INSTABILITIES AND SCALE INVARIANCE IN THE GROWTH OF NANOSTRUCTURES: MESOSCOPIC DESCRIPTIONS

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Talk delivered at Universität Göttingen, May 2003

Sketch of the talk

- Introduction
- Example I: Erosion by ion-beam sputtering

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  - Experimental results
  - Discrete approach
  - Continuum approach
  - Discussion
- Example II: Dynamics of steps on vicinal surfaces

  T. ALA-NISSILA, M. CASTRO, I. KOPONEN, M. RUSANEN
- Conclusions

Introduction

Systems of nanoscopic dimensions feature:

- Fluctuations: thermal origin or externally driven (flux of aggregating units)
- Instabilities $\rightsquigarrow$ pattern formation

Theory of growth has to study the interplay between both trends

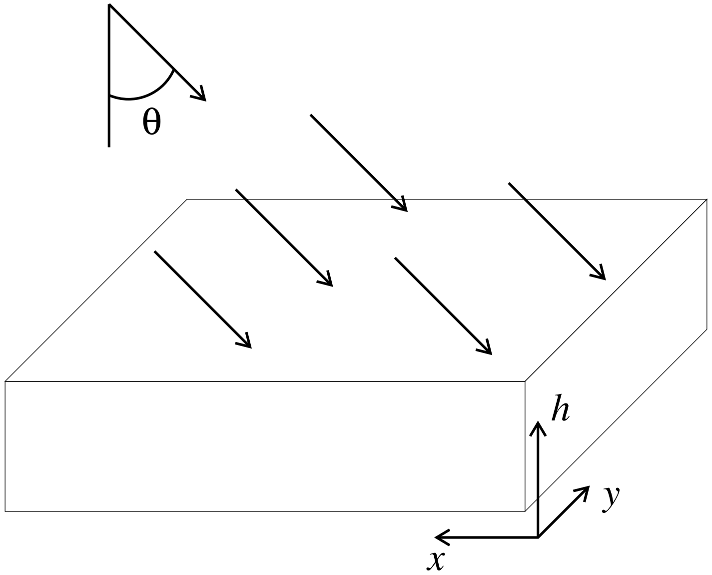
Tools: Non-equilibrium Statistical Mechanics

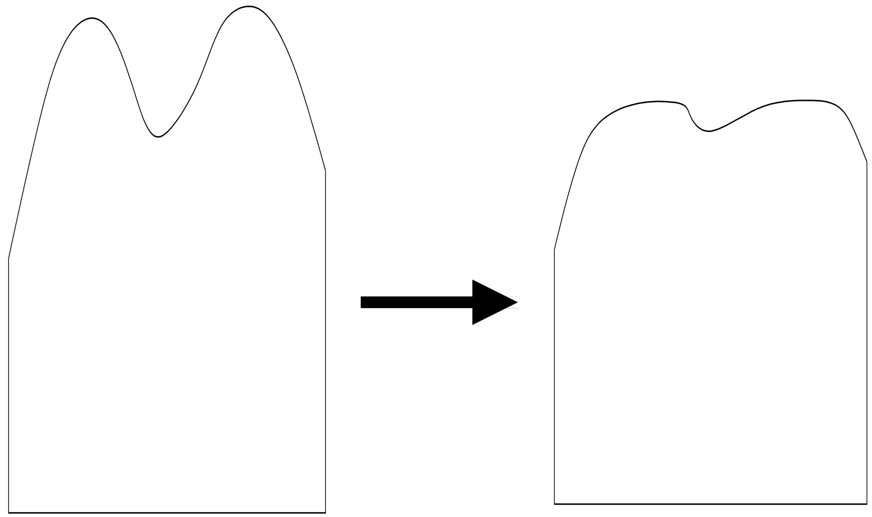
Focus: Coarse-grained description, sensitive to fluctuation effects

Outcome: Universal properties (scaling of fluctuations); also preasymptotic features, relevant to system specifics

Example I: Erosion by ion-beam sputtering

Removal of material from surfaces through the impact of energetic particles





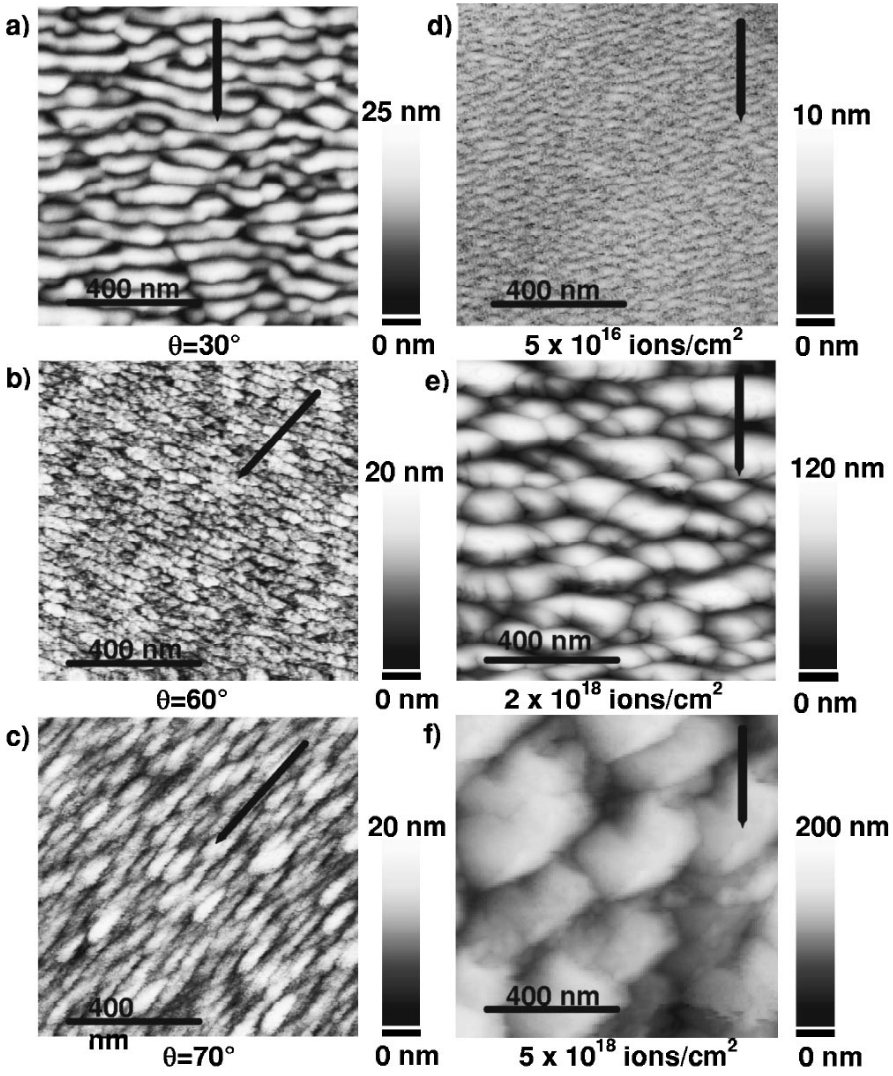
Expect “*pattern removal*” . . .

Employed traditionally for

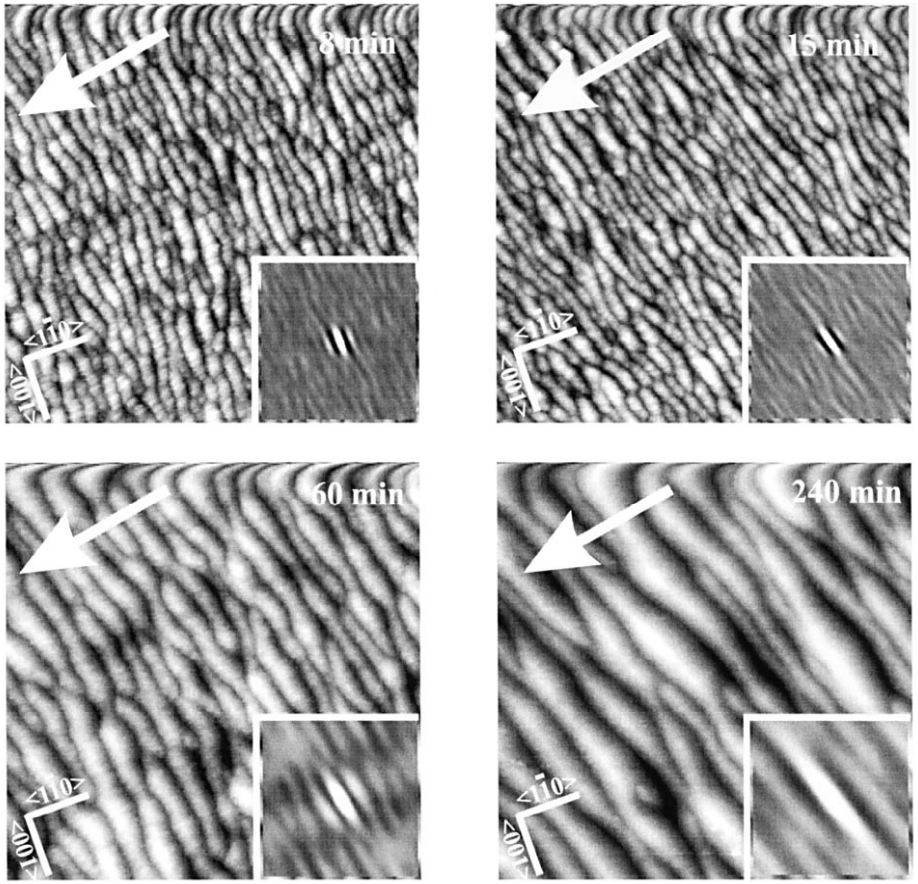
- film fabrication
- surface and depth microanalysis
- surface cleaning and micromachining

Pattern formation

$$\theta \neq 0 \Longrightarrow \textit{ripples}$$

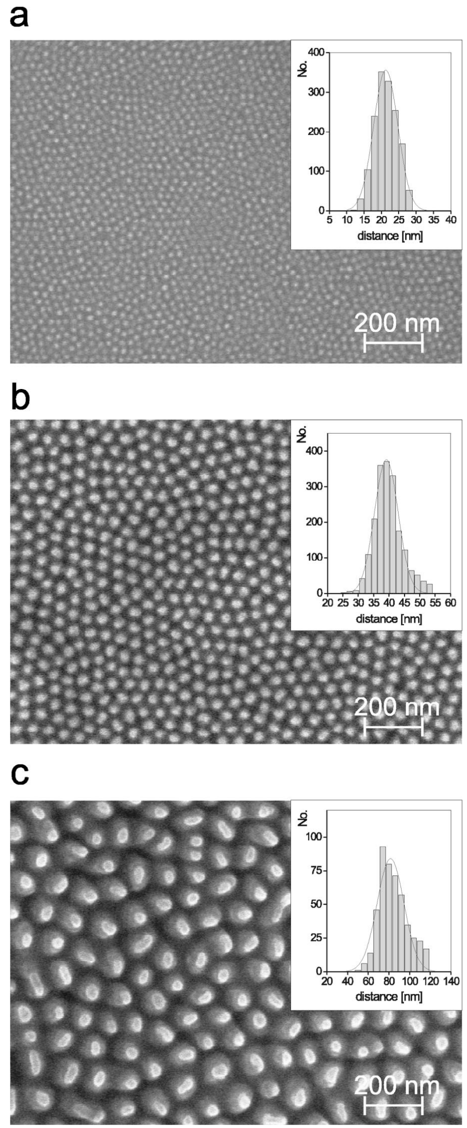


HABENICHT ET AL, PRB '99: 5 keV Xe^+ graphite

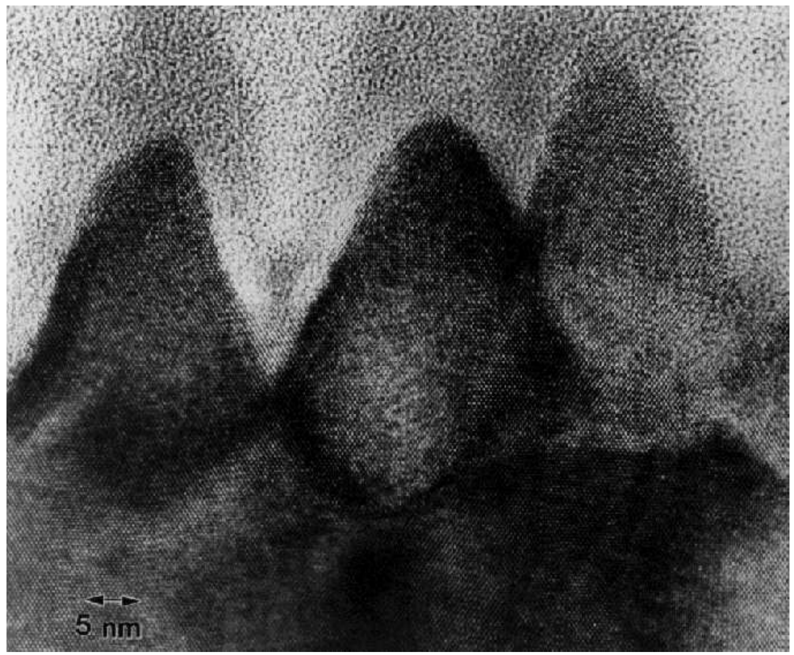


RUSPONI ET AL, PRL '98: 1 keV Ar^+ Cu(110)

