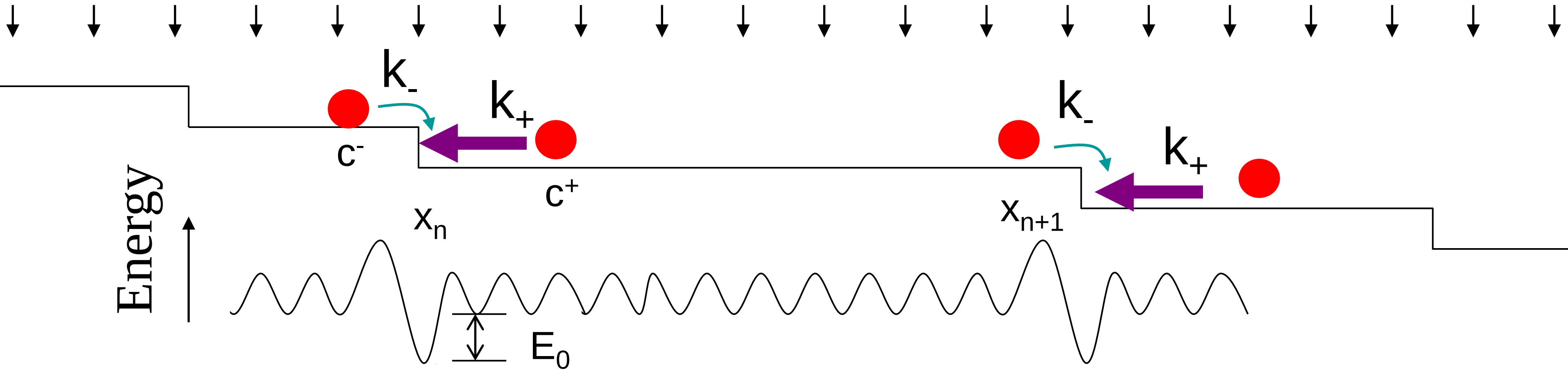
- **Kinetic effect:**

Asymmetric attachment: $k_+ >> k_-$

[Schwoebel, J. Appl. Phys. 40, 614 (1969)]

❖ Competition: Energetics vs. Kinetics

Evolution of Adatoms & Steps



- Equilibrium coverage of adatoms under the step-step elastic interactions $f_n(x_n)$:

$$c_{eq}(x_n) = \exp\left(-\frac{E_0 + Af_n}{k_B T}\right) \qquad f_n = \alpha \sum_{m=\pm 1}^{\pm\infty} \frac{1}{x_{n+m} - x_n}$$

[Tersoff et al., PRL (1995)75, 2730]

- **Adatom diffusion flux:** $-D\frac{\partial c}{\partial x} = k_-\left[c^- - c_{eq}\right]$ $\quad D\frac{\partial c}{\partial x} = k_+\left[c^+ - c_{eq}\right]$

$$c(x_n^-) \neq c(x_n^+) \neq c_{eq}(x_n)$$

- **Step velocity:** $\frac{dx_n}{dt} = k_-[c(x_n^-) - c_{eq}(x_n)] - k_+[c(x_n^+) - c_{eq}(x_n)]$

Equation of Motion

- **Quasi-steady state approximation:**

Low flux

Steps move slowly within the time to approach steady state distribution

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + F(t) \sim 0 \quad \Rightarrow \quad c(x) = -\frac{F}{2D}(x - x_n)^2 + \beta_1(x - x_n) + \beta_0$$

- **Equation of motion of the step:**

$$\frac{dx_n}{dt} = k_-\left[c\left(x_n^-\right) - c_{eq}(x_n)\right] - k_+\left[c\left(x_n^+\right) - c_{eq}(x_n)\right]$$

With proper boundary conditions

$$\frac{dx_n}{dt} = \frac{-Q_{n-1} + Fl_{n-1}\left(\frac{1}{k_-} + \frac{l_{n-1}}{2D}\right)}{\frac{1}{k_-} + \frac{1}{k_+} + \frac{l_{n-1}}{D}} + \frac{Q_n + Fl_n\left(\frac{1}{k_-} + \frac{l_n}{2D}\right)}{\frac{1}{k_-} + \frac{1}{k_+} + \frac{l_n}{D}}$$

$$Q_n = c_{eq}(x_{n+1}) - c_{eq}(x_n)$$

$$l_n = x_{n+1} - x_n$$

Avert Step Bunching: Linear Stability Analysis

- **Perturbation:** $x_{n+1} - x_n = L + q(t)\exp(iKn)$

$dq/dt = \Omega q$ where

$$\Omega = \frac{1-\cos K}{\frac{1}{k_-}+\frac{1}{k_+}+\frac{L}{D}}\left[\frac{\alpha_1 A c_0 S}{k_B T L^2} - F\frac{\frac{1}{(k_-)^2}-\frac{1}{(k_+)^2}}{\frac{1}{k_-}+\frac{1}{k_+}+\frac{L}{D}}\right] + iF\sin K$$

