



Mathematical modeling of kinetic roughening and coarsening during epitaxial growth

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High- T_c superconducting YBCO thin films

- *Superconducting thin film* devices are used in many applications (e.g. high-Q radio frequency devices)
- Model system: *$YBa_2Cu_3O_7$ (YBCO) thin films on MgO* substrate (C-band receiver, Sardinia Radio Telescope)

The Sardinia radio telescope



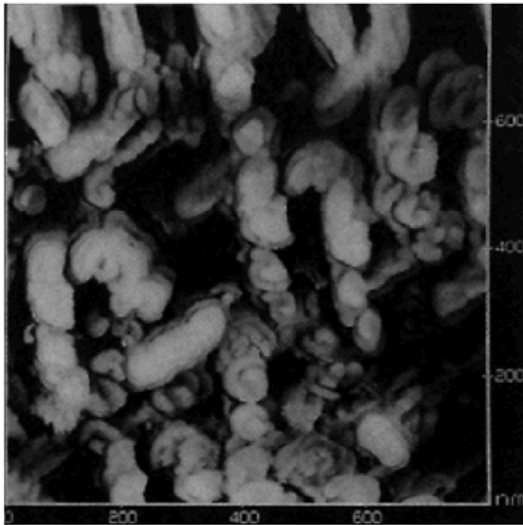
On 30 September 2013, the inaugural ceremony of SRT took place in the presence of the highest local, national and international authorities.

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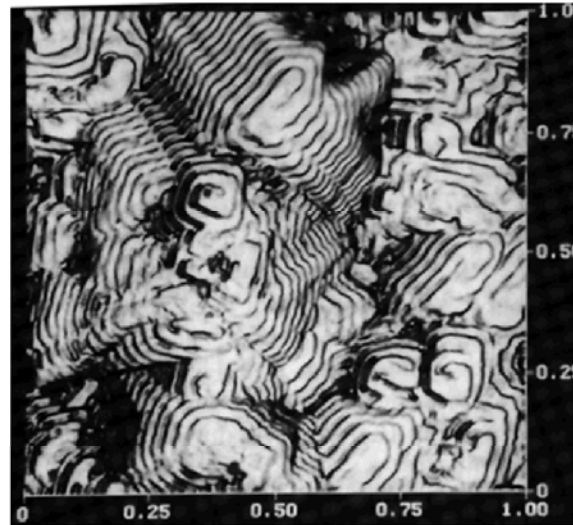
High- T_c superconducting YBCO thin films

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- Model system: *$YBa_2Cu_3O_7$ (YBCO) thin films on MgO* substrate (C-band receiver, Sardinia Radio Telescope)
- Films are grown epitaxially by *deposition* from vapor phase (PVD, e.g., sputtering; CVD, e.g., MOCVD)
- Many aspects of *epitaxial growth* occur far away from equilibrium and are governed by kinetics:
 - *Precursor reactions (gas phase and surface)*
 - *Surface processes (attachment, step motion, pyrolysis...)*
- *Stringent tolerances* on filter characteristics: Films must be of highly uniform thickness and texture.
- *Goal: Development of mathematical tools enabling virtual prototyping and control of robust of high throughput manufacturing processes for complex thin-film systems*

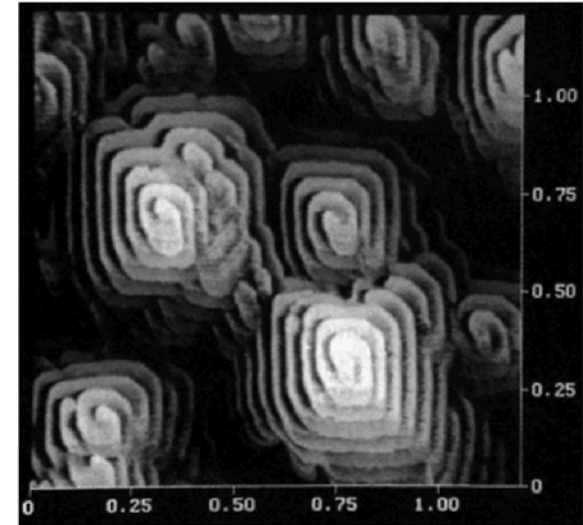
Sputtered YBCO Film on MgO substrate



(a) $h = 10\text{ nm}$



(b) $h = 160\text{ nm}$



(c) $h = 500\text{ nm}$

- Early stages (YBCO/MgO): **Volmer-Weber** island growth (discrete nuclei)
- Intermediate stages: **Spiral growth** (Burton-Frank)
- Late stages: **Coarsening**
 - Spiral step (terrace) height = one unit cell (1.2 nm)
 - Constant terrace width/height ratio $\sim 1/10 - 1/40$
 - **Magic slope!**

I.D. Raistrick & M. Hawley, in: S.L. Shindé & D.A. Rudman (eds.)
Interfaces in High T_c Superconducting Systems, Springer-Verlag, 1994.

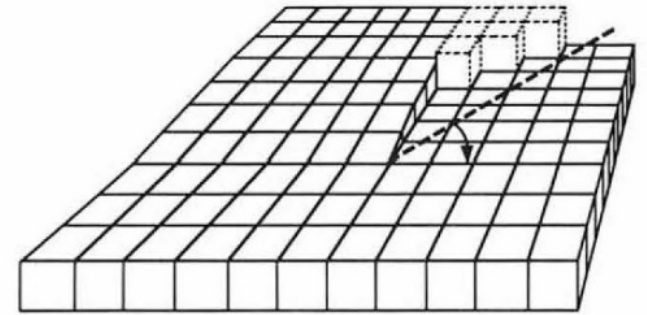
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Continuum film-growth model

- 3D lattice models (Lai & das Sarma, 1991; Zangwill, 1995)

- Assumptions:

- $h_{,t}$ admits Taylor expansion in $\nabla h, \nabla \nabla h,$
- Invariance under $\mathbf{x} \rightarrow -\mathbf{x}$.
- Decay rate no faster than L^{-4} .
- Onsager reciprocity relations.



- Rate equation for surface profile:

$$h_{,t} = F - V(h/\delta) e^{-h/\delta} + \nu \nabla \cdot [(k^{-2} |\nabla h|^2 - 1) \nabla h] - D \nabla^4 h$$

$$\begin{aligned} F &\rightarrow \text{deposition flux} & -V(h/\delta) e^{-h/\delta} &\rightarrow \text{interfacial energy} \\ + \nu \nabla \cdot [(k^{-2} |\nabla h|^2 - 1) \nabla h] &\rightarrow \text{evaporation/condensation}^2 \\ -D \nabla^4 h &\rightarrow \text{capillarity}^1 & k &\rightarrow \text{magic slope} \end{aligned}$$

¹Herring, C, in: *The Physics of Powder Metallurgy*, McGrawHill, 1951.