$\theta \equiv 0 \Longrightarrow dots$

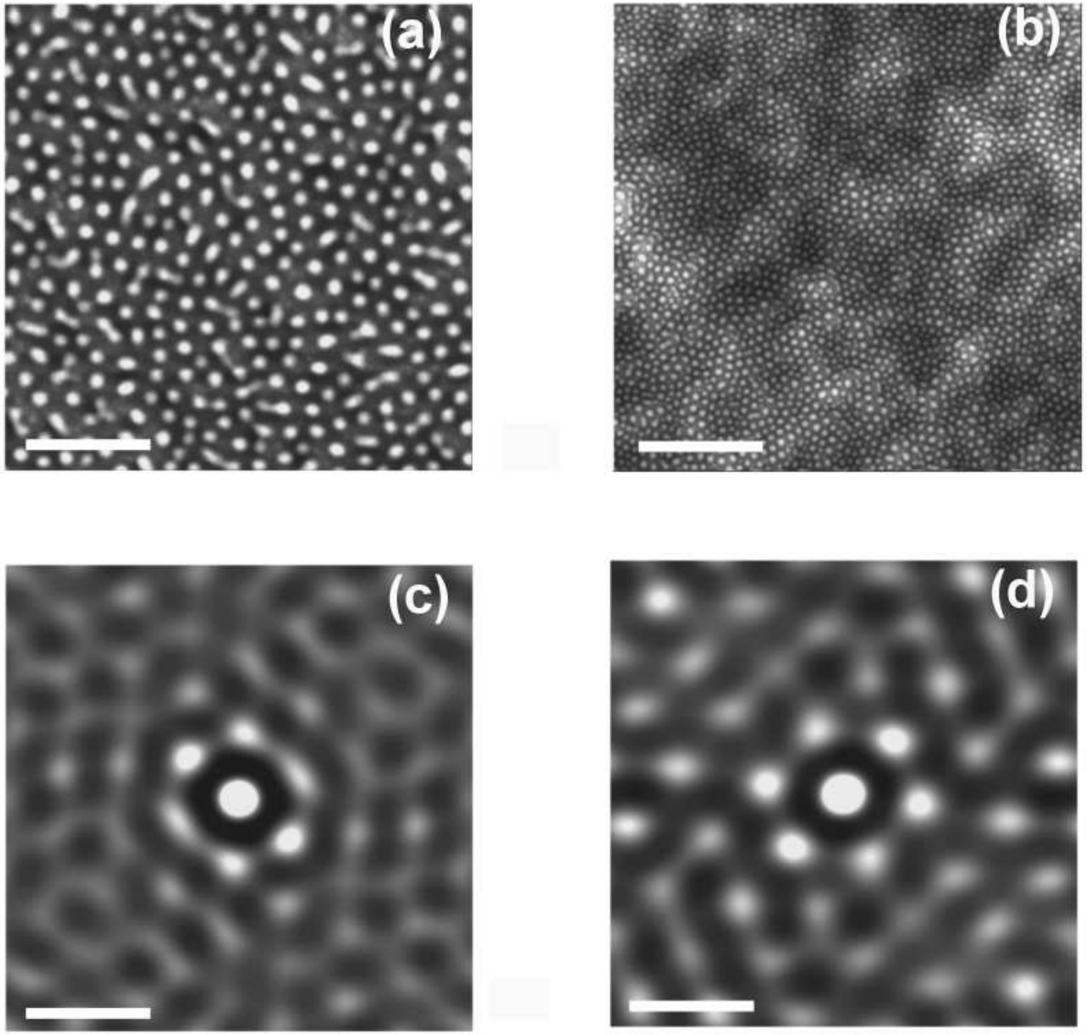


FACSKO ET AL, PRB '02: Ar^+ GaSb



FACSKO ET AL, Science '99: 420 eV Ar^+ GaSb

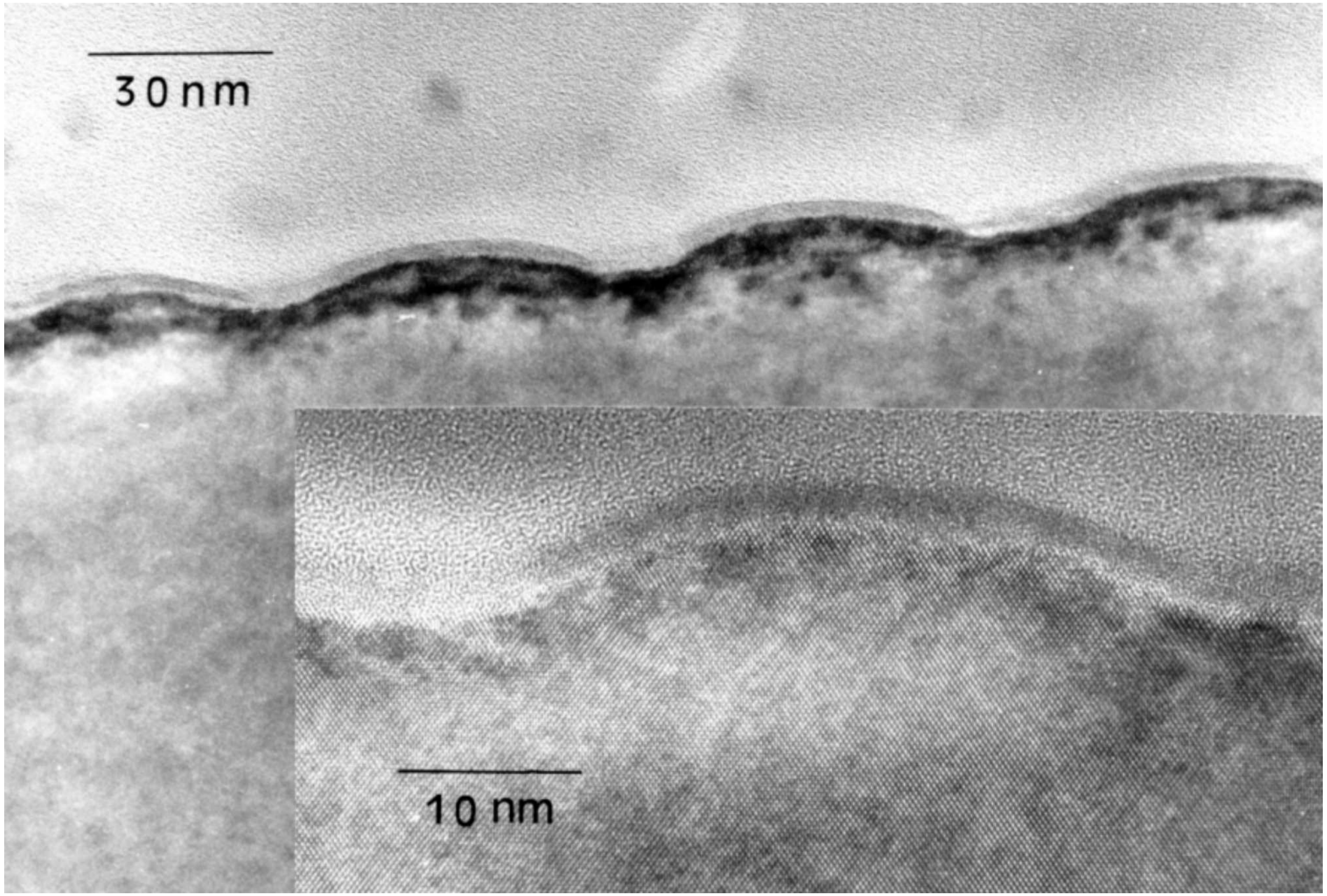
Also obtained on Si



GAGO ET AL, APL '01: 1.2 keV Ar^{+} Si

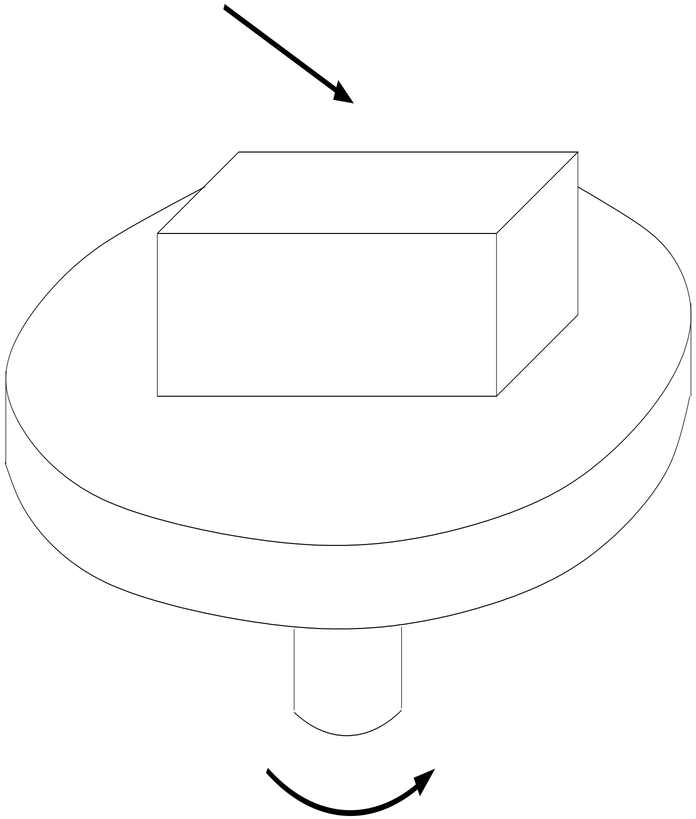
Times: 6 min [(a): 1×1 μm^2]; 960 min [(b): 3×3 μm^2]

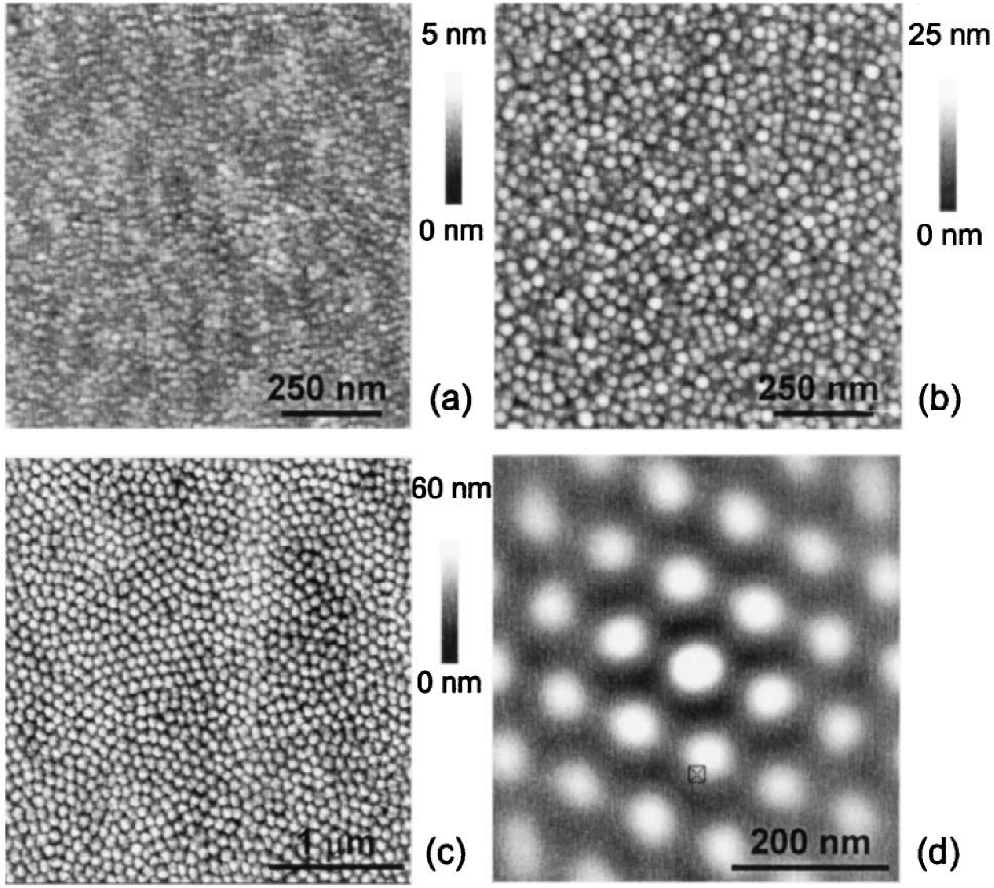
(c), (d): two-dimensional autocorrelation functions over 400×400 μm^2 areas



GAGO ET AL, APL '01: 1.2 keV Ar^+ Si

Can also be obtained for *rotating* targets and $\theta \neq 0$





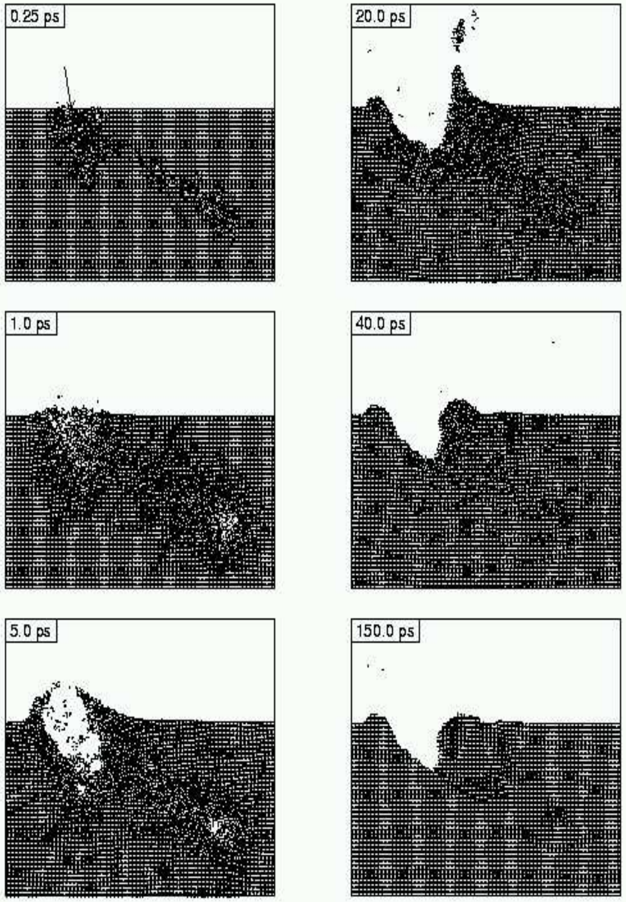
FROST ET AL, PRL '00: 500 eV Ar^+ InP

Times: 10 s (a); 40 s (b); 9600 s (c)

(d) two-dimensional autocorrelation function

Microscopic approach

Highly complex many-body process



Typical scales in Molecular Dynamics

- Time $\approx 10^{-1} - 10^{2}$ ps
- Length $\approx 10 - 100$ Å
- Number of atoms $\approx 10^{5}$

