Nanoscale Morphology Evolution Under Ion Irradiation

PI: Michael J. Aziz, Harvard School of Engineering and Applied Sciences

Contributors: Joy C. Perkinson, Charbel S. Madi, Scott A. Norris

Collaborators: Eitan Anzenberg, Karl F.Ludwig, Kai Nordland, Juha Samela, Laura Bukonte, Marie Backman, Flyura Djurabekova, Michael P. Brenner

Office of Science, U.S. Department of Energy

Harvard School of Engineering and Applied Sciences

Abstract

The use of ion beams has great promise for morphology control in materials synthesis and processing at sub-lithographic length scales. We are experimentally and theoretically studying the fundamental physical principles governing nanoscale surface morphology evolution during ion irradiation at energies low enough that the principal phenomena are observed at the surface rather than in the bulk. Self-organized one- and two-dimensional arrays of nanoscale surface features ("ripples" and "dots") sometimes form spontaneously on initially flat surfaces. If the medium-range order exhibited by the spontaneous patterns could be guided predictably by fundamental understanding combined with known templating methods, then useful periodic structures as small as 7 nm could be generated in high-throughput settings.

Since its discovery nearly half a century ago, it has been suspected that this "sputter pattern" formation is caused by sputter erosion effects. The erosion-based paradigm was established firmly 23 years ago when the destabilizing effect of the surface curvature-dependent sputter yield (atoms removed per incident ion) was incorporated into the linear stability theory of Bradley and Harper (BH) [1]. BH theory's prediction that an initially flat surface will display a pattern-forming instability at all incidence angles is contradicted by our experimental studies on amorphous silicon surfaces, for which there are no potentially confounding effects of singular crystallographic surface energetics and kinetics. We observe rippled surfaces at high angles θ of deviation from normal incidence, *with a transition to a stable flat surface* with decreasing θ. We have discovered that, as far as the stability/instability transition is concerned, *the effect of impact-induced redistribution of atoms that are displaced but not sputtered away is essentially the whole story – not only the cause of stability at low angle, but also the cause of instability at high angle – and that the effect of sputter erosion is essentially irrelevant.* We have arrived at this conclusion from two independent lines of reasoning - one experimental [DOE01], and one theoretical [DOE02]. These papers spell the end of the erosion-based paradigm that has dominated the field for half a century and propose its replacement with a paradigm based on the redistribution of atoms that are displaced, but not removed, by the impact.

[1] R.M. Bradley and J.M. Harper, *J. Vac. Sci. Technol. A* **6**, 2390 (1988).

[DOE01] C.S. Madi, E. Anzenberg, K.F. Ludwig, and M.J. Aziz, *Phys. Rev. Lett.* **106**, 066101 (2011).

[DOE02] S.A. Norris, J. Samela, C.S. Madi, K. Nordlund, M.P. Brenner and M.J. Aziz, *Nature Communications* **2**, 276 (2011).

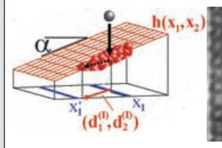
Outlook

- Time-resolved studies of evolution of ripples, hillocks, walls, pits, pores lead to rapidly advancing insight
- Sputter erosion-based paradigm discredited
- Proposed replacement: crater function-based paradigm
- Captures linear regime with no free parameters

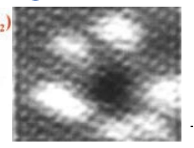
Important future directions:

- Nonlinear behavior based on established linear behavior
- Investigation of non-local effects, e.g. stress; redeposition
- Different materials classes? Compounds? Crystallographic singularities?
- How much control can one possibly have over an evolving topography?

Transcending the limitations of MD: how to extend crater function predictions to a wide range of materials, energies, and length scales?

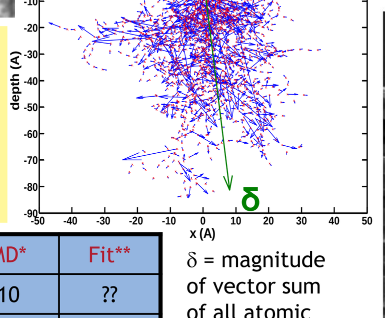


MD, Diamond-Like Carbon, Moseler, Gumbsch, Casiraghi, Ferrari, Robertson, *Science* **309**, 1545 (2005).