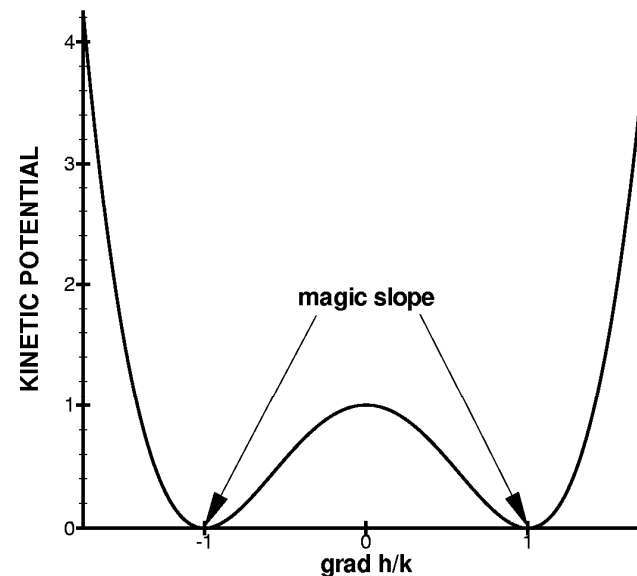
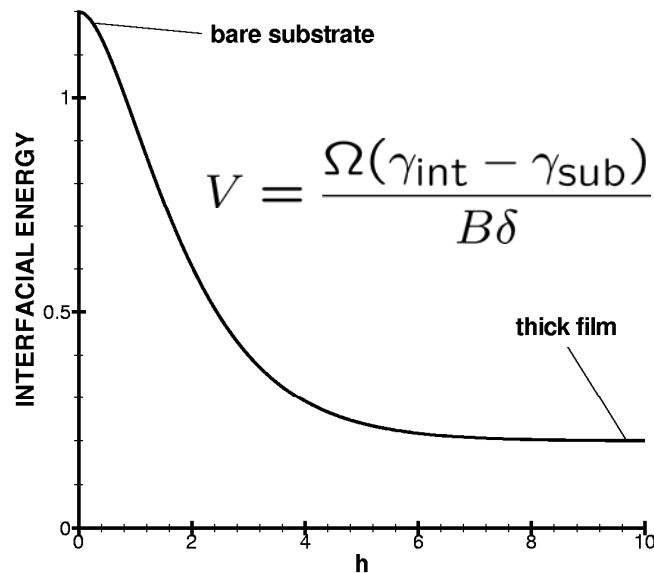
²Mullins, W.W., *Journal of Applied Physics*, **28** (1957) 333.

M. Ortiz, E.A. Repetto & H. Si, *J. Mech. Phys. Solids*, **47** (1999) 697.

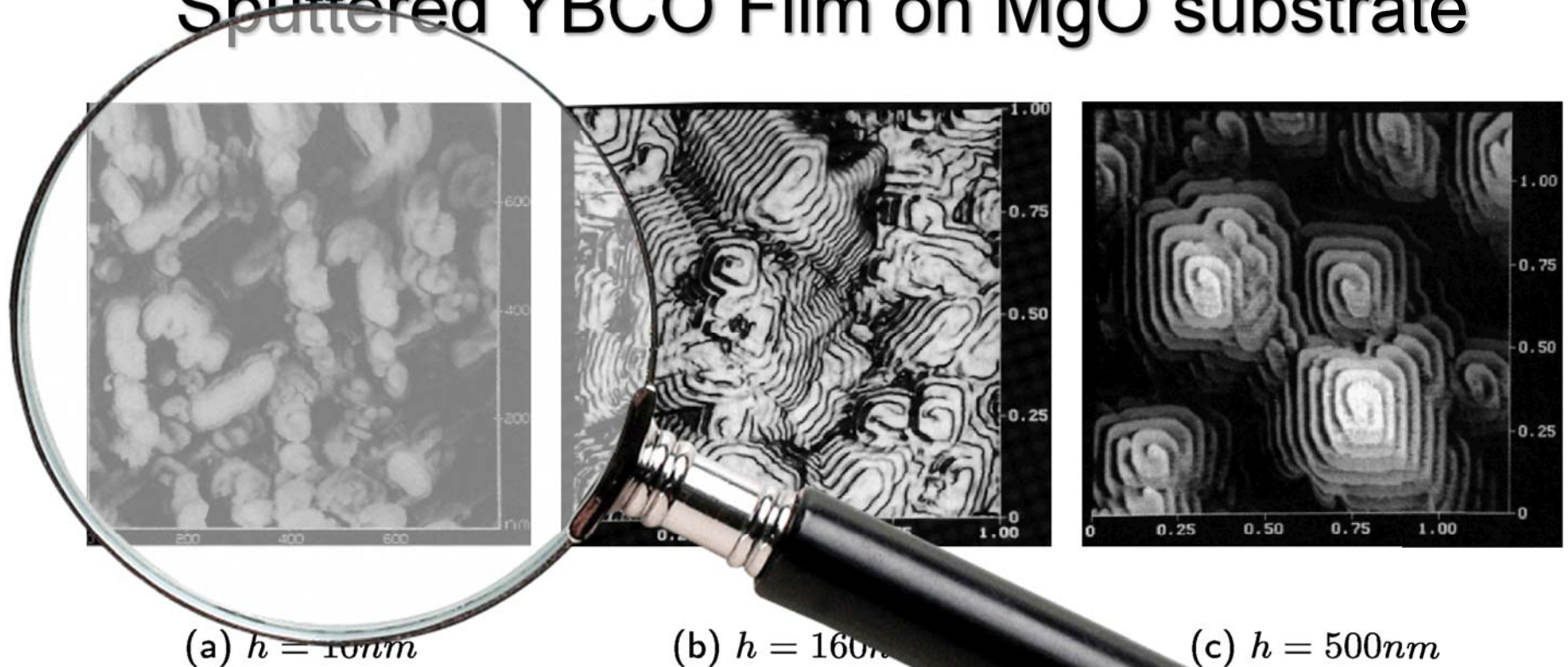
Continuum film-growth model

- Gradient-flow structure!
- From Onsager reciprocity relations: $h_{,t} = -\delta\Phi[h]/\delta h$

- Kinetic potential: $\Phi[h] = \int_{\Omega} \left\{ \overset{\text{interfacial energy}}{-Fh - V(h + \delta)e^{-h/\delta}} + \overset{\text{evaporation condensation}}{\frac{C}{4k^2}(|\nabla h|^2 - k^2)^2} + \overset{\text{capillarity}}{\frac{D}{2}(\nabla^2 h)^2} \right\} d^2x$