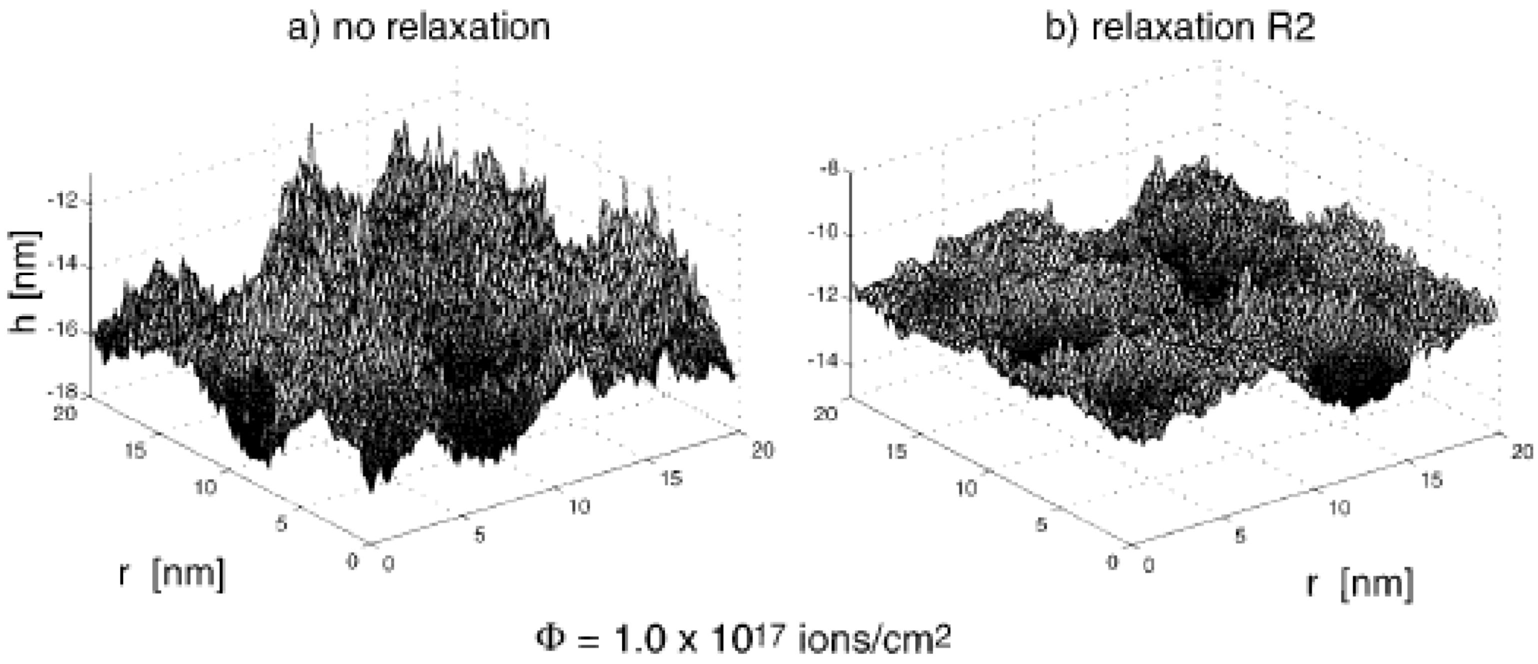
Typical scales in experiments

- Time $\approx 1 - 10^{3}$ s
- Length $\approx 10 - 100$ nm

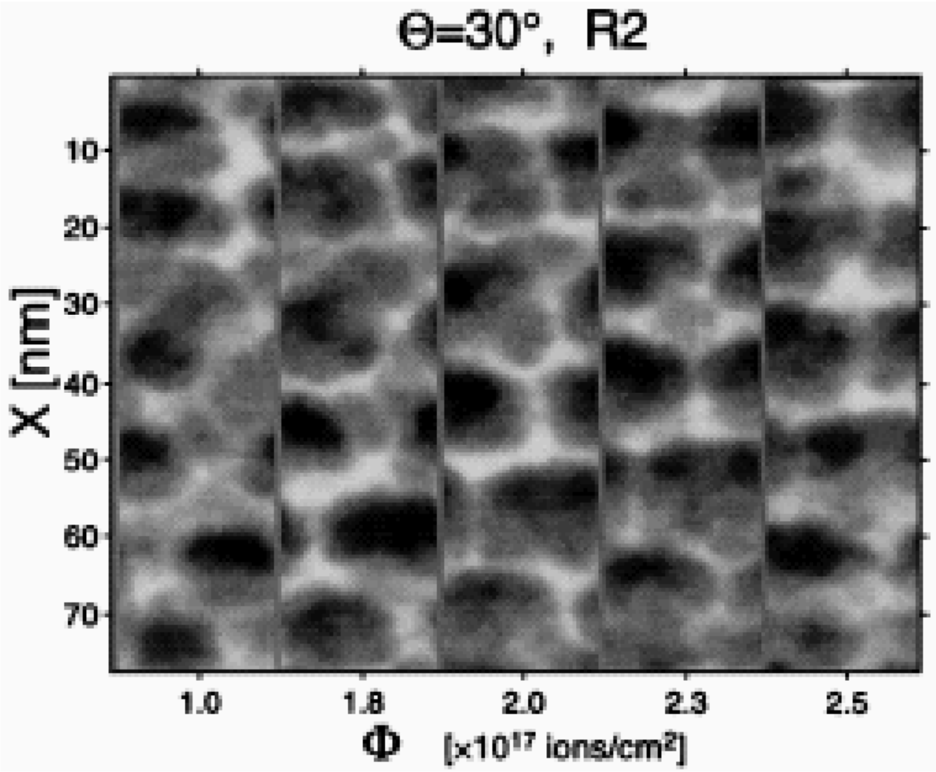
BRINGA ET AL, PRB '01: MD simulation 100 keV Xe onto Au

Kinetic Monte Carlo

Trans. probabilities $W(\mathrm{conf} \to \mathrm{conf}') = \sum_{a=1}^{N} R_a V^a(\mathrm{conf} \to \mathrm{conf}')$



KOPONEN ET AL, PRB '96: 5 keV Ar onto carbon

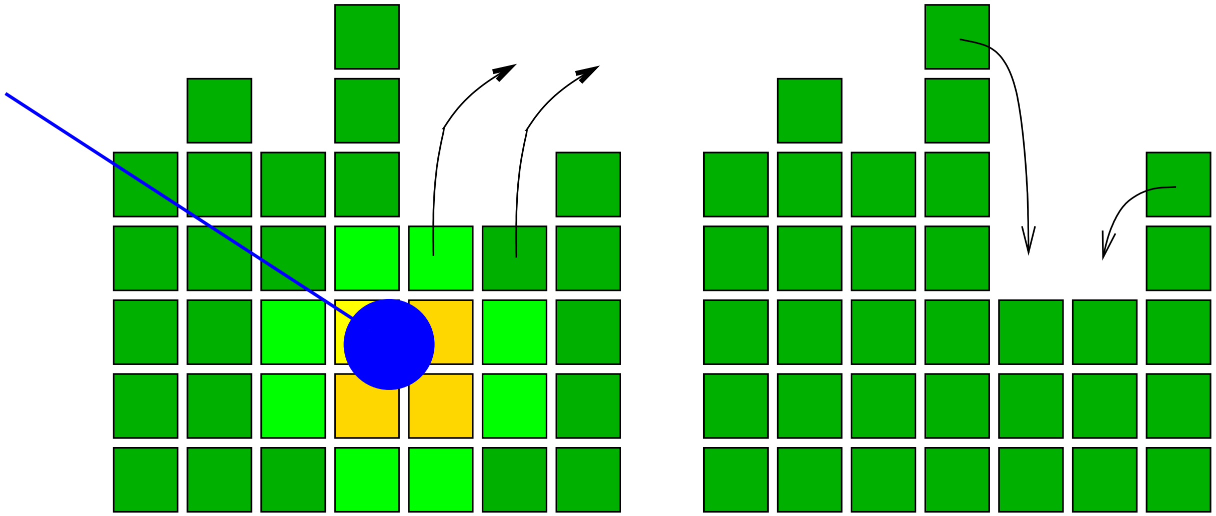


Typical scales in kinetic Monte Carlo

- Time $\approx 1\ \mu$s ($\approx 10^6$ cascades)
- Length ≈ 30 nm

KOPONEN ET AL, PRL '97: kMC simulation 5 keV Ar onto carbon

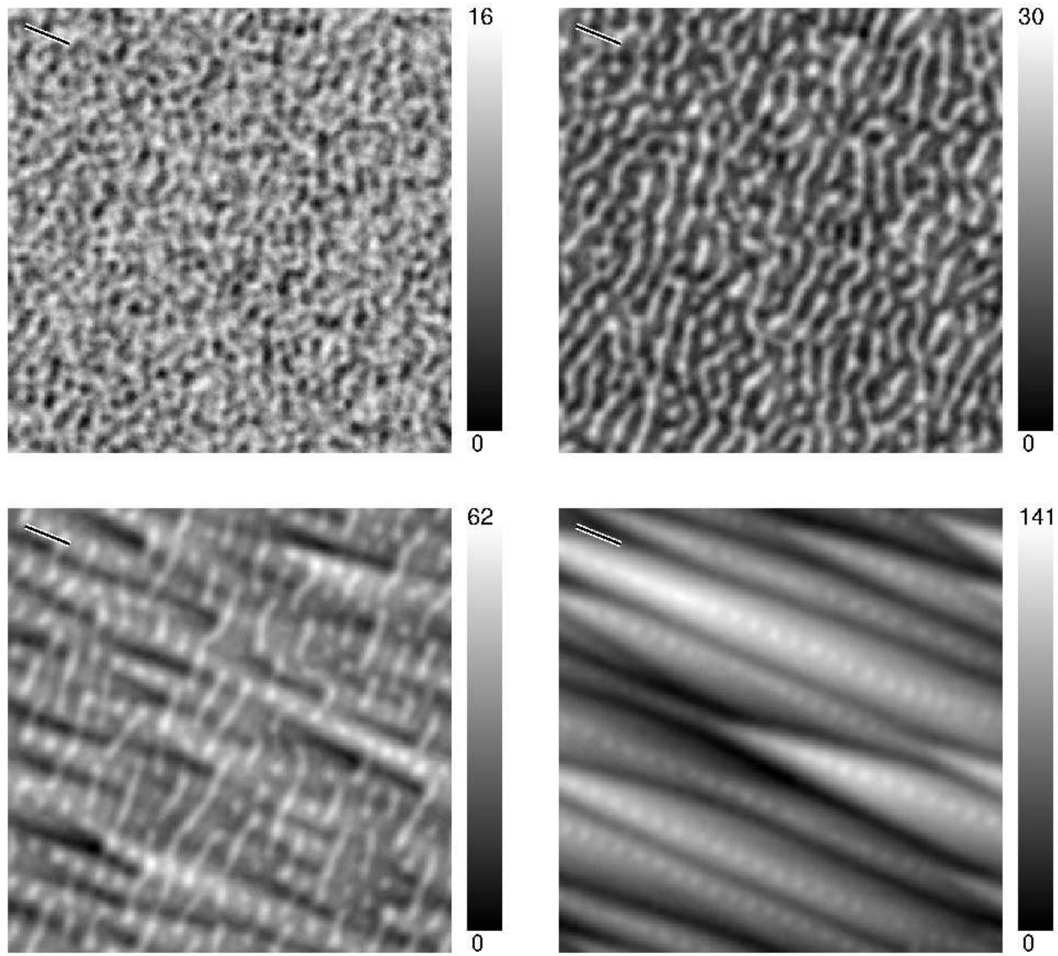
More *coarse-grained* approaches



$$E(x', y', z') = \frac{\epsilon}{(2\pi)^{3/2}\sigma\mu^2} \exp\left(-\frac{(z'+a)^2}{2\sigma^2} - \frac{x'^2+y'^2}{2\mu^2}\right)$$

"Linear cascade" approximation, P. SIGMUND, PR (1969)

Erosion probability $\propto$ Total energy



(a) 3 ML removed

(b) 30 ML

(c) 300 ML

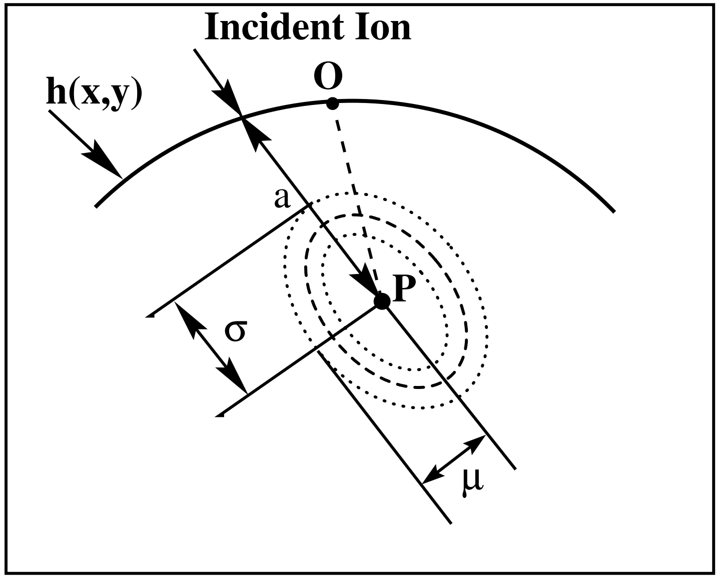
(d) 10^4 ML

HARTMANN ET AL, PRB ‘02

Mesoscopic description

Goal: Compute local erosion velocity

$$v = \frac{\partial h}{\partial t} = \mathcal{V}(\varphi, a, \mu, \sigma, T, J, \ldots)$$