Re Ω > 0 unstable
Re Ω < 0 stable

- **Step flow stability condition:** $\mathrm{Re}\,\Omega < 0$

($k_+ \gg k_-$)

$$\Rightarrow \quad F > \frac{\pi^2 \alpha_1 A c_0 k_-}{k_B T L^2}\left(1 + \frac{L k_-}{D}\right)$$

$$c_0 = e^{-\beta E_0},\ D = D_0 e^{-\beta E_D},\ k_- = \frac{D}{a} e^{-\beta E_{ES}},\ \alpha_1 = \alpha_1(\varepsilon, Y, \nu)$$

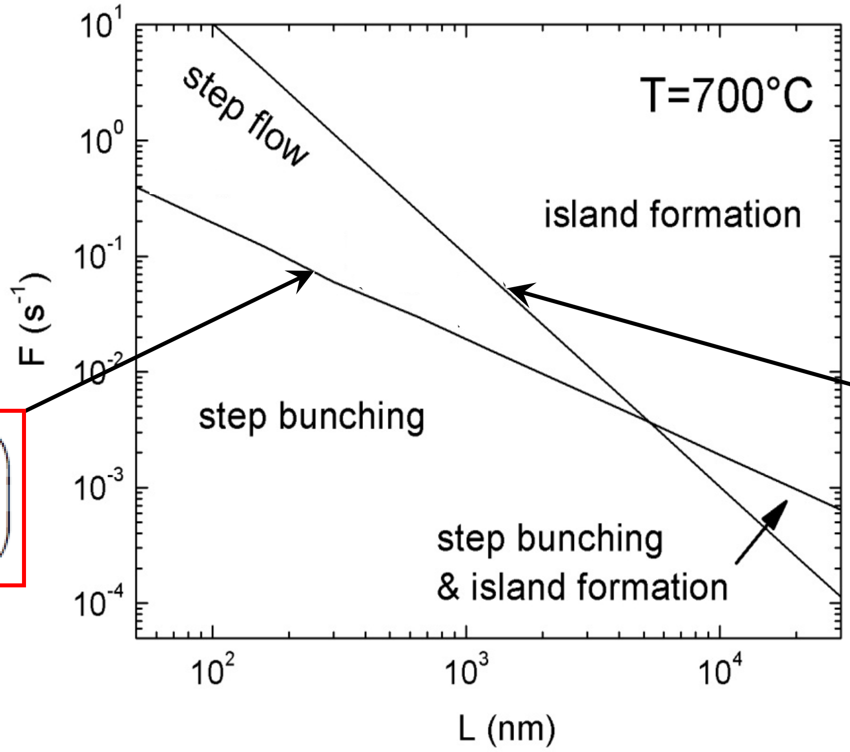
E_{ES} : ES barrier E_D: diffusion barrier E_0: formation energy of an adatom

D : adatom diffusion coefficient L : average terrace width

α_1 : elastic interaction parameter

Growth Mode Diagram

$$F > \frac{\pi^2 \alpha A c_0 k_-}{k_B T L^2}\left(1 + \frac{L k_-}{D}\right)$$

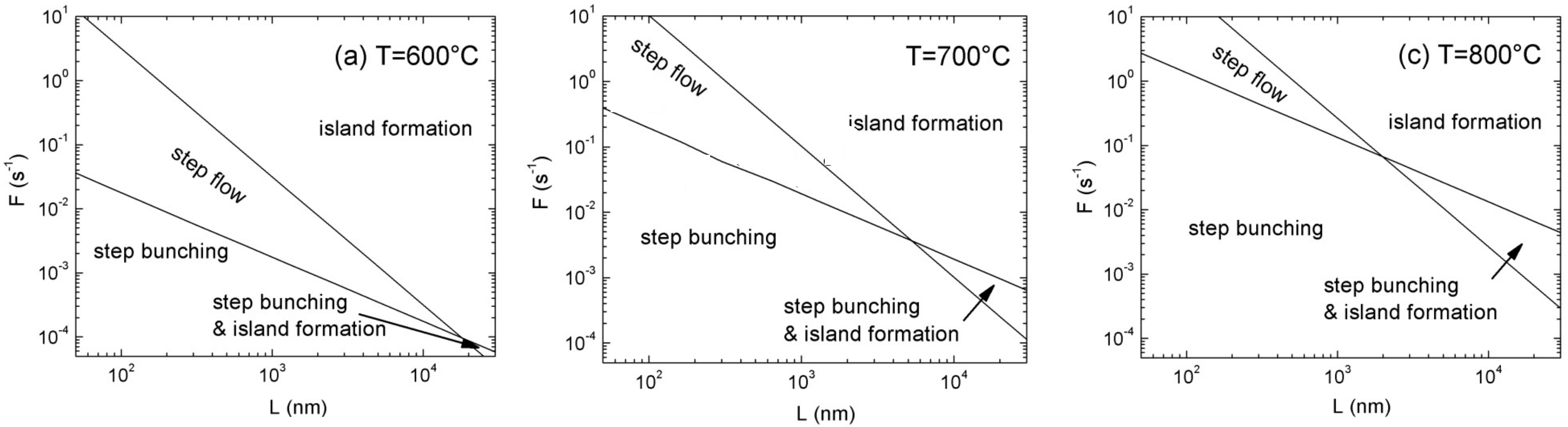


$$F < \frac{2 N_p D}{L^2}$$

- New growth mode: concurrent step bunching and island formation
- Existence of persistent step flow