Sputtered YBCO Film on MgO substrate



- Early stages (YBCO/MgO): **Volmer-Weber** island growth (discrete nuclei)
- Intermediate stages: **Spiral growth** (Burton-Frank)

- Late stages: **Spinning**
 - Spiral step height = one unit cell (1.1 nm)
 - Constant terrace width/height ratio $\sim 1/10 - 1/40$
 - **Magic slope!**

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Kinetics of island nucleation

- Linearized stability analysis

- Linearization: $h_0 \rightarrow h_0 + u$,

$$u_{,t} = -Cu - \nu \nabla^2 u - D \nabla^4 u$$

- Set: $u = Ae^{-\lambda t} e^{-i\mathbf{k} \cdot \mathbf{x}}$,

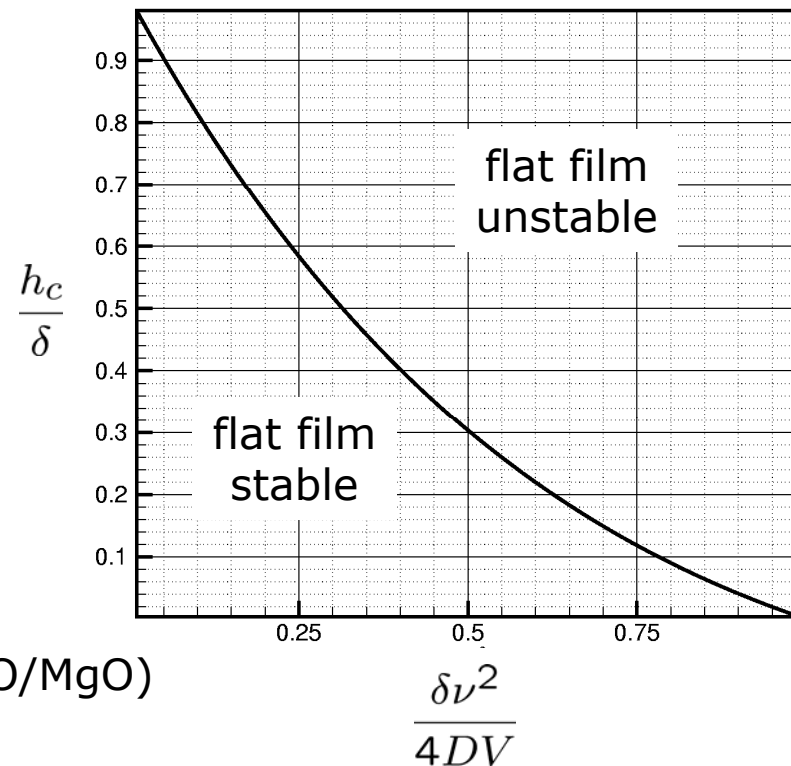
$$\lambda = Dk^4 - \nu k^2 + C$$

- Critical wavelength:

$$k_c = \sqrt{\nu/2D}$$

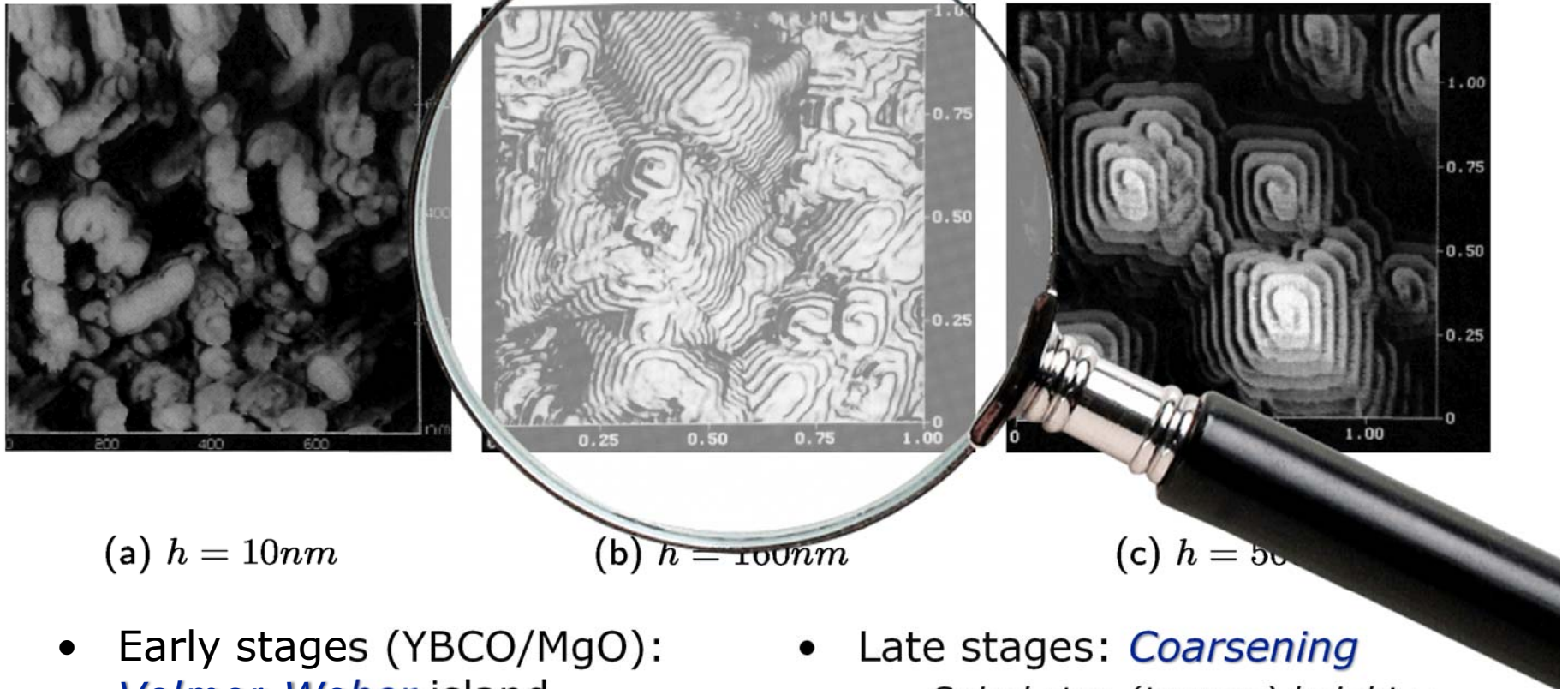
- $h_c = 0 \Rightarrow$ Volmer-Weber. (YBCO/MgO)

- $h_c > 0 \Rightarrow$ Stranski-Krastanow.



Critical thickness h_c .