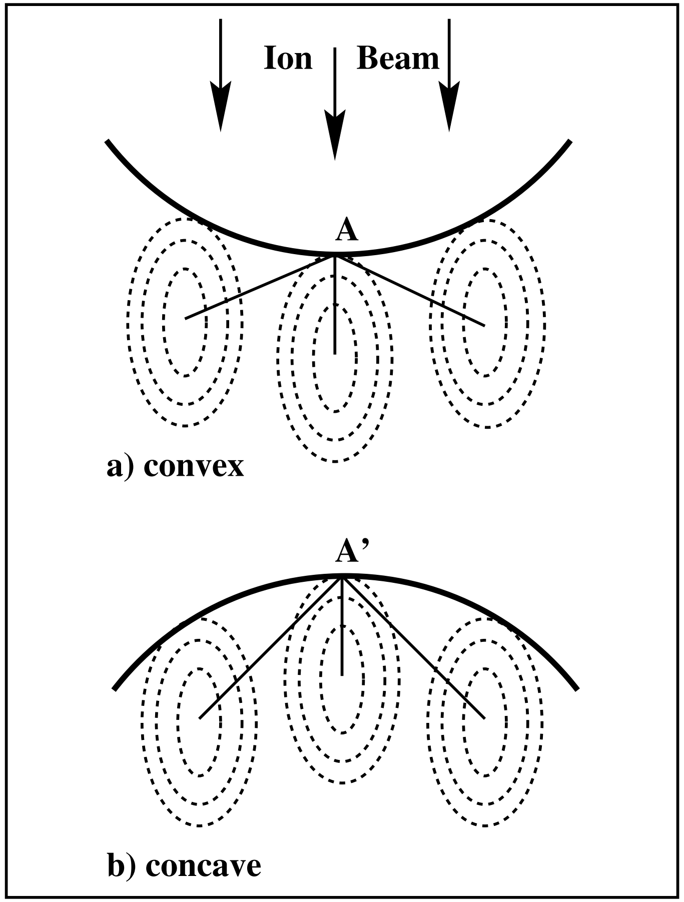


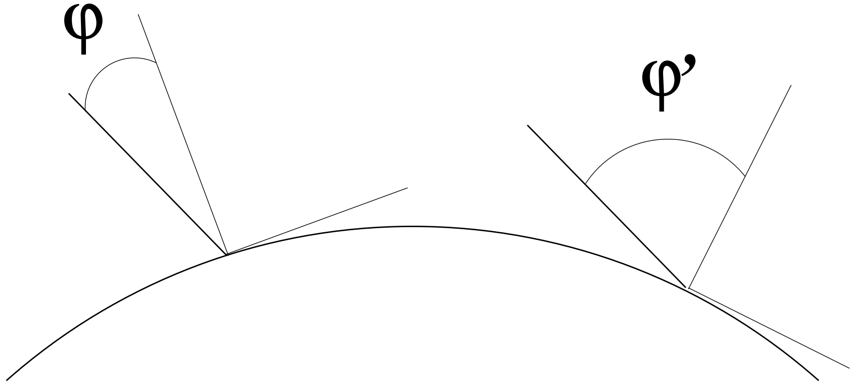
$$E(x', y', z') = \tfrac{\epsilon}{(2\pi)^{3/2}\sigma\mu^2} \exp\left(-\tfrac{(z'+a)^2}{2\sigma^2} - \tfrac{x'^2+y'^2}{2\mu^2}\right)$$

$$v = p \int_{\mathcal{R}} \mathrm{d}\mathbf{r}\, \Phi(\mathbf{r})\, E(\mathbf{r})$$

Perform expansion for small slopes $|\nabla h| \ll 1$

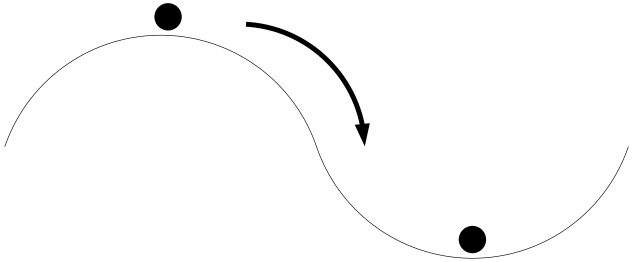
Two important facts:





- Surface features are *amplified* $\rightsquigarrow$ instability
- Effective angle of incidence varies across the surface

Surface diffusion (MULLINS, HERRING '50's)



$$
\begin{aligned}
\vec{\jmath} &= -\nabla \mu \\
\mu &\propto \kappa \quad \text{(curvature)} \simeq -\nabla^2 h
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial h}{\partial t} &= -\nabla \cdot \vec{\jmath} \\
&= -\nabla \cdot (\nabla \nabla^2 h) = -\nabla^4 h
\end{aligned}
$$

In general κ may be anisotropic (metals)

Noise

$$
\frac{\partial h}{\partial t} = \mathcal{F}(h, \nabla h, \ldots) + \eta(\mathbf{r}, t)
$$

$$
\begin{aligned}
\langle \eta \rangle &= J \quad \text{(flux)} \\
\langle \eta(\mathbf{r}, t) \eta(\mathbf{r}', t') \rangle &\simeq J \, \delta(\mathbf{r} - \mathbf{r}') \, \delta(t - t')
\end{aligned}
$$

Full dynamics

(Anisotropic, stochastic) Kuramoto-Sivashinsky equation

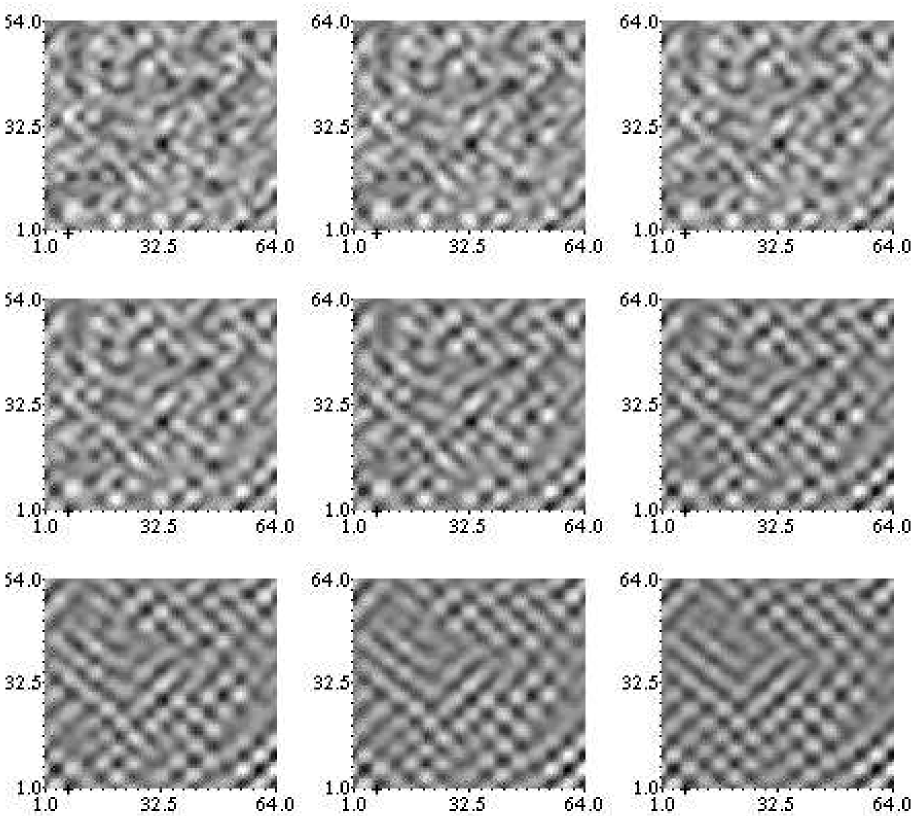
$$\frac{\partial h}{\partial t} = \underbrace{\nu_x \partial_x^2 h + \nu_y \partial_y^2 h}_{\text{“surface tension”}} \underbrace{- D_{xx} \partial_x^4 h - D_{yy} \partial_y^4 h - D_{xy} \partial_x^2 \partial_y^2 h}_{\text{“surface diffusion”}} + \underbrace{\lambda_x (\partial_x h)^2 + \lambda_y (\partial_y h)^2}_{\text{lateral growth}} + \eta$$

Comments

- All coefficients (ν_x, D_{xx}, λ_x) are functions of parameters θ, a, σ, μ, T, J.
- $\nu_y < 0 \quad \forall \theta$ ($\Rightarrow$ *instability*); ν_x changes sign with θ
- $D_{ij} = d_{ij} + \mathcal{K}_{ij}$ with $\begin{cases} d_{ij} \propto \epsilon, \text{ indep. of } T \\ \mathcal{K}_{ij} \propto \frac{1}{T} \exp(-E_{ij}/k_B T) \end{cases}$
- For $\theta = 0$ symmetry is restored in (x, y) plane
  $\Rightarrow \nu_x = \nu_y; \quad \lambda_x = \lambda_y; \quad d_{xx} = d_{yy}; \quad d_{xy} = 0$
- ν_i, D_{ij}, $\lambda_k \propto \epsilon$

Linear theory for $\theta \neq 0$

$$\frac{\partial h}{\partial t} = -|\nu|\nabla^2 h - D\nabla^4 h$$



$$h(k,t) \propto \exp(\omega_k t)$$

$$\omega_k = |\nu|k^2 - Dk^4$$

There exists $k^* \equiv \sqrt{|\nu|/D}$ such that:

$k > k^*$ stable modes

$k < k^*$ unstable modes

$k_0 = k_*/\sqrt{2}$ has a *maximal* growth rate ω_{k_0}

The amplitude of k_0 dominates exponentially fast $\Rightarrow$ *dot structure*

No *hexagonal* ordering

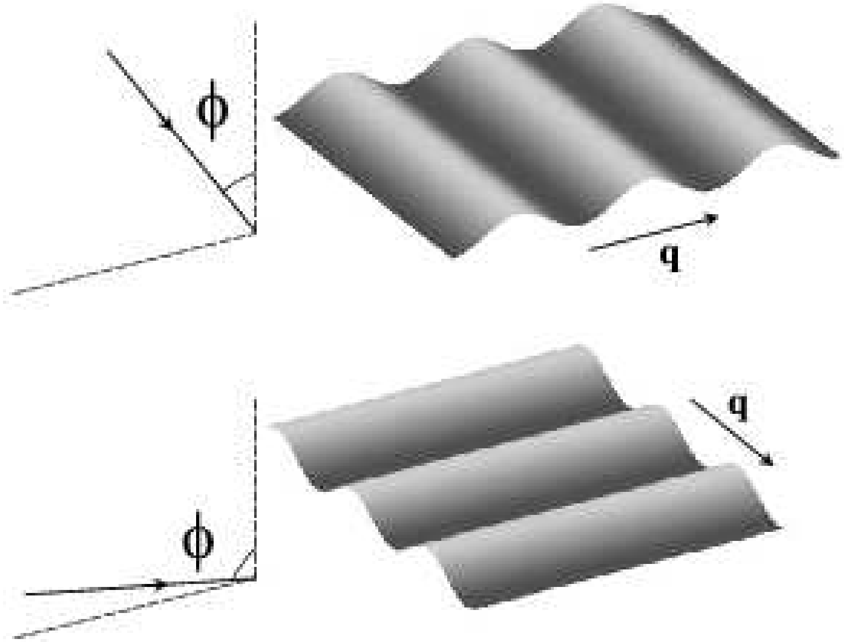
Linear theory for $\theta \neq 0$

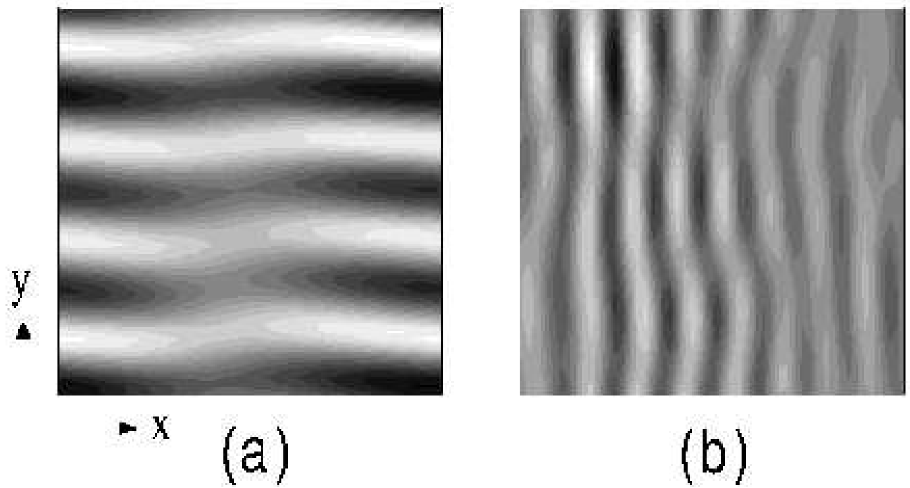
(Bradley & Harper, JVSTA '88)

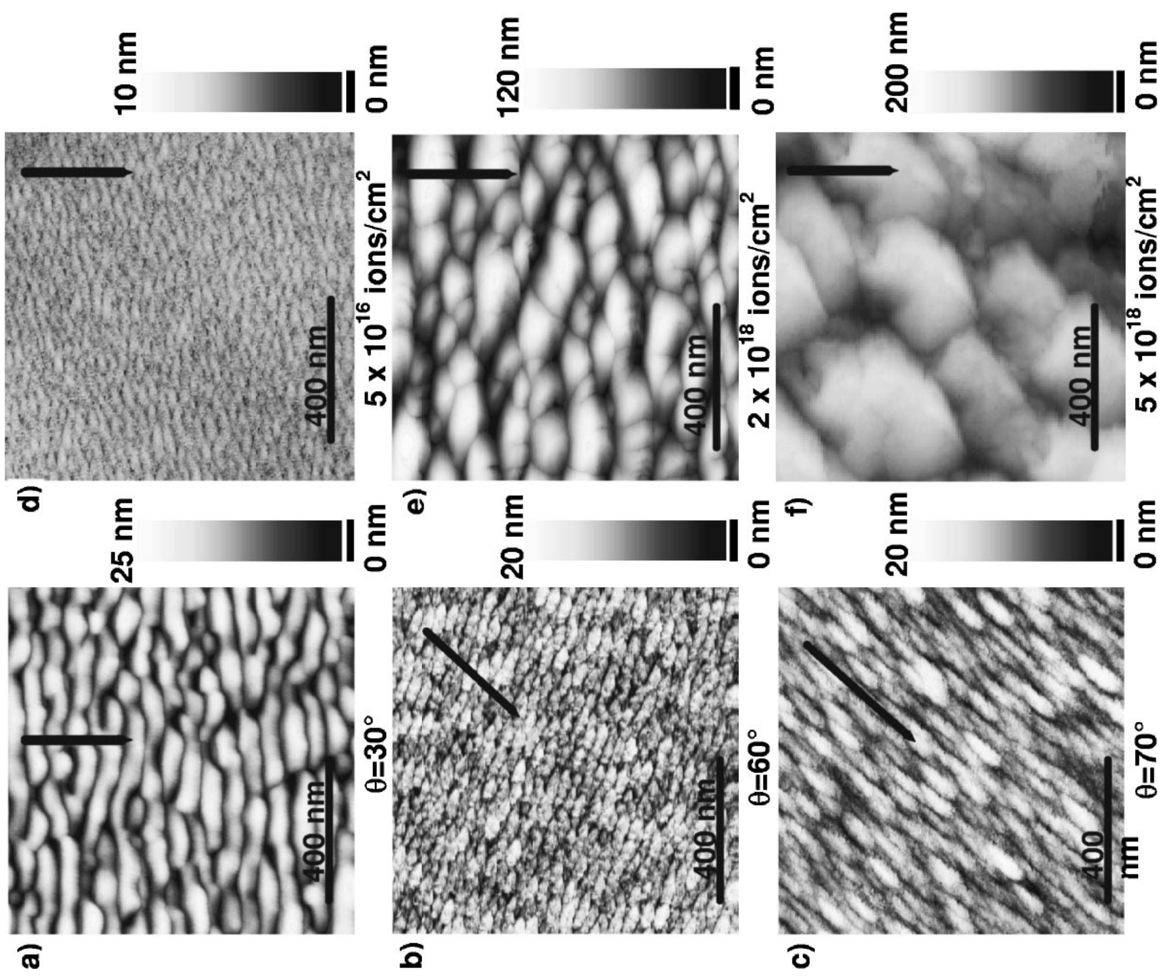
$$h(k,t) \propto \exp\left[(-\nu_x k_x^2 + |\nu_y| k_y^2 - \mathcal{K} k^4)t\right]$$