STM, 1 keV Ne→Ag(001) Constantini, Buatier de Mongeot, Boragno, Valbusa, *PRL* **86**, 5 (2011).

Monte Carlo calculation of binary collision cascades



δ = magnitude of vector sum of all atomic displacements

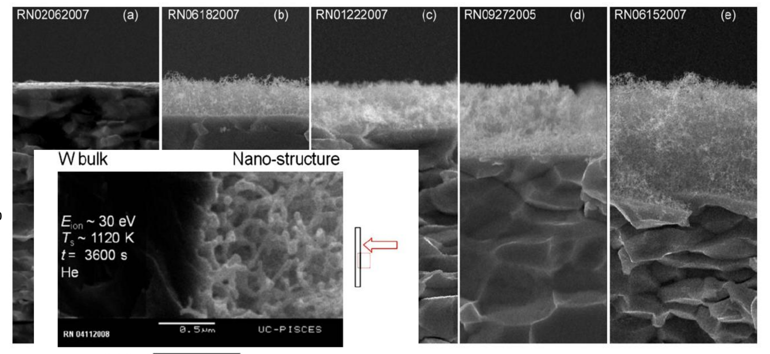
δ (nm) Ar → Si	MC	MD*	Fit**
E = 250 eV	3	10	??
E = 1000 eV	9	??	70

* Stillinger-Weber potential

** Our fit of the Carter-Vishnyakov model to our experimentally measured dispersion relation

Implications for Fusion Reactor Walls

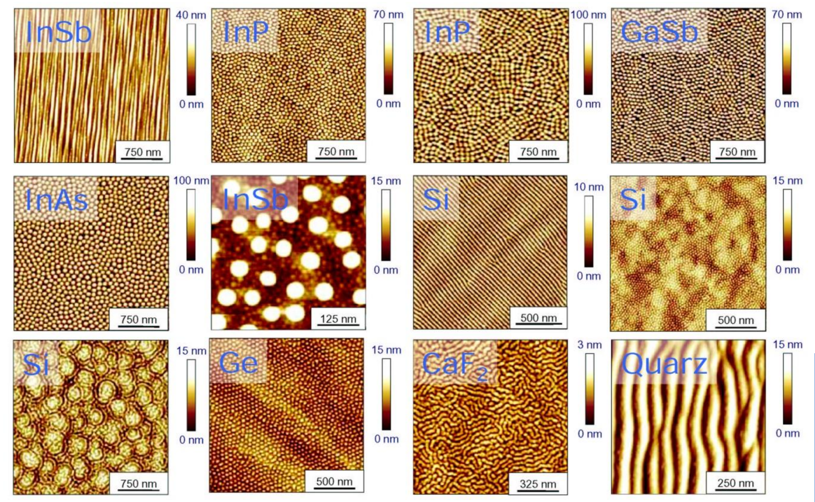
Our discovery has potential implications for the formation of a mysterious nanoscale topography leading to surface degradation of tungsten plasma-facing fusion reactor walls. Low sputter yield (atoms removed per incident particle) has been an important design criterion in the selection of tungsten for surfaces that must be exposed to large plasma particle fluxes for extended periods. This work shows that a sputter yield of zero is an insufficient design criterion for morphologically stable solid surfaces under energetic particle irradiation, and ultimately crater function engineering considerations may provide a more refined materials design criterion.



M.J. Baldwin and R.P. Doerner, "Helium induced nanoscopic morphology on tungsten under fusion relevant plasma conditions", *Nucl. Fusion* **48**, 035001 (2008).

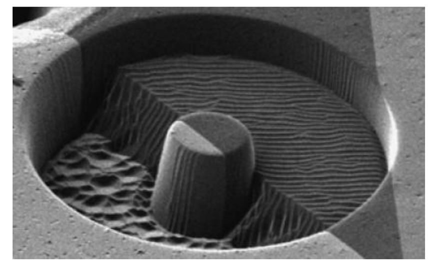
Irradiation-Induced Nanoscale Pattern Formation

Self-organized "Sputter Patterns"



Unpublished image courtesy of Bashkim Ziberi, Leibniz-Institut für Oberflächenmodifizierung.

Topographical Instabilities: "Bug" or "Feature"?