Sputtered YBCO Film on MgO substrate



(a) $h = 10\text{ nm}$

(b) $h = 100\text{ nm}$

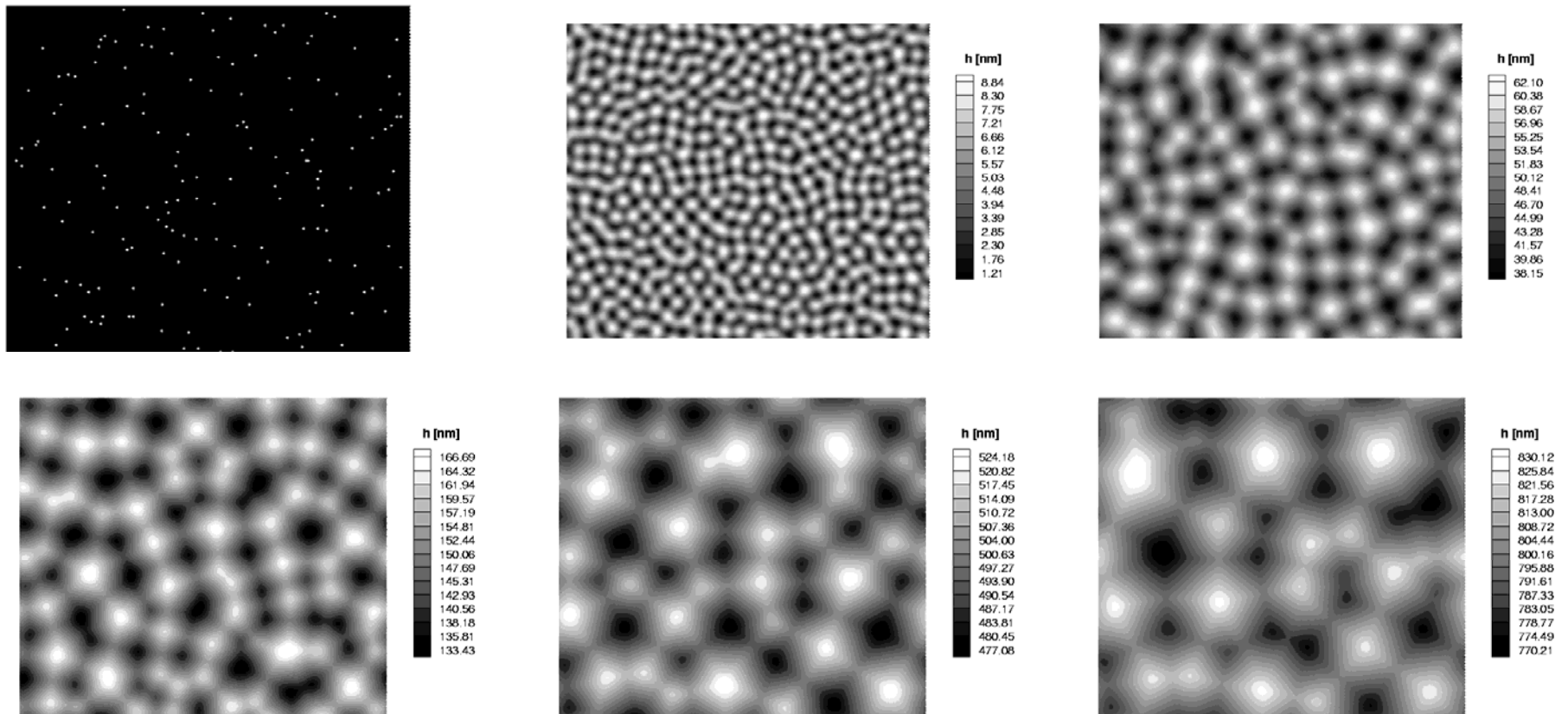
(c) $h = 500\text{ nm}$

- Early stages (YBCO/MgO): **Volmer-Weber** island growth (discrete nuclei)
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Kinetics of surface roughness



Level contours of surface height (nm).
(direct simulation by finite-differences)

Kinetics of surface roughness

- For $h \gg \delta$, kinetics reduce to

$$h_{,t} = F + \nu \nabla \cdot [(k^{-2} |\nabla h|^2 - 1) \nabla h] - D \nabla^4 h$$

- Taking averages: $\langle h \rangle_{,t} = F$
- Roughness profile: $h = \langle h \rangle + h'$

- Rate equation for roughness profile:

$$h'_{,t} = \nu \nabla \cdot [(k^{-2} |\nabla h'|^2 - 1) \nabla h'] - D \nabla^4 h' = \frac{\delta \Phi}{\delta h}$$

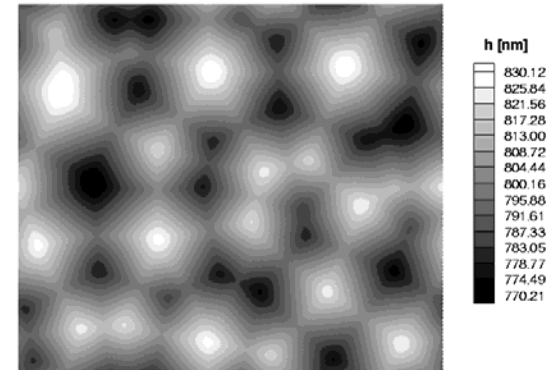
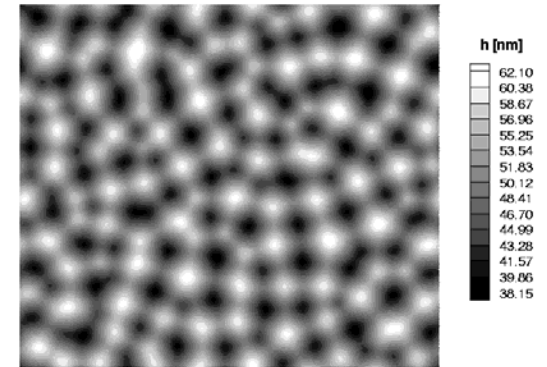
- Kinetic potential for roughness profile:

$$\Phi[h'] = \int_{\Omega} \left(\frac{\nu}{4k^2} (|\nabla h'|^2 - k^2)^2 + \frac{D}{2} (\nabla^2 h')^2 \right) dx$$