Small θ: $\nu_x < \nu_y < 0$

Large θ: $\nu_y < \nu_x$ and $\nu_y < 0$

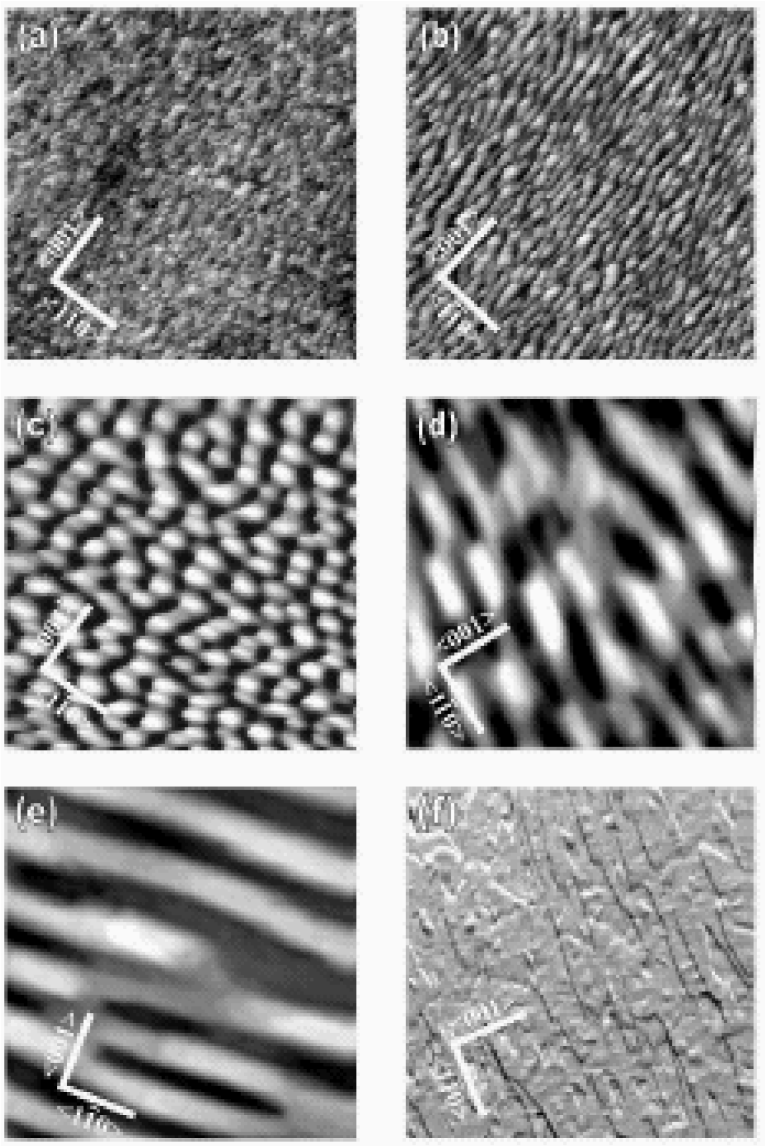






a)
400 nm
θ=30°
25 nm
0 nm
b)
400 nm
θ=60°
20 nm
0 nm
c)
400 nm
θ=70°
20 nm
0 nm
d)
400 nm
5 x 10^16 ions/cm^2
10 nm
0 nm
e)
400 nm
2 x 10^18 ions/cm^2
120 nm
0 nm
f)
400 nm
5 x 10^18 ions/cm^2
200 nm
0 nm

Effects of anisotropy

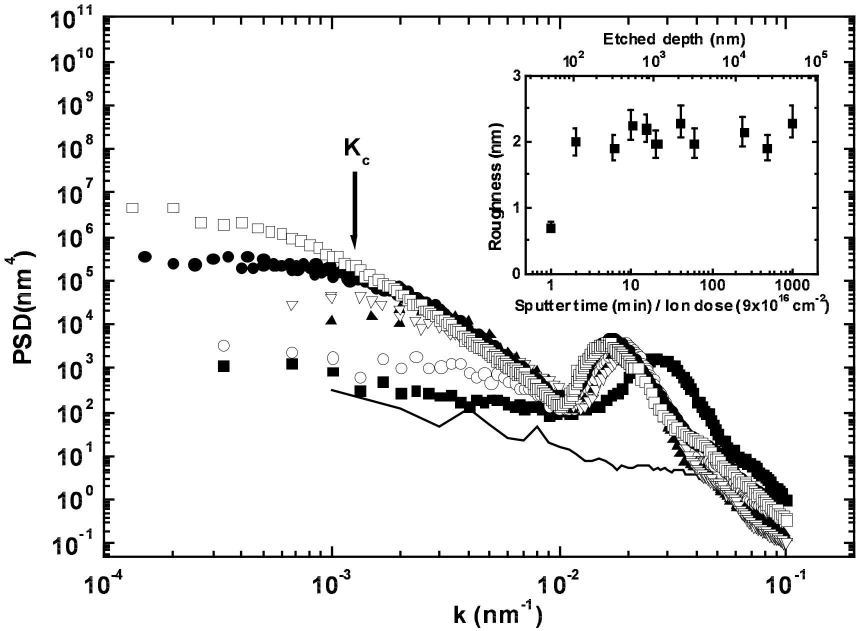


COSTANTINI ET AL, JPC '01: 1 keV Ar^+ Ag(110)

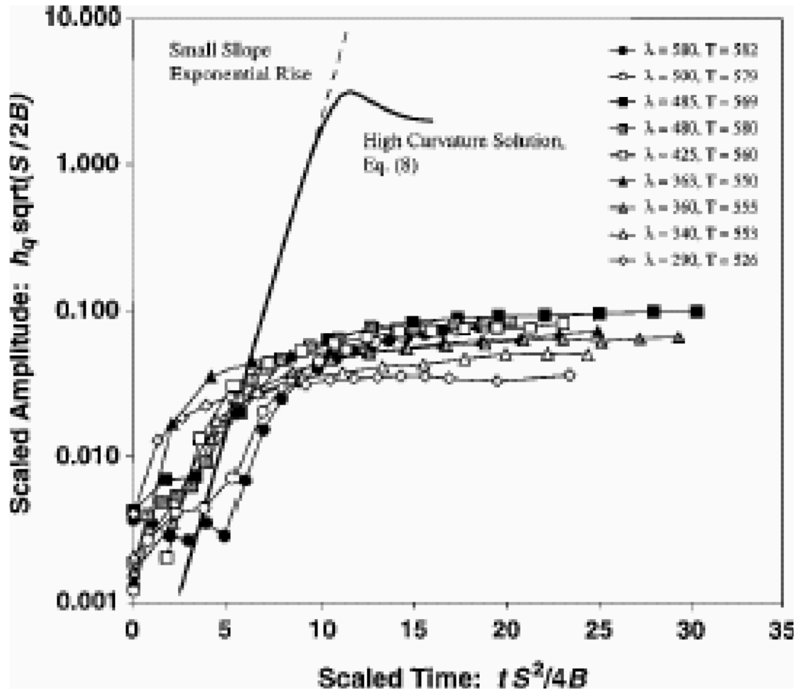
When surface diffusion is thermally activated ($d_{ij} = 0$), anisotropies $[E_{ij}(T)]$ allow selection of ripple direction by tuning T

Limitations of BH (linear) theory

The actual surface (rms) roughness *saturates* with time, rather than *diverge* exponentially



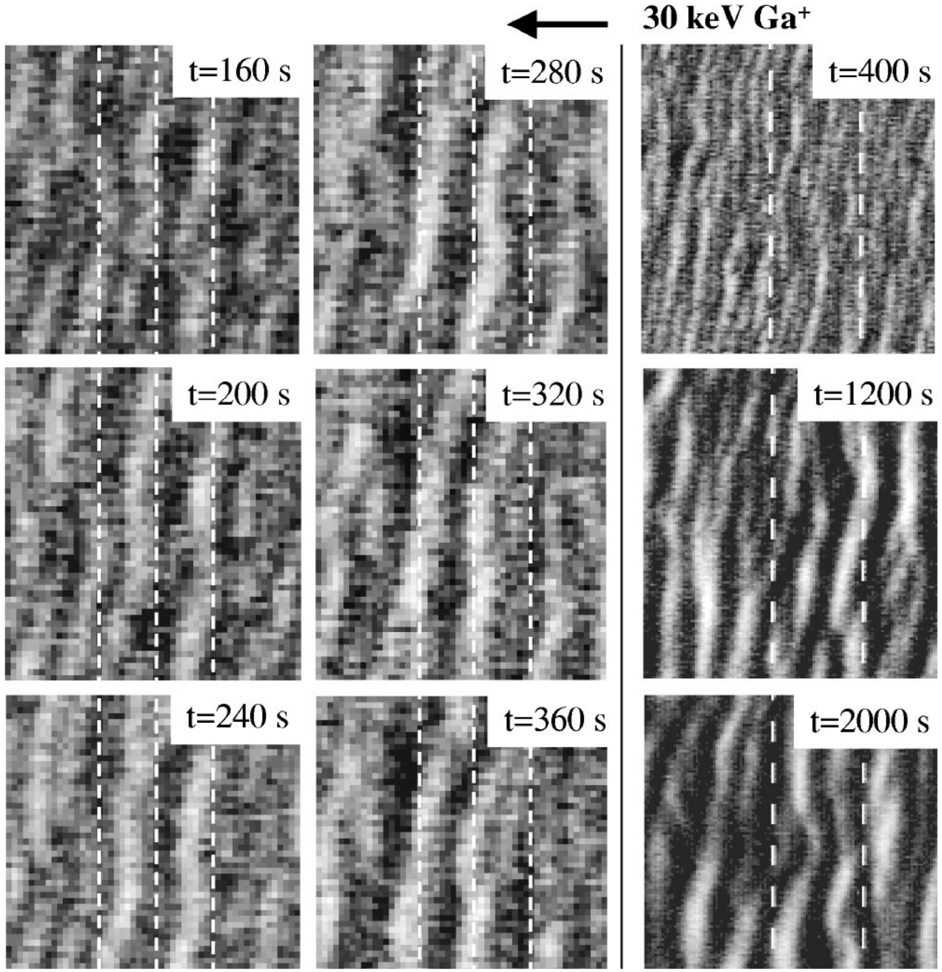
GAGO ET AL, APL '02: 1.2 keV Ar, Si

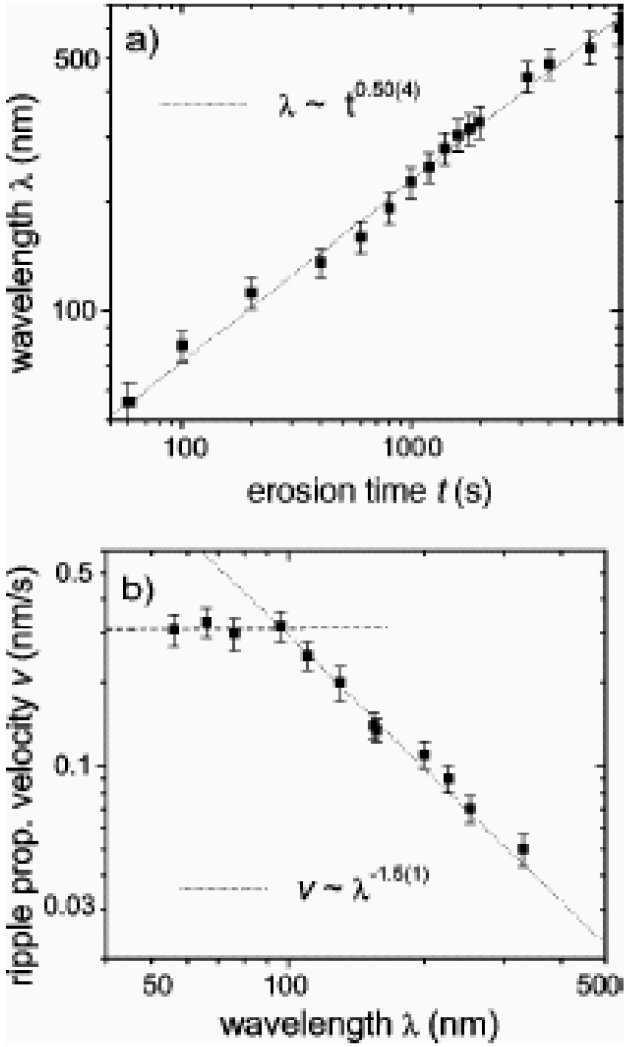


ERLEBACHER ET AL, JVSTA '00: 750 eV Ar, Si

Limitations of BH (linear) theory

The actual ripple amplitude *coarsens* with time, rather than *stay* constant



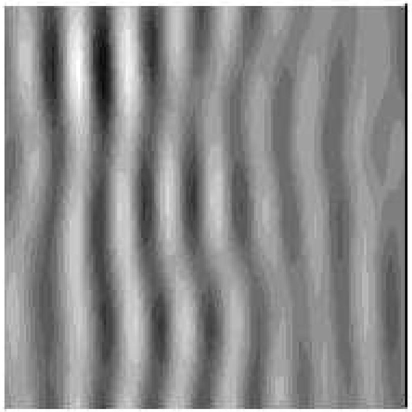


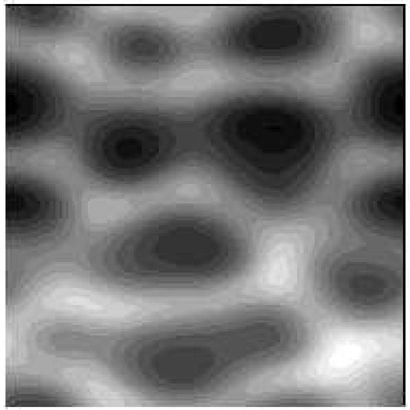
HABENICHT ET AL, PRB '02: 30 keV Ga onto Si