Growth Mode Diagram *(continued)*

❖ Temperature Dependence



To avert step bunching

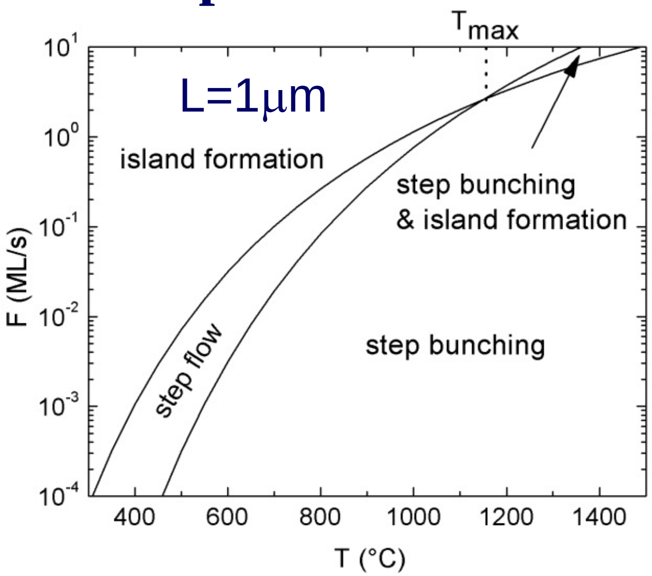
$$F > \frac{\pi^2 \alpha A c_0 k_-}{k_B T L^2}\left(1+\frac{Lk_-}{D}\right) \sim \begin{cases} \frac{1}{L^2}\exp\left(-\frac{E_0+E_D+E_{ES}}{k_B T}\right) & \text{small L} \\ \frac{1}{L}\exp\left(-\frac{E_0+E_D+2E_{ES}}{k_B T}\right) & \text{large L} \end{cases}$$