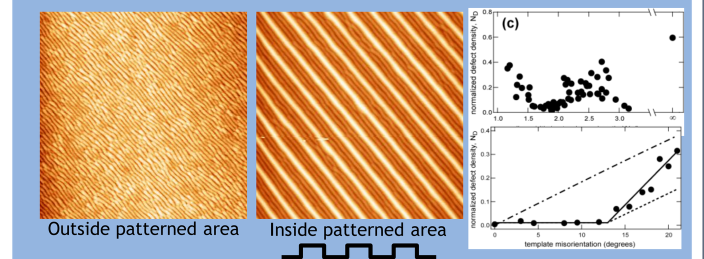
30 keV Ga^+ Focused Ion Beam (FIB)→ Cu with grain boundary

Volkert and Minor, *MRS Bull.* **32**, 389 (2007).

Variety of Patterns

- High-throughput self-assembled patterns
- Wide range of length scales (7 nm – hundreds of nm)
- Short- and long-range order
- Ultrasmoothening of surfaces under certain conditions
- Patterns form on metals, semiconductors, and insulators

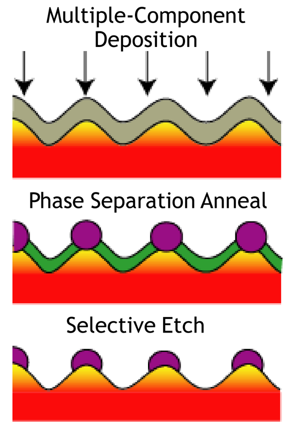
Lateral Templating: How much control can you possibly have over pattern evolution across an entire area by manipulating only the boundaries?



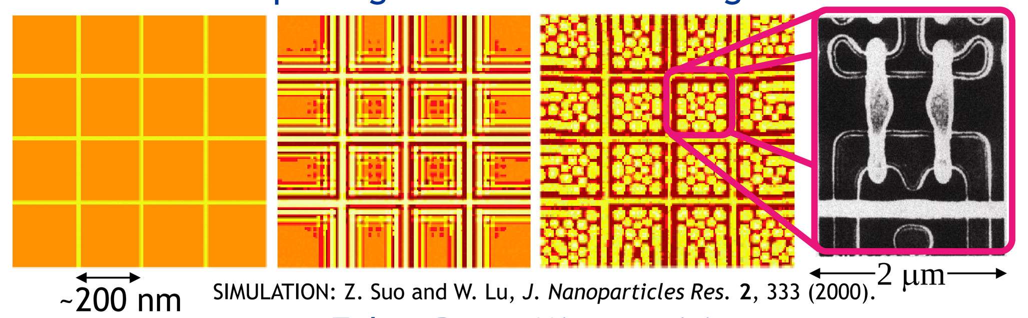
Cuenat, George, Chang, Blakely, Aziz, *Advanced Materials* **17**, 2845 (2005).

Wouldn't it be nice…

Vertical templating for materials integration



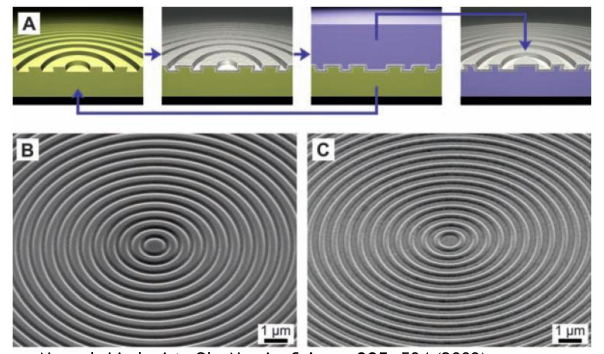
Lateral templating to control lateral organization



SRAM element (Fujitsu)

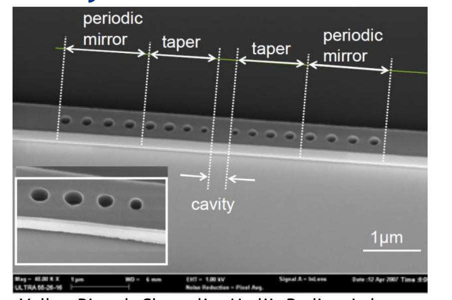
SIMULATION: Z. Suo and W. Lu, *J. Nanoparticles Res.* **2**, 333 (2000).