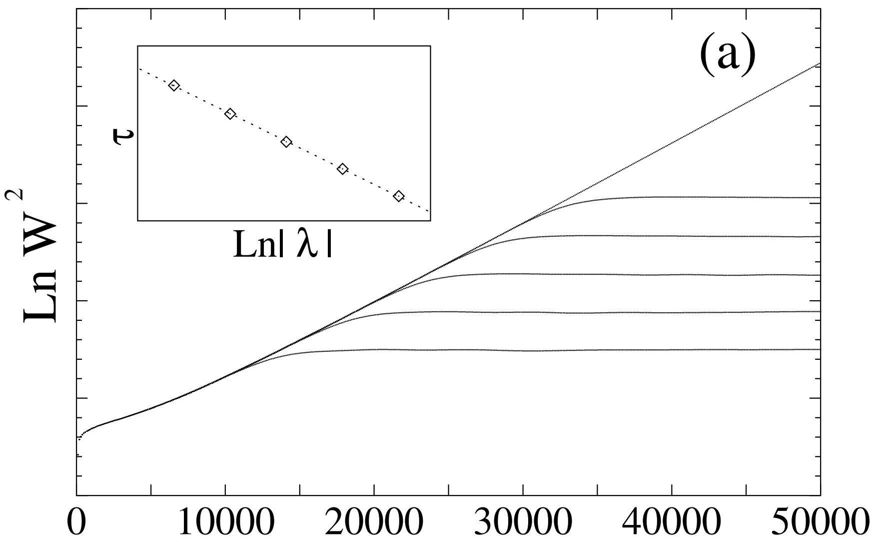
Rodolfo Cuerno, Universidad Carlos III de Madrid

Non-linear dynamics ($\theta \neq 0$)

$\lambda_x \lambda_y > 0$







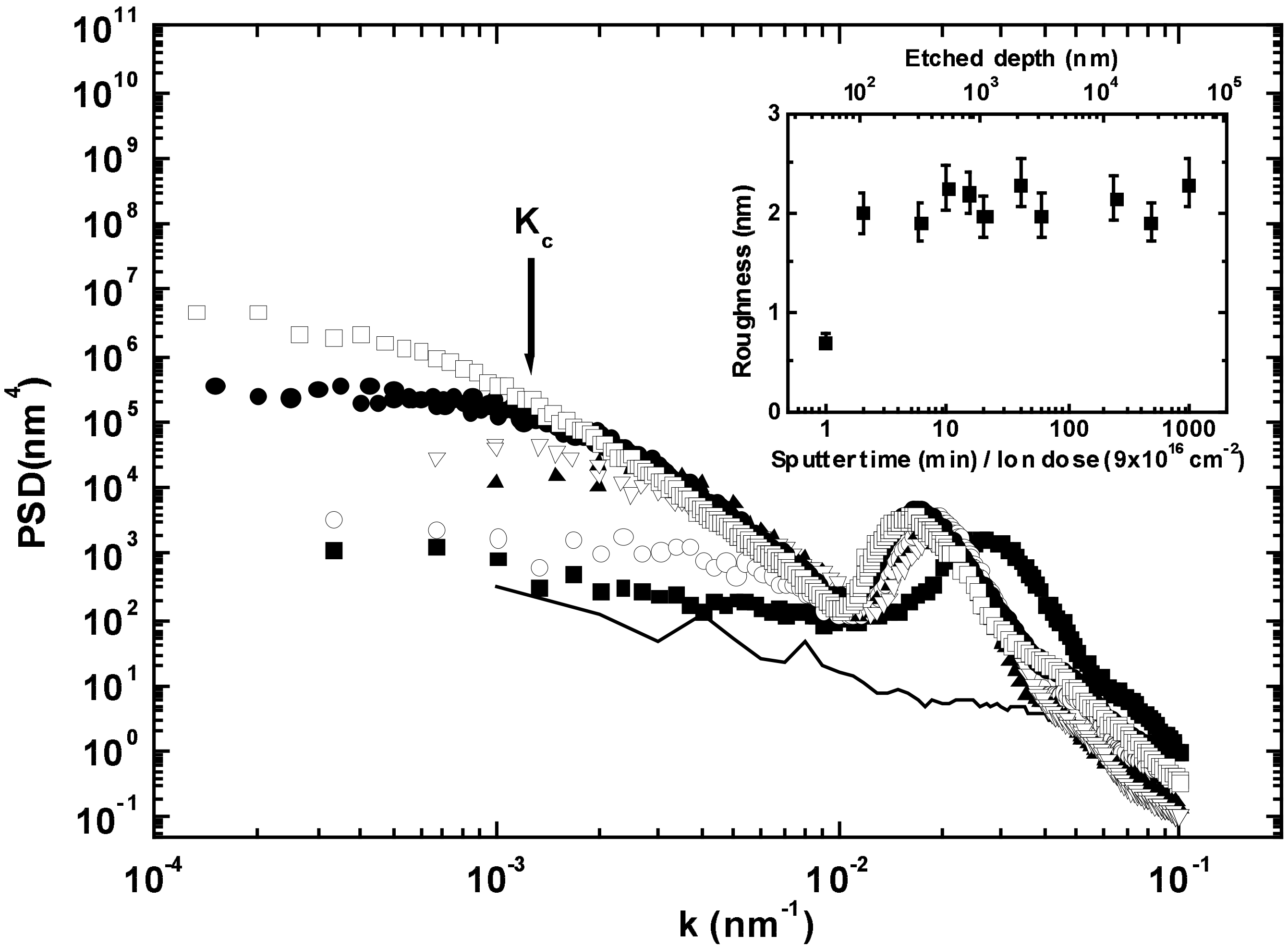
PARK ET AL, PRL '99

Crossover time τ = onset for kinetic roughening

$$\nu \partial_x h \sim \lambda (\partial_x h)^2 \Rightarrow \nu \frac{W_0}{\ell^2} \sim \lambda \frac{W_0^2}{\ell^2} \quad \Rightarrow \quad \left. \begin{array}{l} W_0 \sim \nu/\lambda \\ W_0 \sim \exp(\nu\tau/\ell^2) \end{array} \right\} \Rightarrow \tau \sim \frac{\mathcal{K}}{\nu} \log(\nu/\lambda)$$

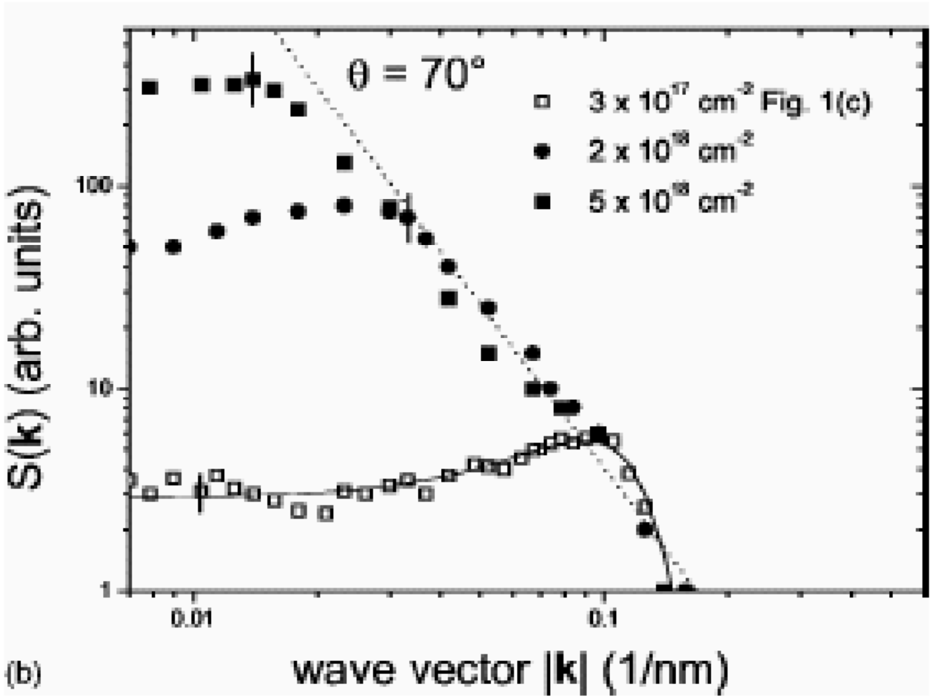
Talk delivered at Universität Göttingen, May 2003

Kinetic roughening

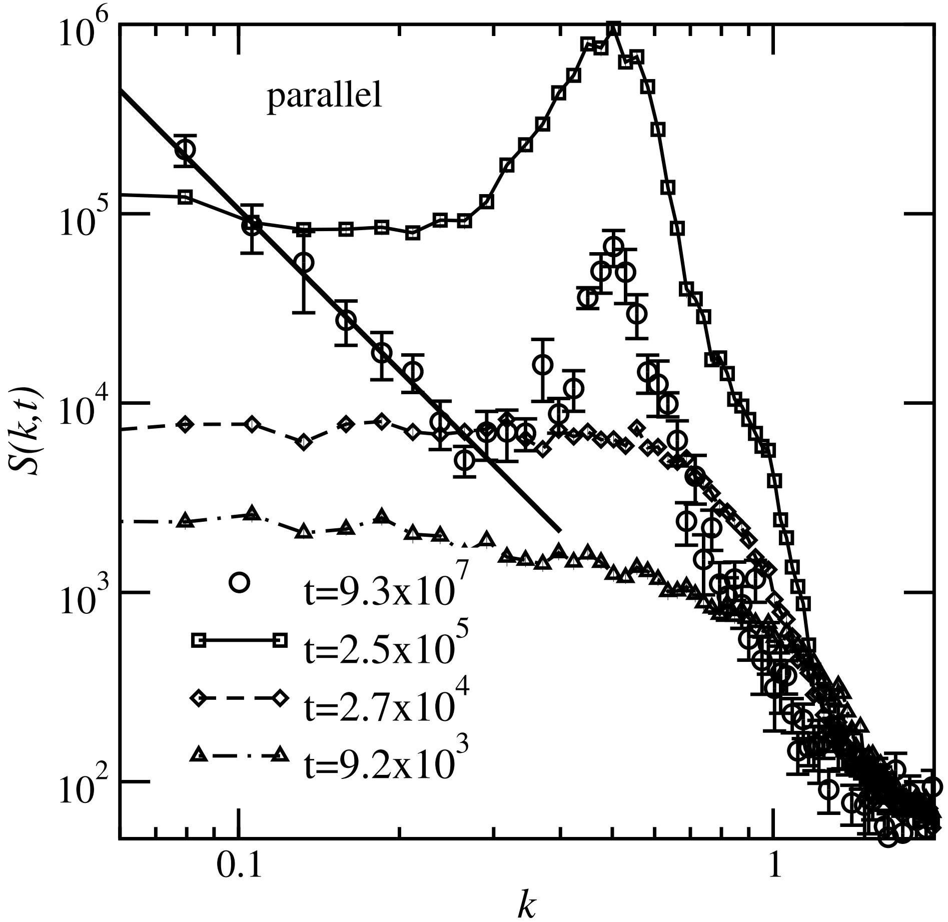


GAGO ET AL, APL '02: Ar onto Si

Kinetic roughening (2)

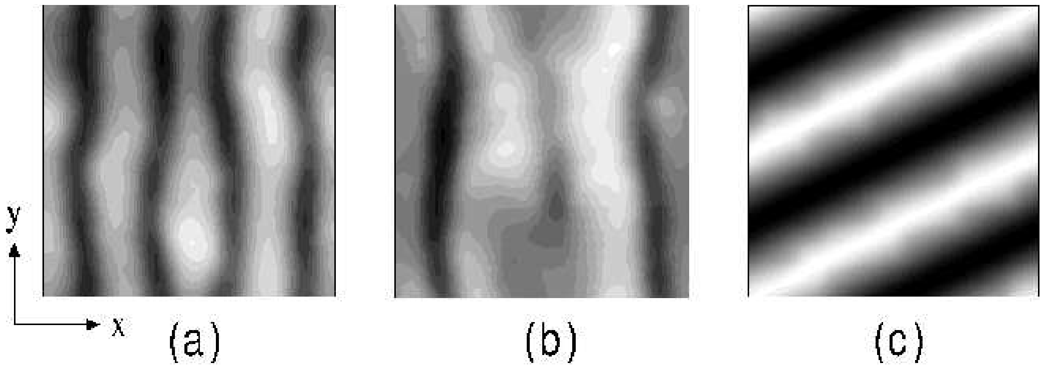


HABENICHT ET AL, PRB '99: 5 keV Xe^{+} graphite

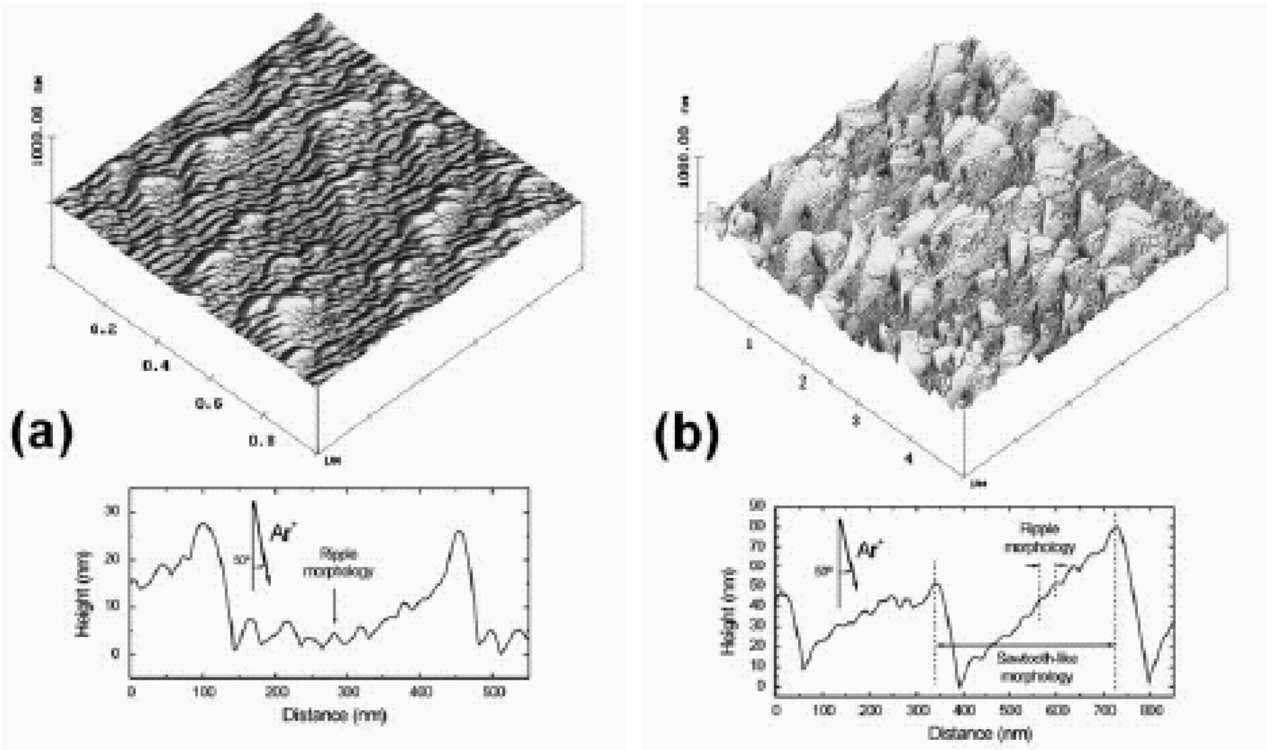


HARTMANN ET AL, PRB '02: MD simulations

$\boxed{\lambda_x \lambda_y < 0}$ Ripples prevail with *large roughness*: *shadowing* effects may be relevant