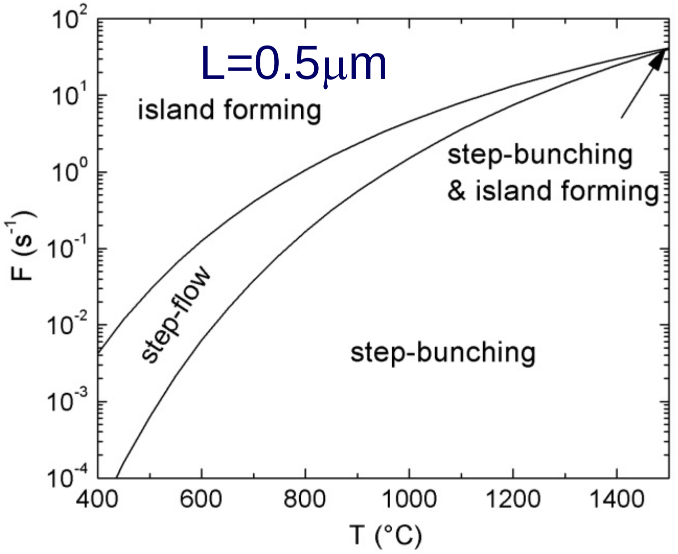
To avert island formation

$$F < \frac{2N_p D}{L^2} \sim \frac{1}{L^2}\exp\left(-\frac{E_D}{k_B T}\right)$$

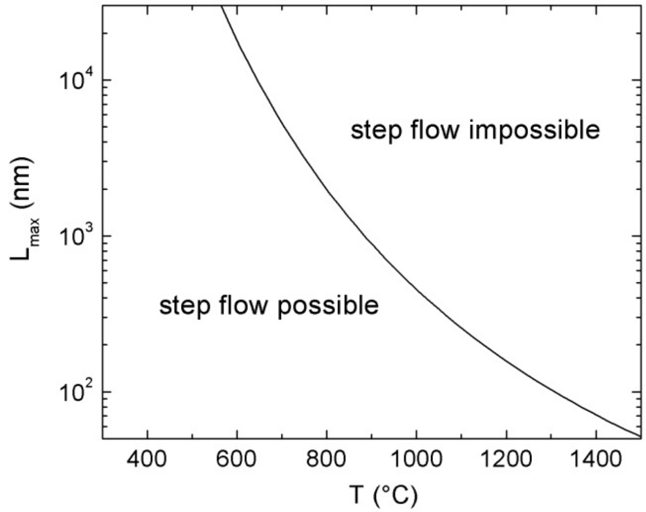
Growth Mode Diagram *(continued)*

❖ Flux vs Temperature





❖ Maximum Terrace Width

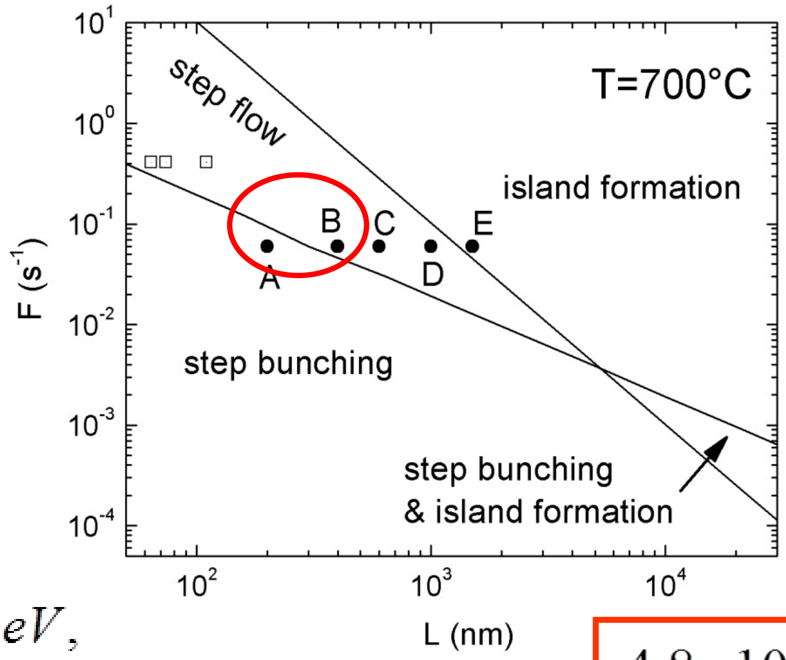


$$L_{max} = \frac{D}{k_-}\left(\frac{2k_B T N_p D}{\pi^2 A \alpha_1 c_0 k_-} - 1\right)$$

Experiments & Theory

[Hong et al., Phys. Rev. Lett. 95, 095501(2005)]

F=0.06 ML/s



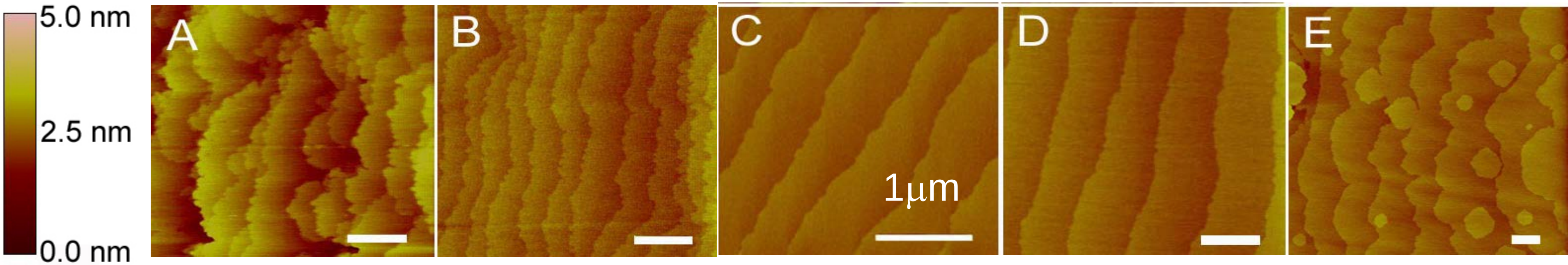
Parameters found:

$$E_0 = 0.8eV, E_D = 0.9eV,$$

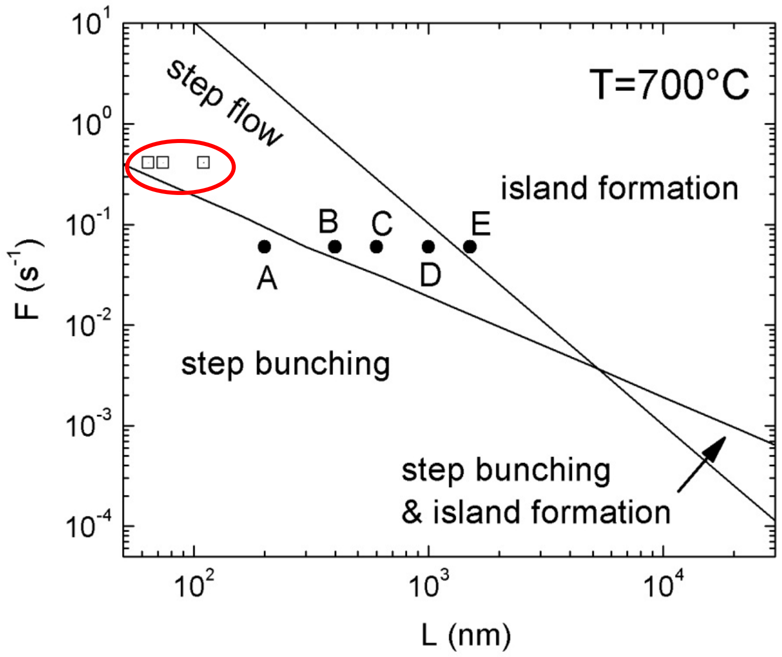
$$E_{ES} = 0.1eV, D_0 = 2.3\times10^{11}\,nm^2/s$$