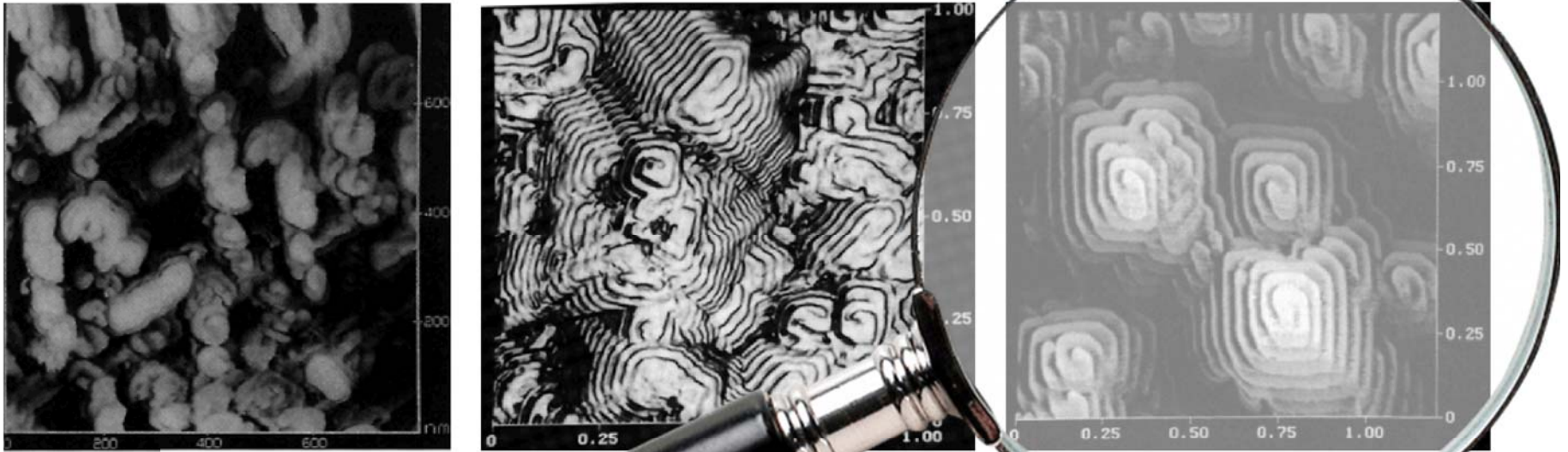
- Roughness measure: $w^2 = \langle h^2 \rangle - \langle h \rangle^2$,

$$\frac{1}{2} (w^2)_{,t} = \frac{1}{|\Omega|} \int_{\Omega} \left(\nu \underbrace{(1 - k^{-2} |\nabla h'|^2)}_{\text{anti-diffusion}} |\nabla h'|^2 - \frac{D}{2} (\nabla^2 h')^2 \right) dx$$

roughening driven by anti-diffusion!



Sputtered YBCO Film on MgO substrate



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(c) $h = 500\text{nm}$

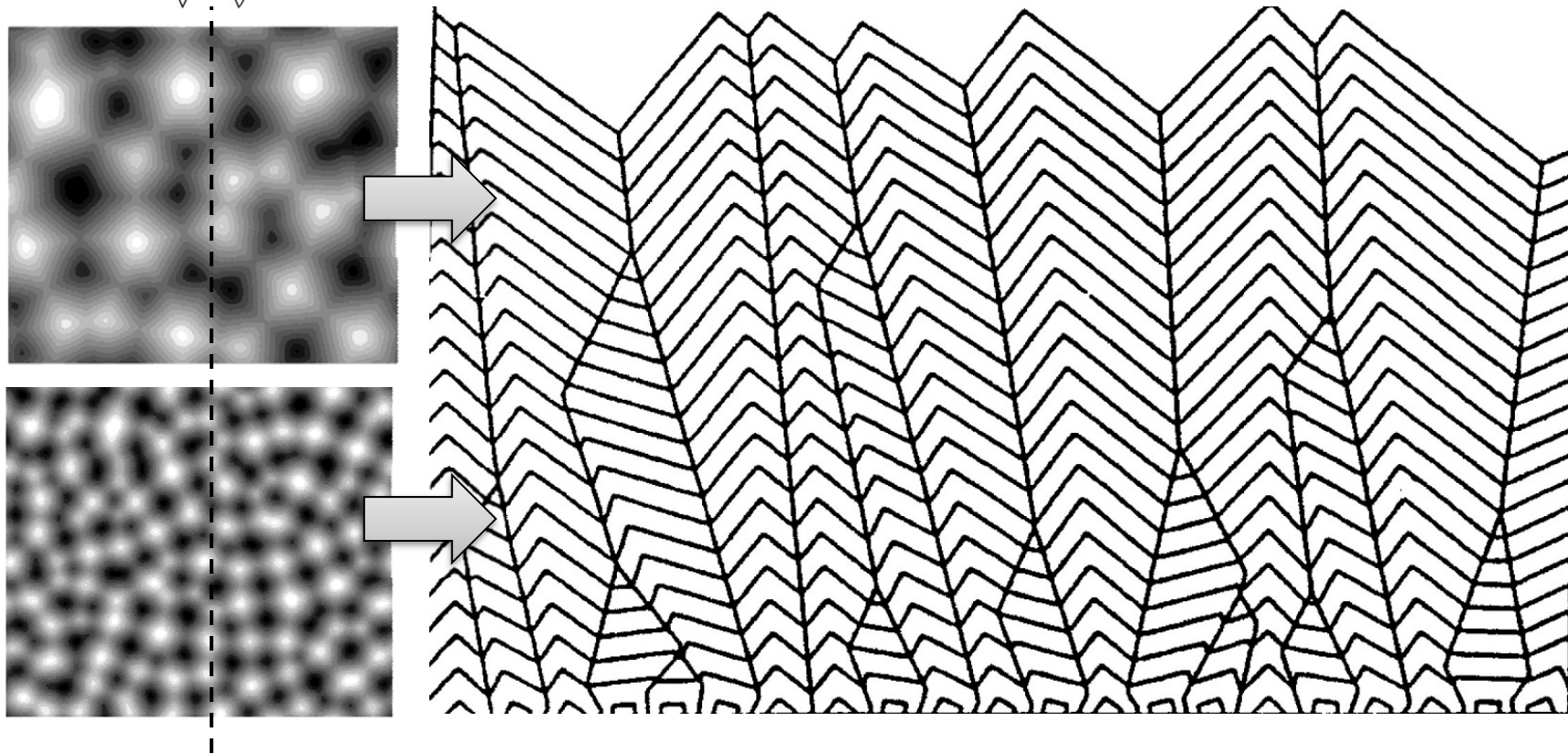
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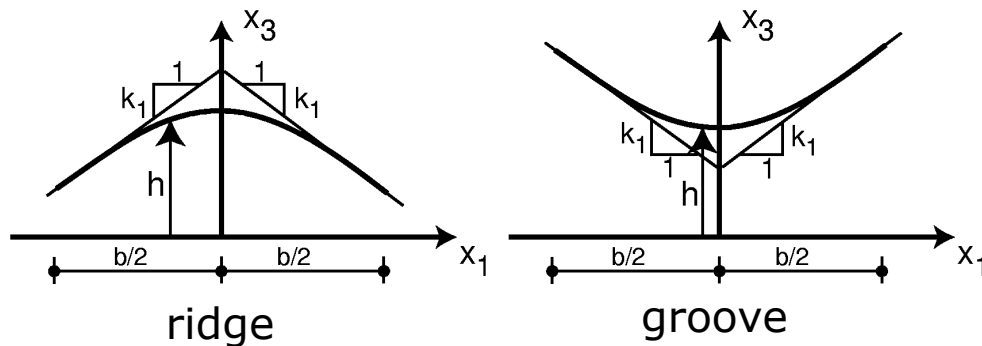