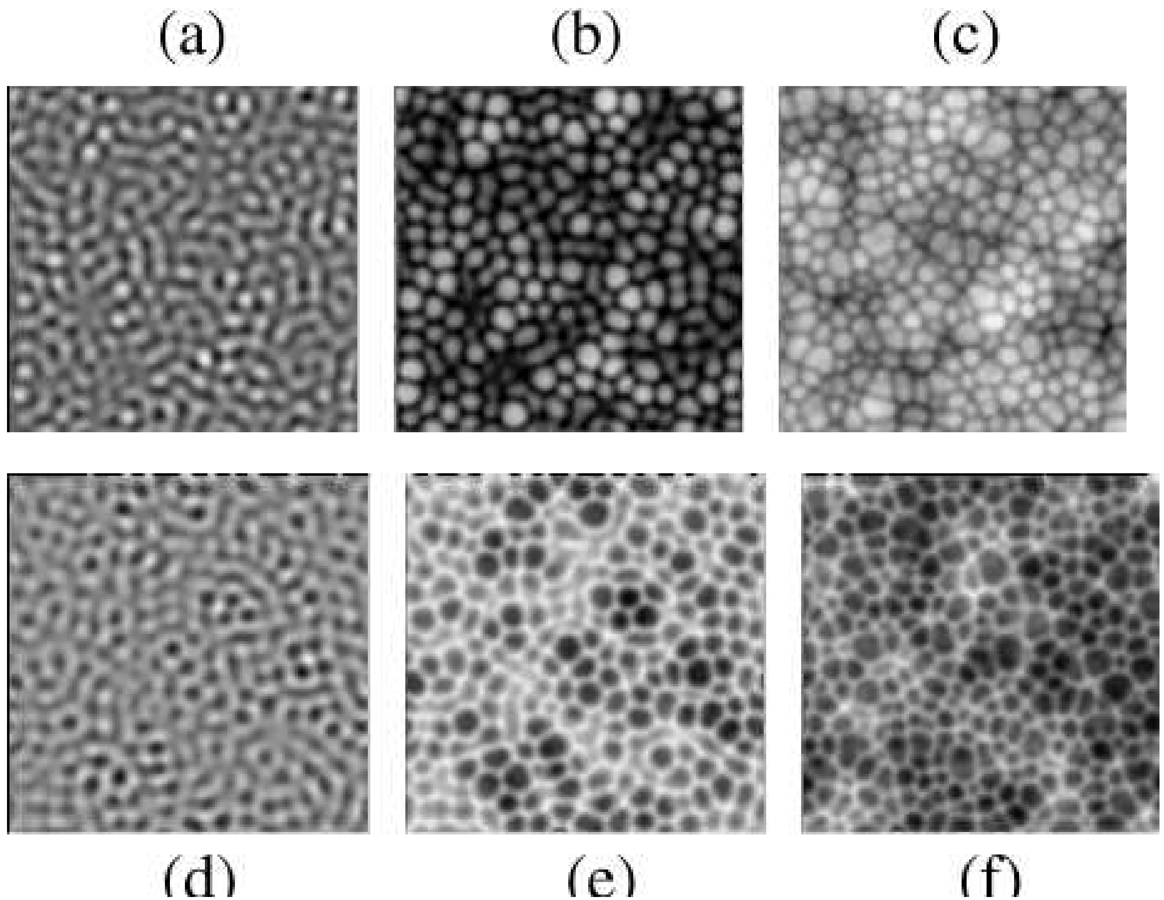
PARK ET AL, PRL '99



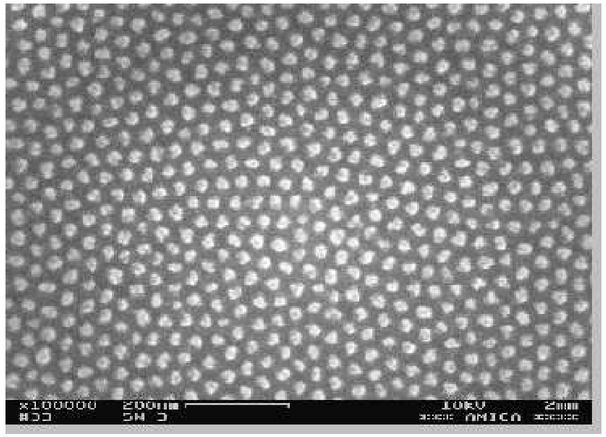
GAGO ET AL, Nanotechnol. '02

Non-linear dynamics ($\theta = 0$)

Dots are formed, but *not* with the proper ordering



KAHNG ET AL, APL '01



FACSKO ET AL '00

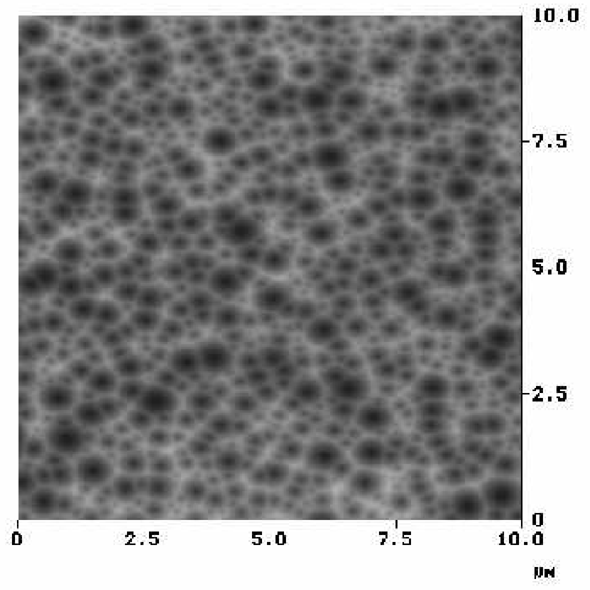
Other sputtered systems might be described by the nKS equation:

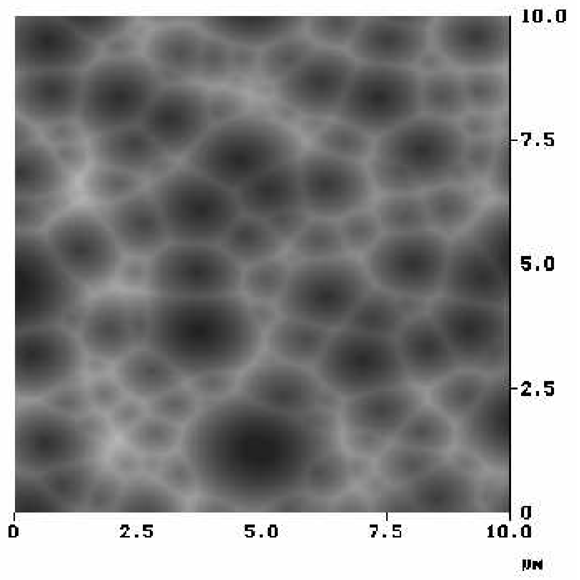
Amorphous carbon films (KOPONEN ET AL, JAP '97)

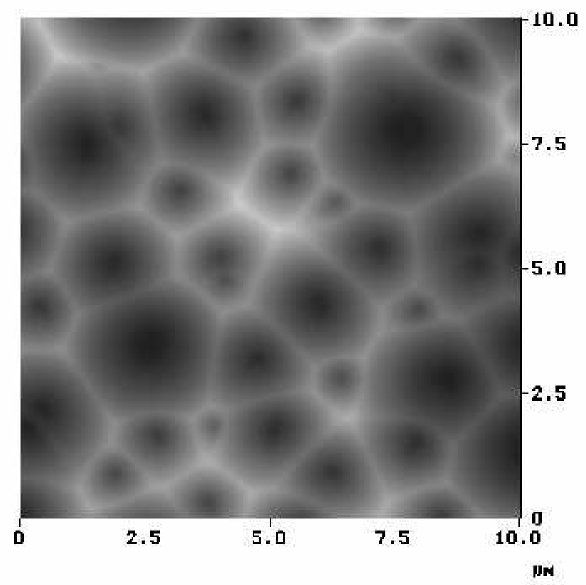
Ge bombarded at low energy (CHEY ET AL, PRB '95)

Other sputtered systems might be described by the nKS equation:

Si within a magnetron (with M. CASTRO, M. G. HERNÁNDEZ, L. VÁZQUEZ)



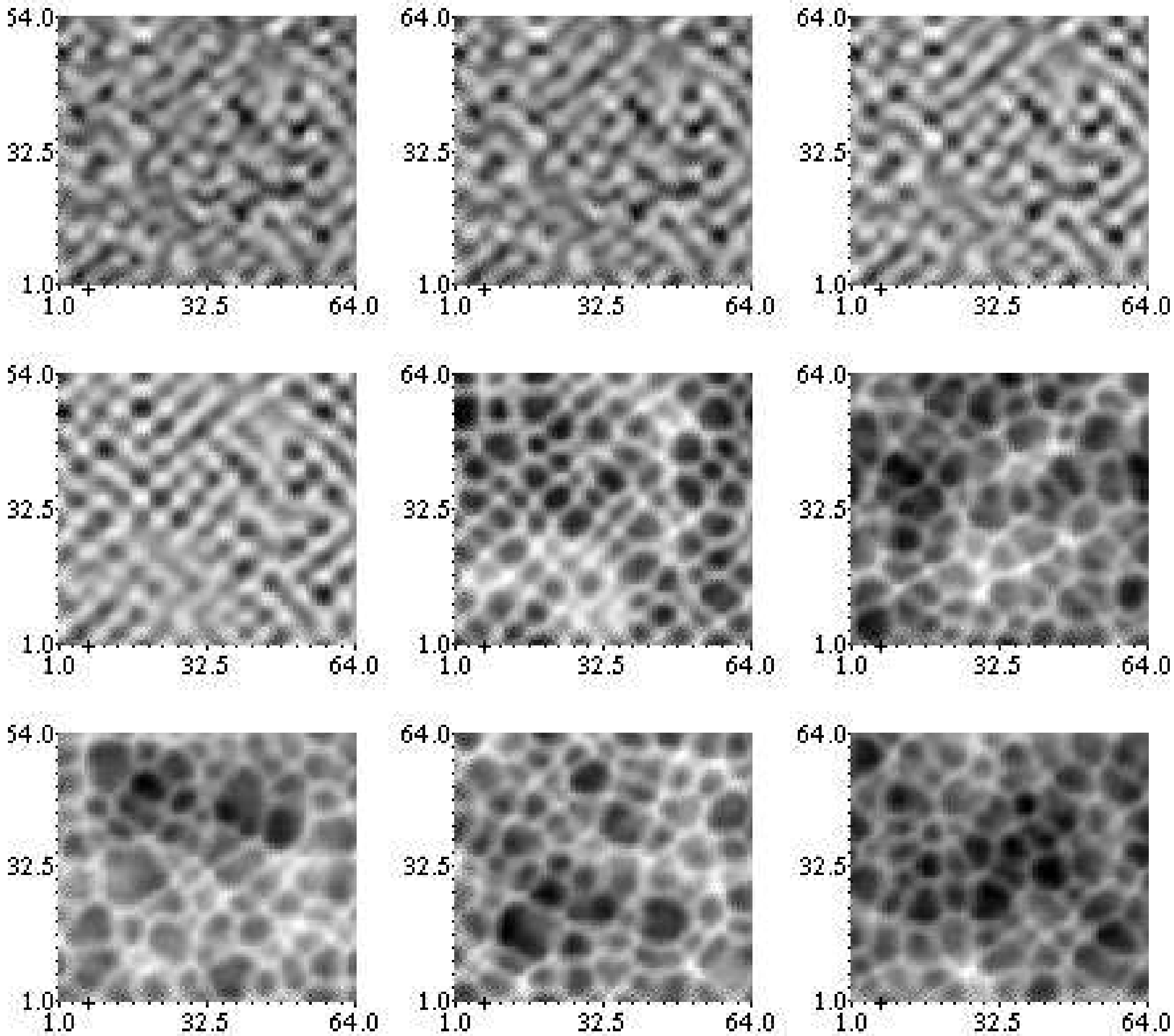




(M. CASTRO)

Cell ("dot") coarsening

Dot statistics ⇝ relevance of noise



Continuum description of IBS (a summary)

- Full dynamic equation *cannot* be described out of symmetry arguments: (cf. $\partial_t h = |\nu| \partial_x^2 h + \lambda(\partial_x h)^2 + \eta$, Kardar, Parisi, Zhang)
- (Qualitative) Agreement in terms of energy and flux dependencies (for thermally suppressed diffusion)
- Agreement in terms of pattern formation + stabilization
- Universality class for kinetic roughening? (need extremely long experiments)
- Disagreements:

  Dot formation:
  - In-plane ordering

  Ripple formation:
  - Wavelength coarsening
- Mechanisms not considered thus far may play a role (viscous flow, shadowing effects, . . .)