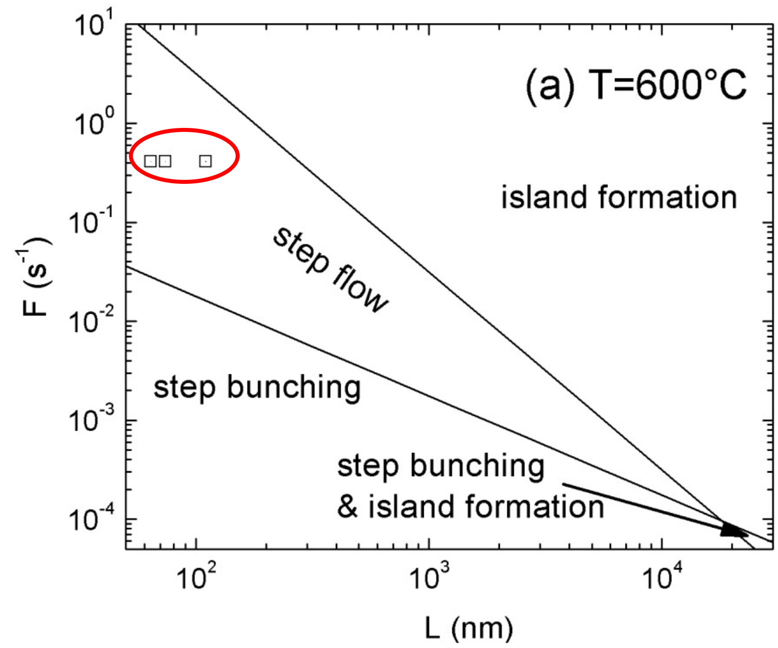
$$4.8\times10^6 < D < 1.1\times10^7\,nm^2/s$$

$$1.02 < E_0 + 2E_{ES} < 1.15eV$$



Experiments & Theory *(continued)*





Experimental data points:

J. Choi *et al.*, Appl. Phys. Lett. **79**, 1447 (2001)

G. Rijnders *et al.*, Appl. Phys. Lett. **84**, 505 (2004)

Can We Determine the Stability of the Step Flow in the Early Stage?

- **Time evolution of step position:**

$$dx_n / dt = V\left[\left(x_{n+1} - x_n\right), \left(x_{n+2} - x_n\right), \ldots, \left(x_{n-1} - x_n\right), \left(x_{n-2} - x_n\right), \ldots\right]$$

V : translational symmetry in the system is conserved

- Step-width evolution:

$$d\delta_n / dt = \sum_{m=\pm 1}^{\pm\infty} \left(\delta_{n+m} - \delta_n\right) \partial V / \partial r_m \quad \delta_n(t) = x_{n+1}(t) - x_n(t) - L$$

- Fourier transformation: $\hat{\delta}(K,t) = \sum_{n=-\infty}^{+\infty} \delta_n(t) \exp(-iKn)$ $\qquad \hat{\delta}(K,t) = \hat{\delta}(K,t_0) \exp\left[\Omega(K)(t - t_0)\right]$

$$\longrightarrow \quad \partial\hat{\delta} / \partial t = \Omega \hat{\delta} \qquad \Omega(K) = \sum_{m=\pm 1}^{\pm\infty} \left[\exp(iKm) - 1\right] \partial V / \partial r_m$$

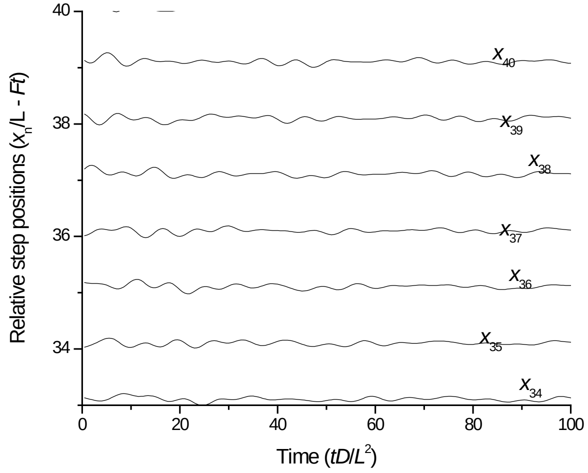
- **Determination of the stability of the step flow:** $\mathrm{Re}[\Omega] = \frac{1}{t - t_0} \ln \left| \frac{\hat{\delta}(K,t)}{\hat{\delta}(K,t_0)} \right|$