Smooth Metals for Plasmonics



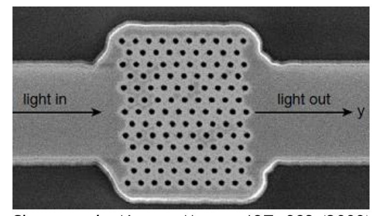
Nagpal, Lindquist, Oh, Norris, *Science* **325**, 594 (2009).

Fabry-Perot Microcavities

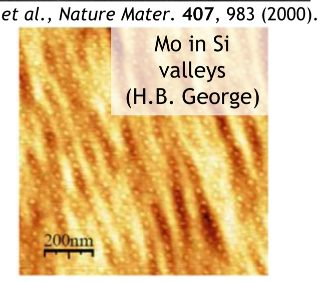


Velha, Picard, Charvolin, Hadji, Rodier, Lalanne, Peyrade, *Optics Express* **15**, 16090 (2007).

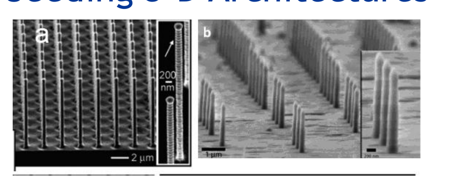
Photonics



Chow *et al.*, *Nature Mater.* **407**, 983 (2000).

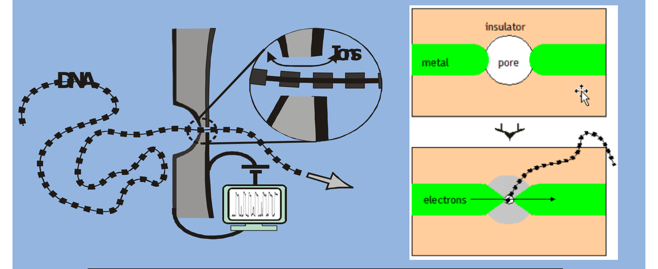


Seeding 3-D Architectures



Pokroy, Epstein, Persson-Gulda, Aizenberg, *Adv. Mater.* **21**, 463 (2009).

Integrating Electrodes into Nanodevices



materials class	nanopores close?
insulators	Y
metals	Y
semiconductors	Y

George, Hoogerheide, Madi, Bell, Golovchenko, Aziz, "Ion Sculpting of Nanopores in Amorphous Metals, Semiconductors, and Insulators", *APL*, **96**, 263111 (2010).

Key Issues

There is a phenomenological linear stability theory (Bradley-Harper) for isotropic single-component materials, infinitesimal amplitudes.

It fails in some fundamentally important ways. Why?

Not understood:

- Microscopic mechanisms
- Possible on-local effects, e.g. stress, redeposition (linear regime)
- Anisotropy; alloys and compounds (linear regime)
- Nonlinear behavior (large slope, curvature)

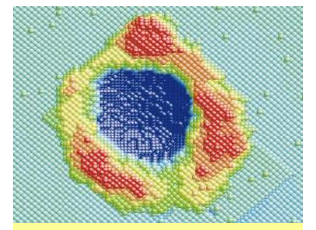
Control:

- Range of morphologies accessible
- Limits to size (vertical and lateral), regularity, flexibility
- Manipulation by boundaries
- Manipulation via external fields

Theoretical

We have developed a new theoretical methodology for predicting the governing partial differential equation for surface evolution from the accumulation of topographic responses to individual ion impacts. The local response (the "crater function") can be obtained by experiment (e.g. STM images) or simulation (e.g., Molecular Dynamics (MD)). Although no two craters are completely identical, it's only the average over many craters that matters. The theory exploits a separation in length scale between the topographic changes due to a single ion impact and the emerging pattern. It also exploits a separation in time scale between the "prompt regime", in which kinetic energy-induced sputter erosion and bombardment-induced surface mass transport go to completion, and the "gradual regime" in which thermally-activated morphological relaxation processes occur. The theory derives, *without any free parameters*, the *S* coefficients in Eq. 1 (there is one for each independent spatial dimension, *x* and *y*) from the crater functions. A flat surface is stable if both *Sx* and *Sy* are positive; if either is negative the surface is unstable. Prior to this work, the best models for the *S* coefficients contained adjustable parameters, and in many cases there was no way to reliably estimate the magnitude of those parameters.