Example II: step dynamics on vicinal surfaces

Vicinal surface: orientation close to that of a high symmetry surface ⇝ steps

Steps have equilibrium *roughness*, that can be characterized

WANG ET AL. ‘90

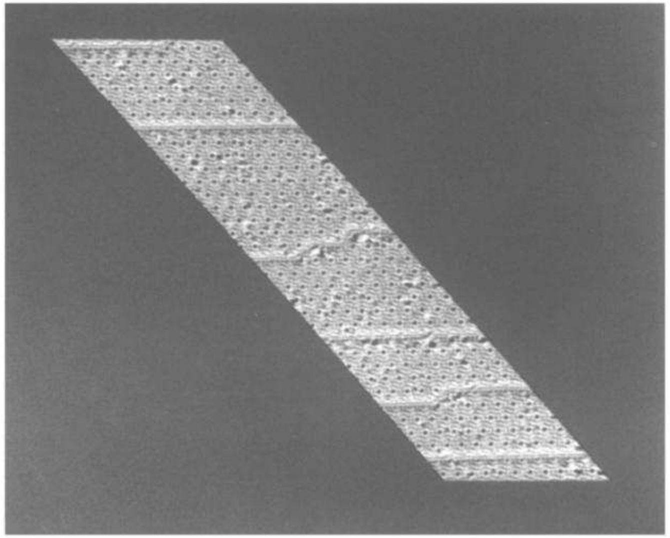
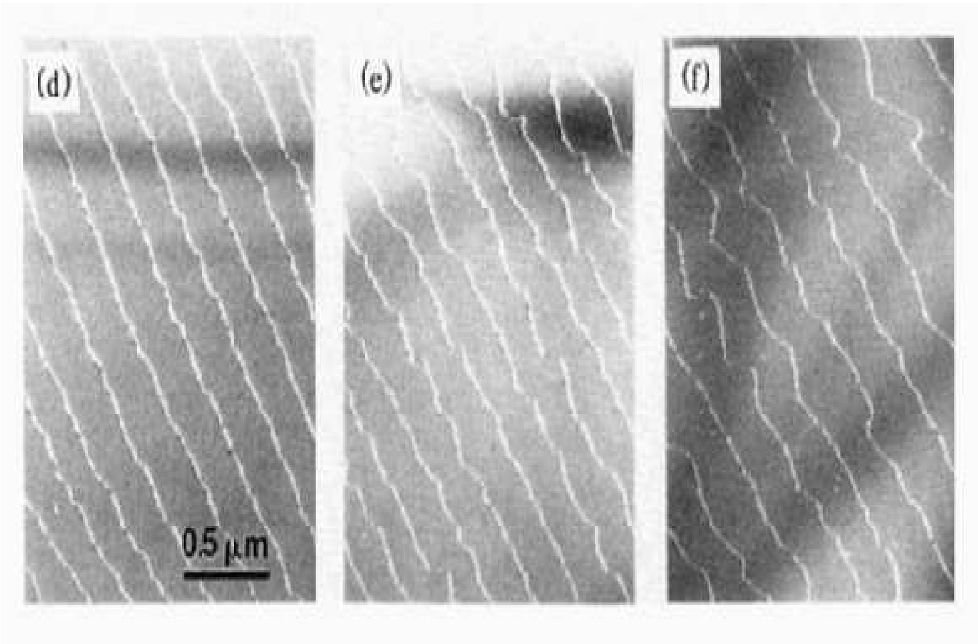


FIG. 1. Scanning-tunneling-microscope image of a ~800 Å×200 Å region of a stepped Si surface misoriented by 1.2° towards the [$\bar{1}\bar{1}2$] direction. Notice that the kink spans one (7×7) unit cell.

TUNG ET AL. ‘90

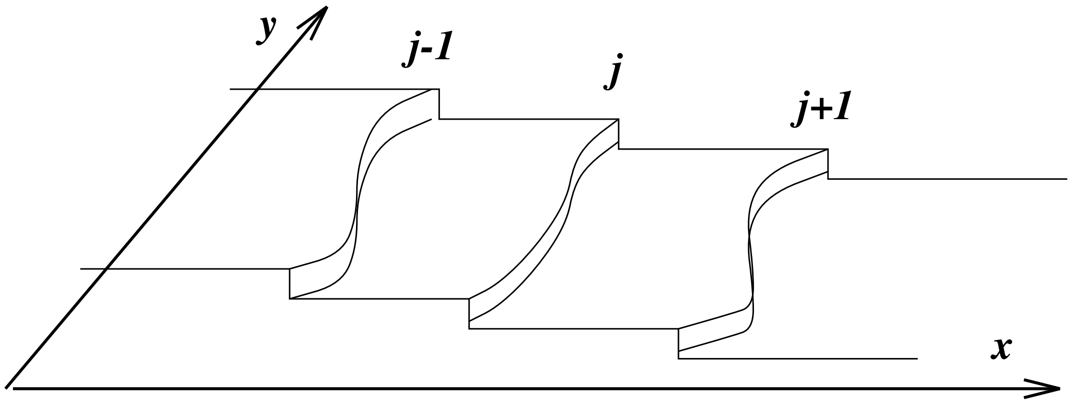


d) Si [2 $\bar{1}$ $\bar{1}$]; (e) 1 ML; (f) 2 ML

Under growth conditions, steps move and their roughness evolves

Rodolfo Cuerno, Universidad Carlos III de Madrid

Negligible nucleation: step flow



Adatom density $c(\mathbf{r},t)$ on terrace

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \frac{c}{\tau} + J - \nabla\cdot\mathbf{q} + j$$

$\mathbf{q}$ = fluctuations in diffusion current

j = flucts. adsorption/desorption

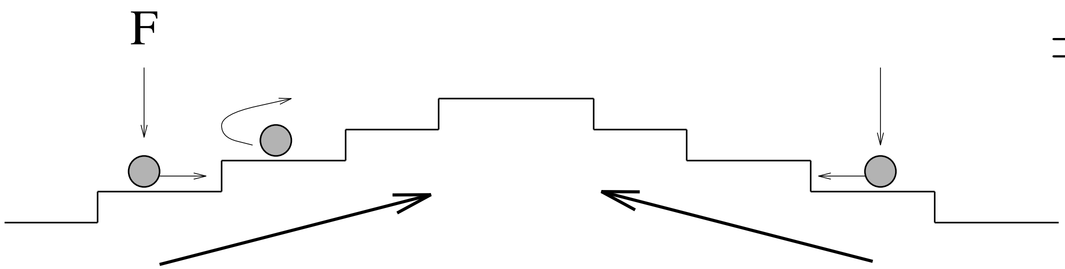
Attachment/dettachment at steps

$$\pm\mathbf{n}\cdot(D\nabla c - \mathbf{q})|_{\mathrm{step}} = k_\pm(c - c_{\mathrm{eq}} + j_\pm)$$

$+$ = at ascending step

$-$ = at desdending step

$k_\pm$ = kinetic coeffs. for attachment

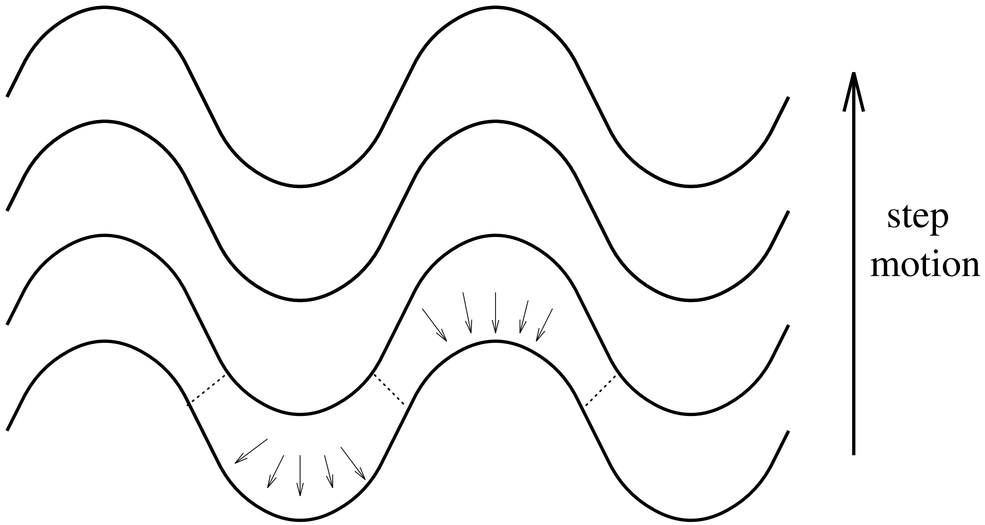


Velocity $\quad \mathbf{v}\cdot\mathbf{n} = \mathbf{n}\cdot(D\nabla\mathbf{c} - \mathbf{q})|_+ - \mathbf{n}\cdot(D\nabla\mathbf{c} - \mathbf{q})|_- + \left[\nabla_{\mathrm{s}}^2\kappa_{\mathrm{s}}\right]$

Talk delivered at Universität Göttingen, May 2003

EHRLICH-SCHWOEBEL barrier ⇒ instability

If attachment depends on side of step ($k_+ \neq k_-$) ⇒ *meandering* instability in step profile



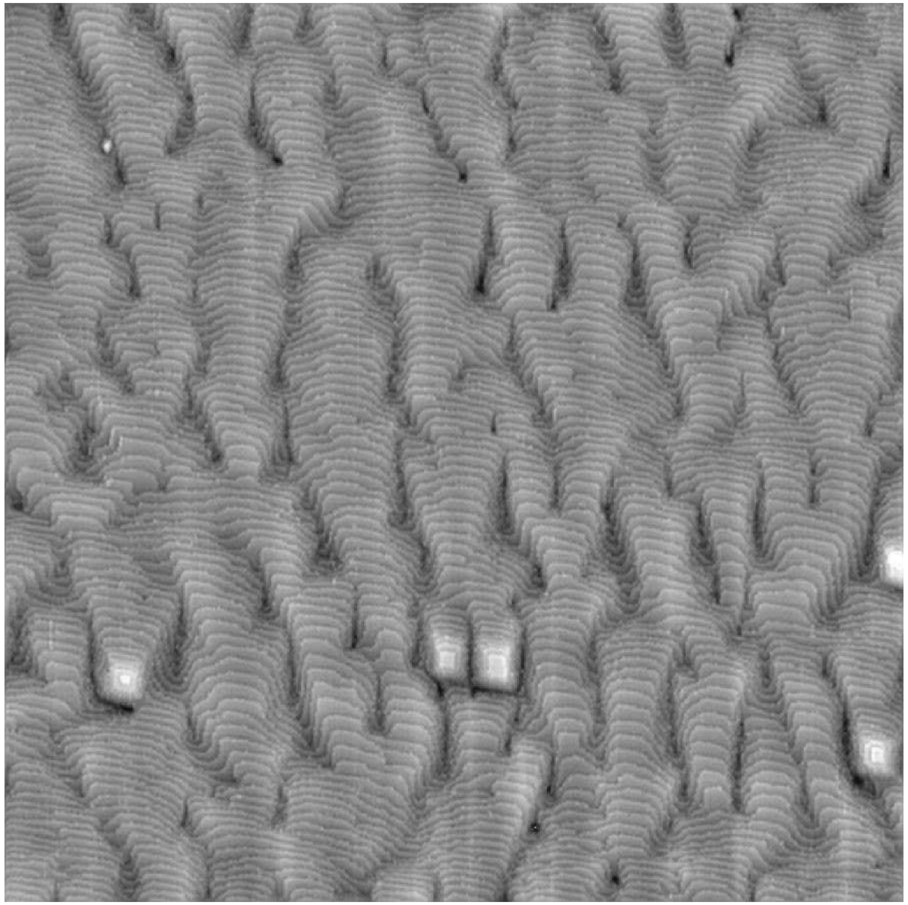
BALES, ZANGWILL, PRB ‘90

Protrusions “*screen*” indentations

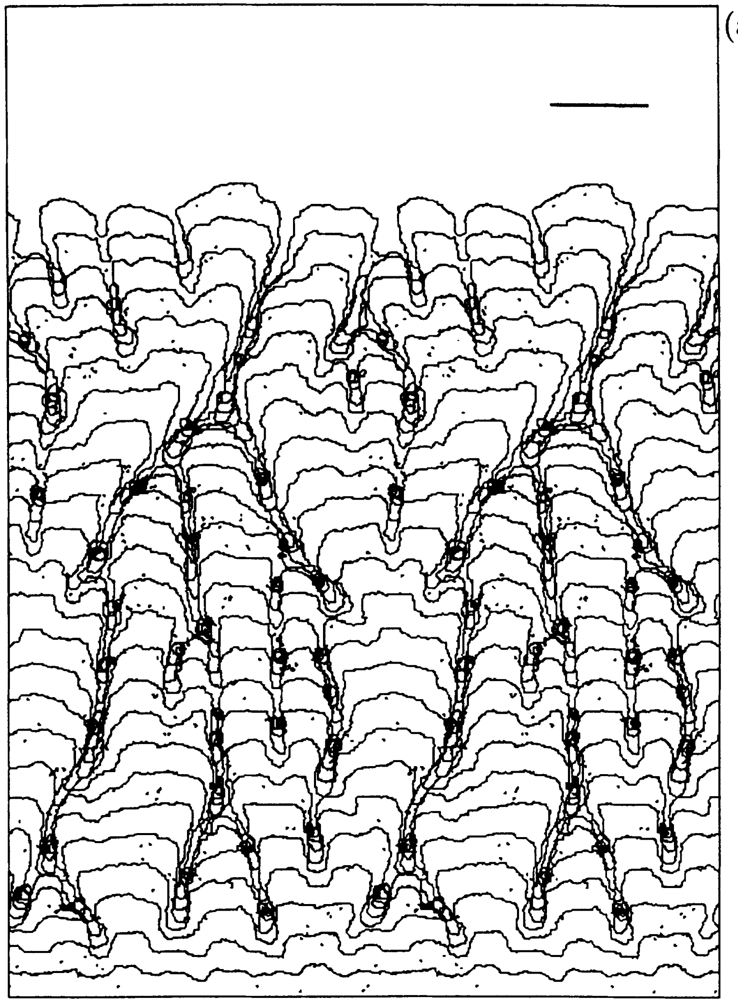
Analogous to Mullins-Sekerka instability in solidification (*snowflakes*)

Evolution equation for a single step is the Kuramoto-Sivashinsky equation (KARMA, MISBAH, PIERRE-LOUIS, . . ., late 90’s)

Can be generalized to trains of steps, no desorption, etc.



MAROUTIAN ET AL, PRB '01: Cu (1 1 17)



SAITO & UWAHA, PRB '94: kinetic MC

Agreement is *not* complete though (wavelength dependence with flux, . . .)

$\rightsquigarrow$ further work is needed

Conclusions

- Tools developed in the study of non-equilibrium systems can be employed for the study of growth systems with nanometer size features (growth, erosion, microfluids)
- Although the formalism is adapted to the study of asymptotic properties (esp. in the case of scale invariance), equations cannot be derived merely from symmetry arguments
- Careful attention must be paid to system specifics
- Still, advantage can be taken from developments on universal or generic models. Specifically, the latter studies can assess parameter regions for pattern formation, or e.g. surface disordering