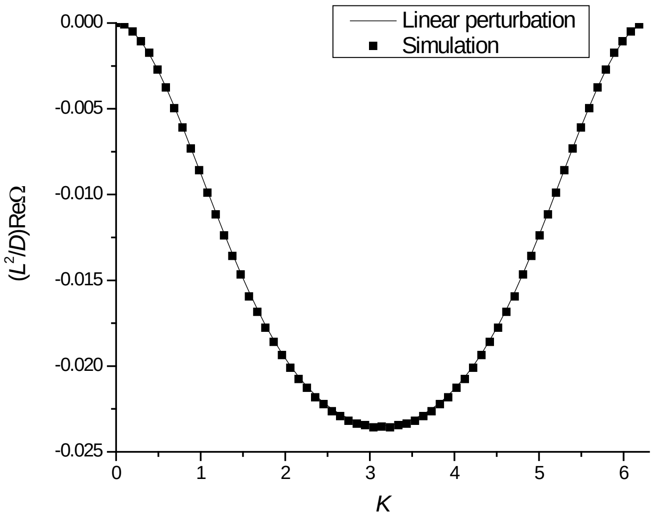
Step positions at two different times:

System parameters and growth mode can be determined!

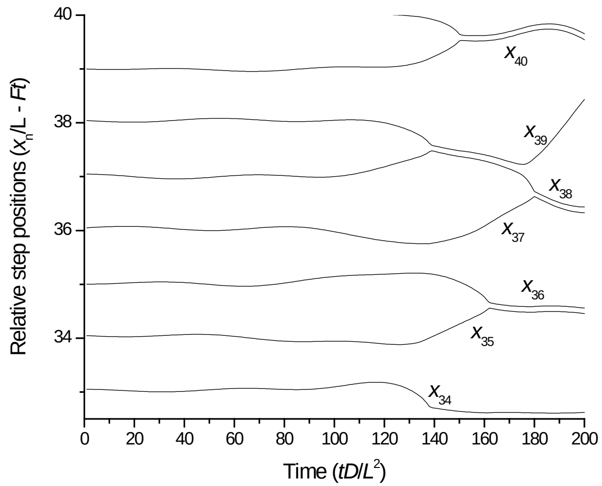
Fourier analysis of the dynamics

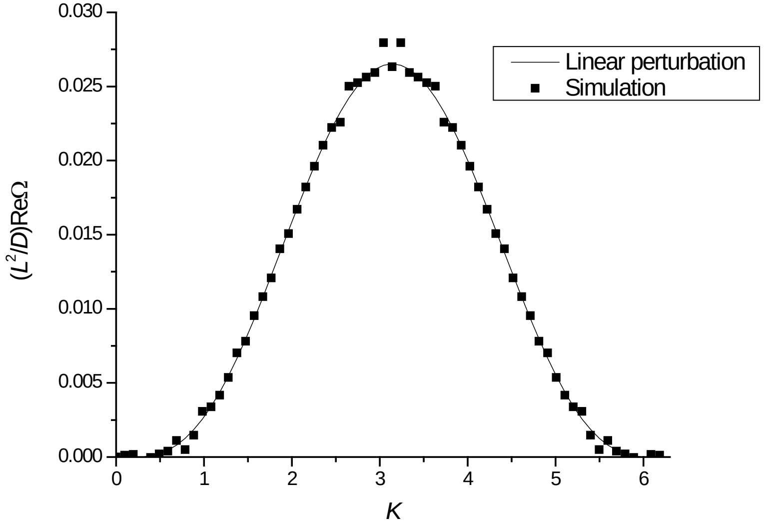
- **Stable: Step Flow (high flux)**





- **Unstable: Step Bunching (low flux)**





Any Thickness Dependence in Step Flow?

Evolution of steps in the "step bunching" region

- **Time evolution of the step position**

$$x_n = L(n + Ft) + \Delta(t)\sin(2\pi n / N), \quad \Delta(t) = \Delta(0)e^{\Omega t}$$

$$\Rightarrow \quad \mathrm{Re}\,\Omega = \frac{1}{t - t_0}\ln\left|\frac{\hat{\delta}(K,t)}{\hat{\delta}(K,t_0)}\right| \approx \frac{\alpha_1 A c_0 D}{k_B T L^3}\left[1 - \frac{L}{L^*}\frac{\pi^2}{K(2\pi - K)}\right](1 - \cos K)$$