Kinetics of island coarsening



- Islands are separated by sharp interfaces
- Preferred slope is maintained within islands
- Islands grow selectively and cover smaller islands

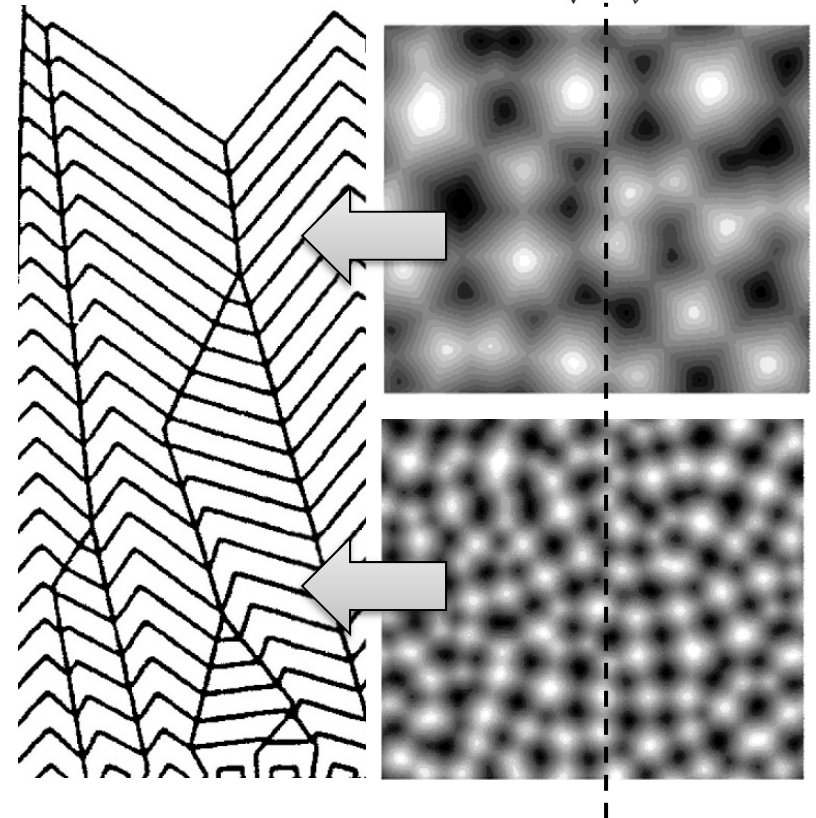
Kinetics of island coarsening



- Large islands $\sim$ small capillarity
- $D \rightarrow 0$, sharp-interface approximation.
- Boundary layer width: $l = \sqrt{D/2\nu} \rightarrow 0$.
- Relaxation time: $\tau = D/2\nu^2 \rightarrow 0$.

- Limiting kinetic potential: $\Phi_0[h] = \int_{\mathcal{S}} \sqrt{2\nu D} [2k_1^3(s)/3k] ds$,
 $\mathcal{S} \equiv$ singular set of the profile.

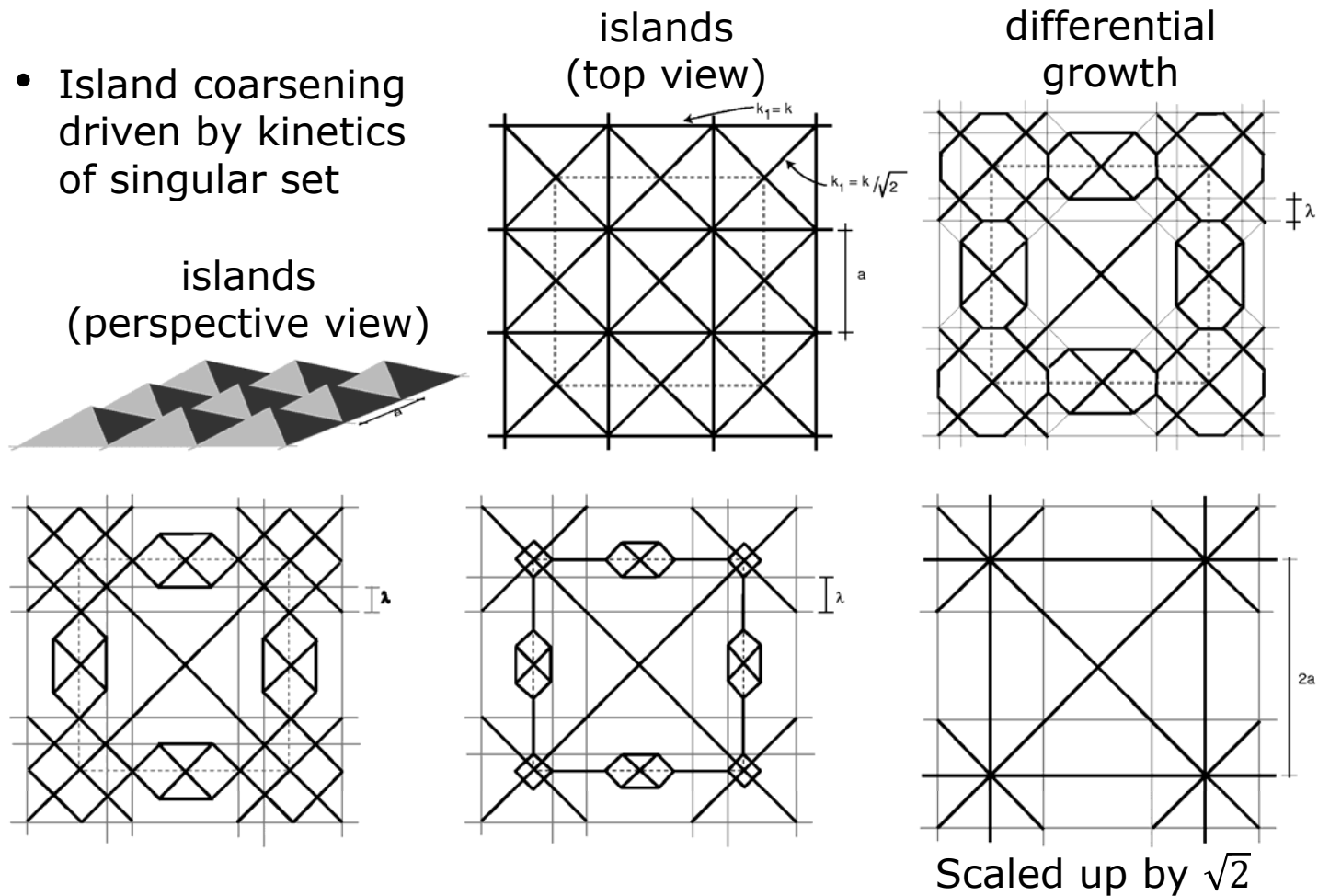
- Limiting kinetics: $h_{,t} = -\delta\Phi_0[h]/\delta h$.