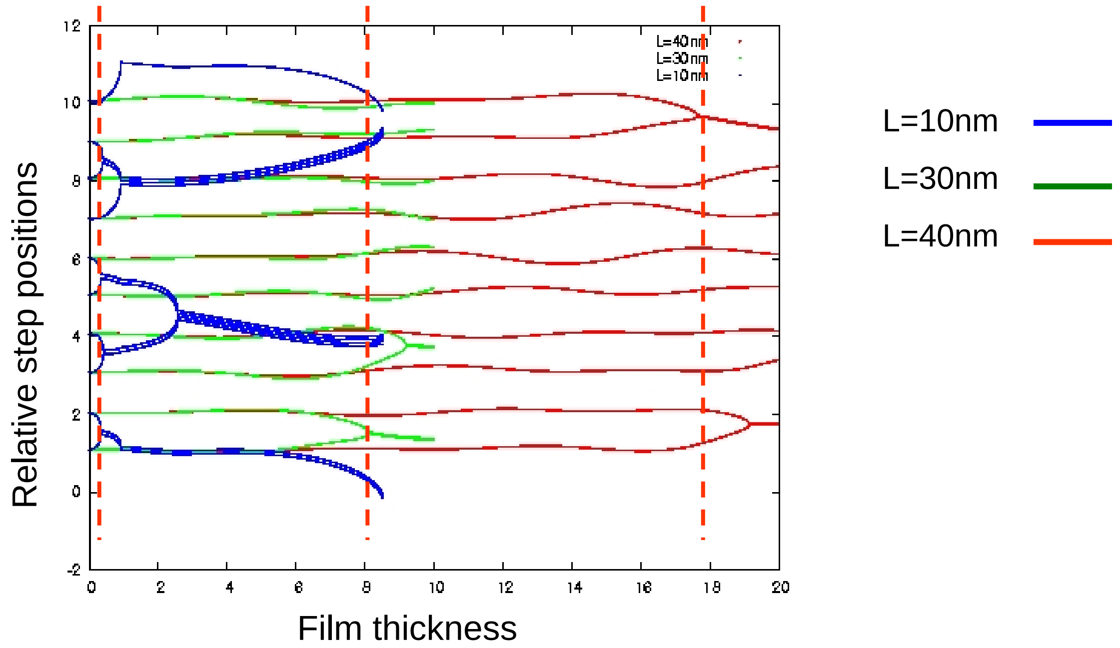
Maximum at $K=\pi$

L^*: critical terrace width above which a persistent step flow occurs

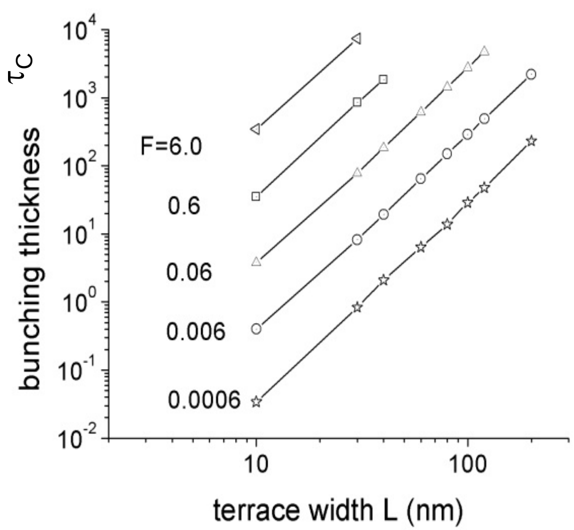
$$\frac{\tau_C}{F} \approx C\frac{k_B T L^3}{\alpha_1 A c_0 D}\left(1 - \frac{L}{L^*}\right)^{-1}$$

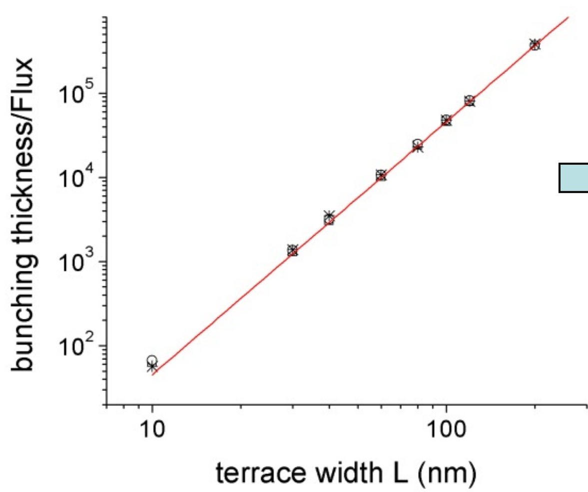
For a film thickness $t < t_C$: step-flow occurs in the step bunching regime

Numerical Results



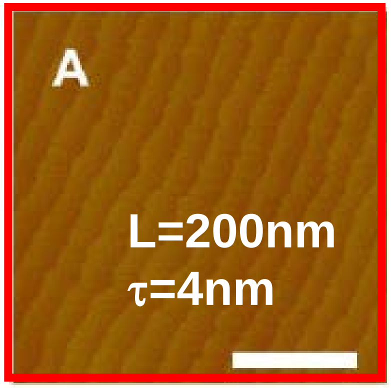
Scaling behavior of film growth is also numerically confirmed

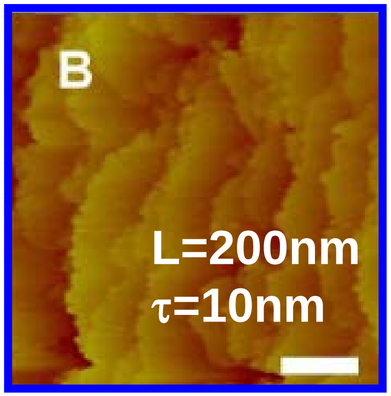


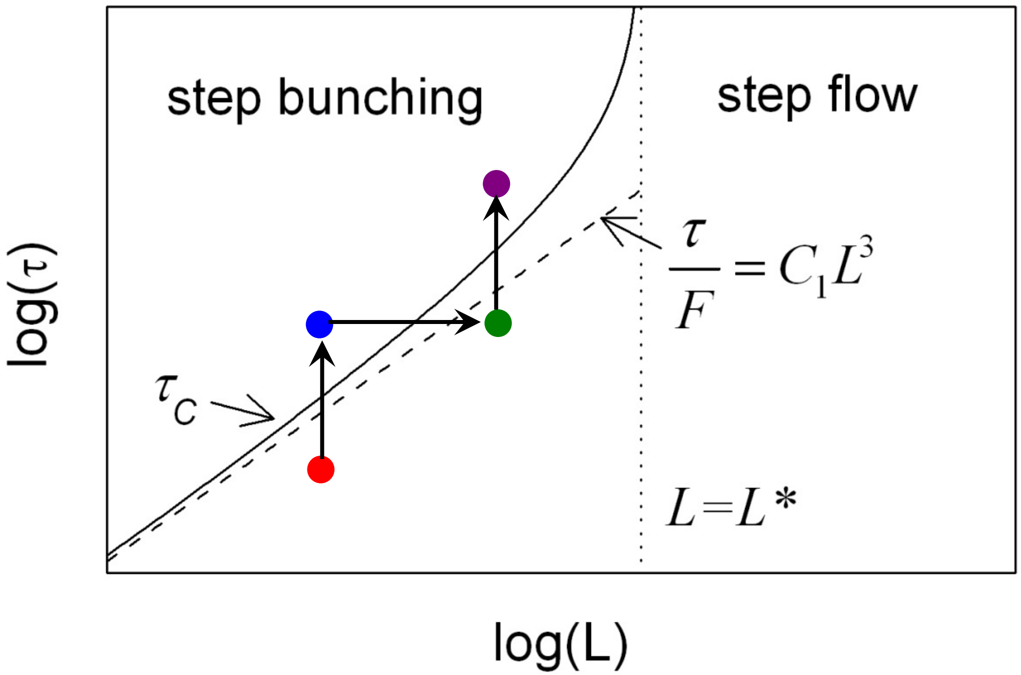


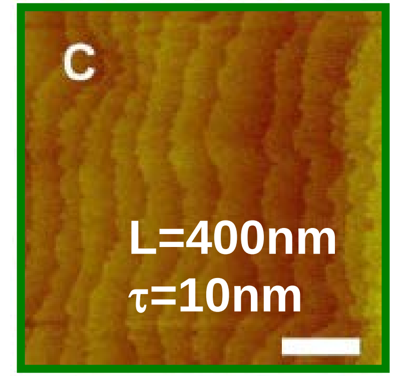
$$\frac{\tau_C}{F} = \frac{\tau_C'}{F'}$$

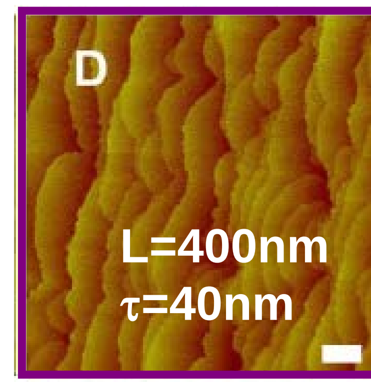
Experiments & Theory



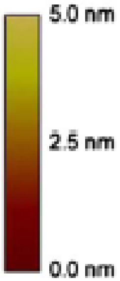








[M.Yoon et al., Phys. Rev. Lett. 99, 055503 (2007)]



- Existence of a critical thickness !
- Under certain thickness, always step flow observed at a given conditions
- System parameters can be extracted

Summary on Step Bunching

- *Persistent* step flow is possible by satisfying the conditions of averting island formation and averting step bunching.

- Even in the step bunching growth region, step flow can be achieved below critical thickness, where scaling behavior between critical thickness and flux is predicted.

- System parameters can be extracted using the growth-mode diagram and scaling behavior.