Coarsening driven
by kinetics of singular set!

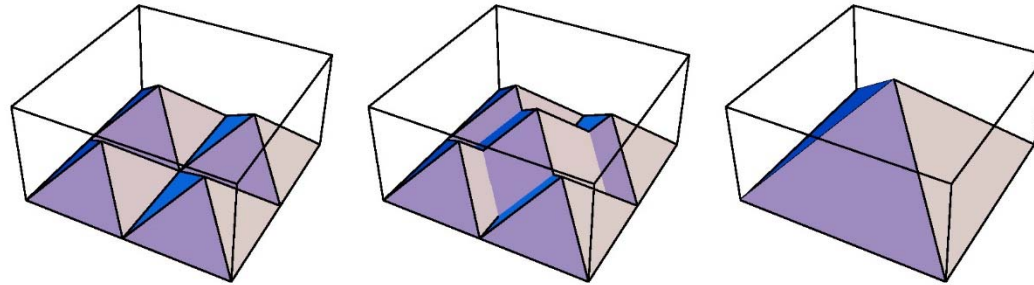
Kinetics of island coarsening

- Island coarsening driven by kinetics of singular set



Evolution of singular set (ridges and grooves).

Kinetics of island coarsening



- Effective kinetic equation:

$$h_{1,t} = \frac{80}{3} \frac{\sqrt{2\nu D} k^4}{12h_1^2 - 4ah_1k + 3a^2k^2}, \quad h_1 < ak$$

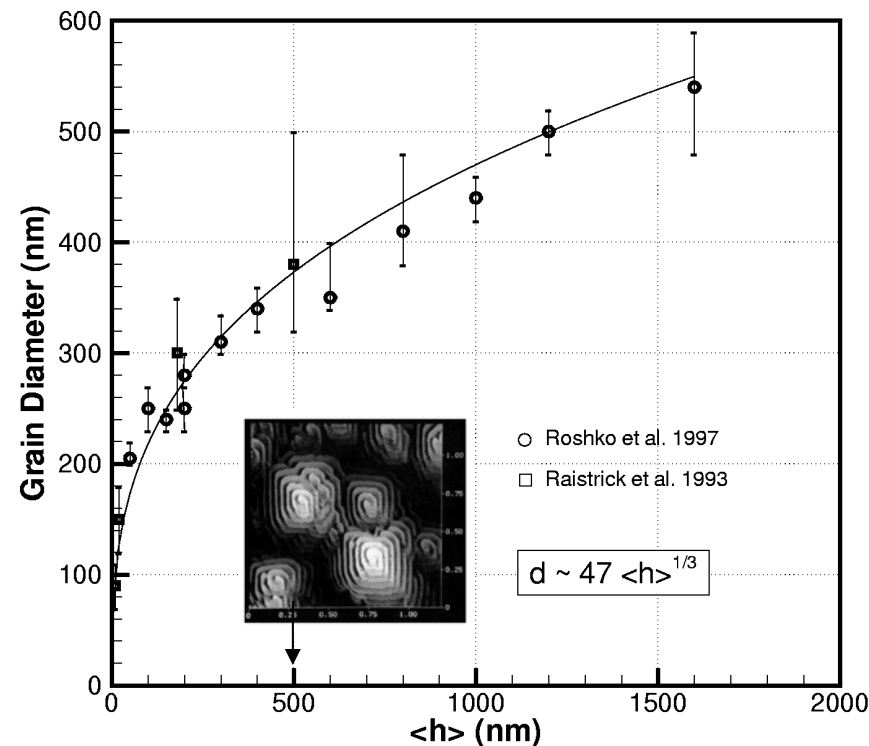
$$h_{1,t} = \frac{16}{3} \frac{\sqrt{2\nu D} k^4}{-20h_1^2 + 60ah_1k - 29a^2k^2}, \quad h_1 > ak$$

- Grain-size growth law:

$$d = \left(\frac{280}{59} \frac{\sqrt{2\nu D} k}{F} \langle h \rangle \right)^{1/3} \sim \langle h \rangle^{1/3}$$

- Island size scales as 1/3 power of film thickness!

Kinetics of island coarsening



Grain diameter d vs. average film thickness $\langle h \rangle$. Theoretical fit to data of Raistrick and Hawley (1993) and Roshko *et al.* (1997).

- We prove mathematically that the ***1/3 scaling is optimal***¹ (it is both an upper bound and a lower bound).

¹S. Conti and M. Ortiz, *J. Mech. Phys. Solids*, **56** (2008) 1885.
M. Ortiz, E.A. Repetto & H. Si, *J. Mech. Phys. Solids*, **47** (1999) 697.

Extension to strained-film growth

- Rate equation for surface profile:

$$h_{,t} = F + \nu \nabla \cdot [(k^{-2} |\nabla h|^2 - 1) \nabla h] - D \nabla^2 (\nabla^2 h - \gamma^{-1} U)$$

where $U(x_1, x_2)$ is the volume free-energy density at $x_3 = h(x_1, x_2)$.

- Assume:

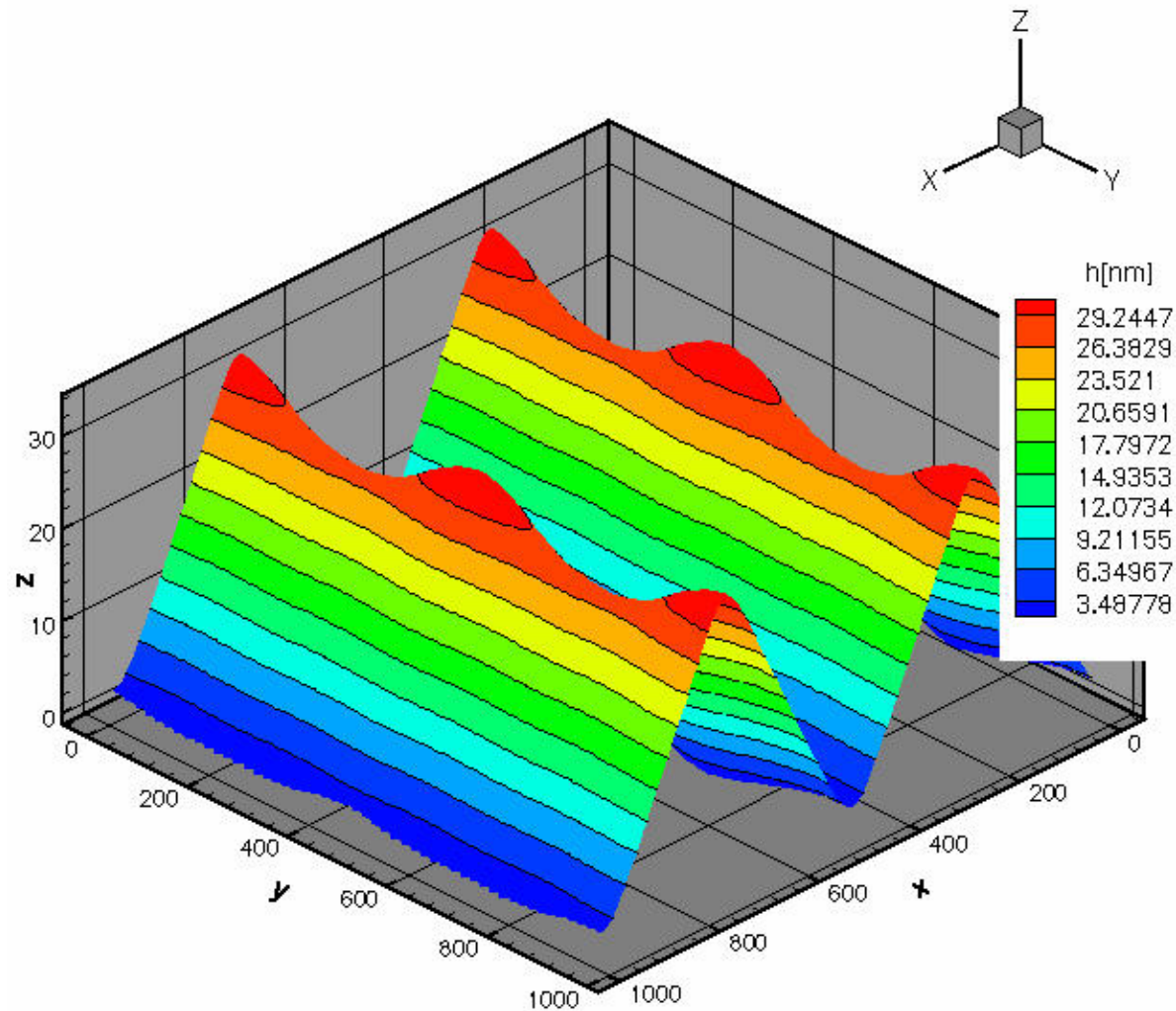
- Shallow waviness: $|\nabla h| < \varepsilon \ll 1$.
- Small thickness: $\langle h \rangle / d < \varepsilon \ll 1$, $d \equiv$ in-plane dimension.

- Asymptotic form of the elastic energy as $\varepsilon \rightarrow 0$:

$$E \sim - \int_{\Omega} \int_{\Omega} \frac{1}{2} G_{ik}(\mathbf{x} - \mathbf{x}') t_i(\mathbf{x}) t_k(\mathbf{x}') d\Omega d\Omega'$$

- Effective tractions: $t_i \sim -\sigma_{i\beta}^* h_{,\beta} - (h c_{i\beta kl} \epsilon_{kl}^p)_{,\beta}$.

Extension to strained-film growth



Surface profile snapshots, uniaxial misfit strain,
 $t = 0, 200, 300, 400, 500, 600$ s

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Extension to strained-film growth

- Elastic film, $h = \langle h \rangle + u$, linearize:

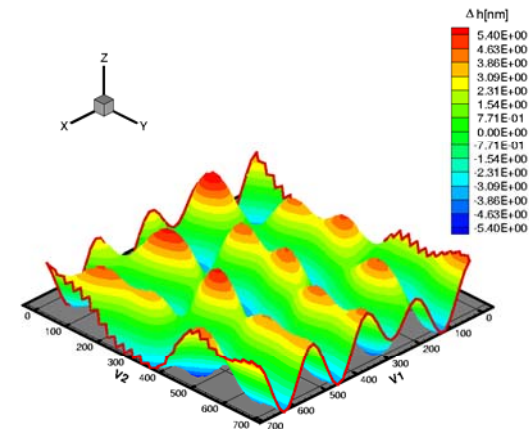
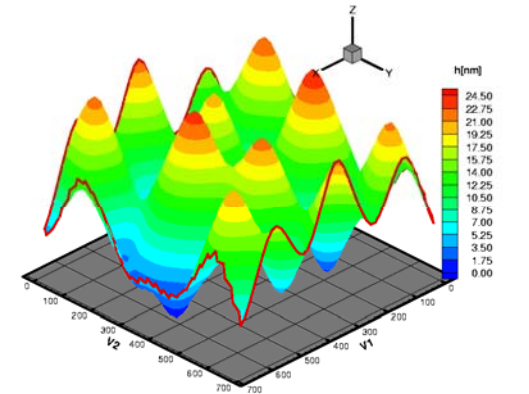
$$u_{,t} = -\nu \nabla^2 u - D \nabla^2 (\nabla^2 u - \gamma^{-1} U)$$
- Set: $u = A e^{\lambda t} e^{i \mathbf{k} \cdot \mathbf{x}}$
- Biaxial stress: $k_1 = k_2 = k$,

$$\lambda = -2\nu k^2 + 4Dk^4 - 4\sqrt{2}Dk^3\gamma^{-1}\sigma^{*2}/E'_s$$
- Steady profile: $\lambda = 0$,

$$k \sim \sqrt{2}\sigma^{*2}/\gamma E'_s, \quad \text{for } \sigma^* \text{ large.}$$
- Uniaxial stress: $\sigma_{11}^* = \sigma^*$, $k_1 = k$, $k_2 = 0$,

$$\lambda = -\nu k^2 + Dk^4 - 2Dk^3\gamma^{-1}\sigma^{*2}/E'_s$$
- Steady profile: $\lambda = 0$,

$$k \sim 2\sigma^{*2}/\gamma E'_s, \quad \text{for } \sigma^* \text{ large.}$$



Biaxial and uniaxial stress

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Summary and conclusions

- Continuum model of YBCO film growth predicts:
 - Initial Volmer-Weber island growth.
 - ‘Magic slope’.
 - $t^{1/3}$ coarsening law.
- Asymptotic expansion leads to simple expression for elastic energy in the limit of small thickness, shallow profile.
- The effects of elastic strain are:
 - Islands become more ‘dome-like’.
 - Islands tend to elongate and to align into lattices.
 - Coarsening rate is slowed down.
 - A stationary island size becomes possible.
- *Beyond shallow surfaces?* Grooving? Overhangs? Cracks?

Thank you!