A Parameter-Free Theory



MD, Xe → Au(111), Nordlund

General surface response

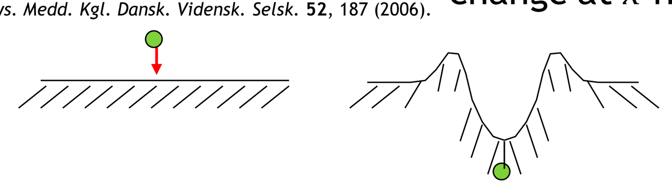
$$\frac{\partial h(x,t)}{\partial t} = \int J(x')\Delta h(x-x';b)\,dx'$$

Aziz, *Mat. Fys. Medd. Kgl. Dansk. Vidensk. Selsk.* **52**, 187 (2006).

J: irradiation flux

$b \equiv \partial h/\partial x = \tan\theta$

Δh: crater function: height change at x from impact at x'



→ PDE, with coefficients *determined*

$$\frac{\partial h}{\partial t} = -F(b) + S_x(b)\frac{\partial^2 h}{\partial x^2} + S_y(b)\frac{\partial^2 h}{\partial y^2} - B\nabla^4 h \quad (1)$$

Norris, Brenner, Aziz, *J. Phys. Cond. Matt.* **21**, 224017 (2009).

$F(b)$: sputter yield vs. slope b

$S_{x,y}(b)$: curvature coefficient

B: surface diffusion

Norris Theory: Abbreviated Math

Norris, Brenner, Aziz, *J. Phys. Cond. Matt.* **21**, 224017 (2009).

Norris, Samela, Bukonte, Backman, Djurabekova, Nordlund, Madi, Brenner, Aziz, *Nature Communications*, 2:276 (2011).

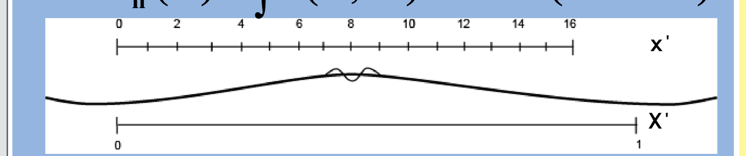
Main steps of the analysis:

1. Flux-weighted integration of nearby impacts

$$v_n^P(\mathbf{x}) = \int J(\mathbf{x}')\Delta h(\mathbf{x}-\mathbf{x}')d(\mathbf{x}')$$

2. Separate length scales using a small parameter

$$v_n^P(\mathbf{x}') = \int R(\mathbf{x}',\mathbf{X}')d\mathbf{X}' \qquad (\mathbf{X}' = \varepsilon\mathbf{x}')$$



3. Taylor expansion and term rearrangement

$$v_n^P(\mathbf{x}') = \left[\int R\,d\mathbf{x}'\right]_{X'=0} + \varepsilon\nabla_{X'}\cdot\left[\int R\,\mathbf{x}'\,d\mathbf{x}'\right]_{X'=0} + \ldots$$

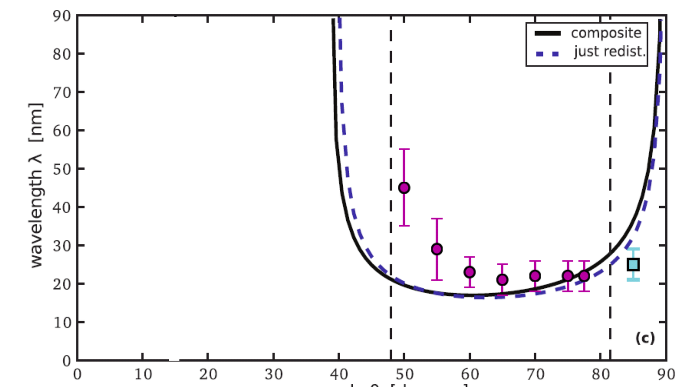
Moment Form

$$v_n(\mathbf{x}) = \left[IM^{(0)}\right] + \varepsilon\nabla\cdot\left[IM^{(1)}\right] + \frac{1}{2}\varepsilon^2\nabla\cdot\nabla\cdot\left[IM^{(2)}\right] + \ldots$$

- Moments converge more rapidly than full crater functions
- Moments can also be split into erosive and redist. parts
- Frequently discussed effects lie in different moments
  - Erosive yield is in $M^{(0)}_{erosive}$
  - "Bradley-Harper Effect" is in $M^{(1)}_{erosive}$
  - Surface currents are in $M^{(1)}_{redist.}$
  - Craters are (mostly) in $M^{(2)}_{redist.}$

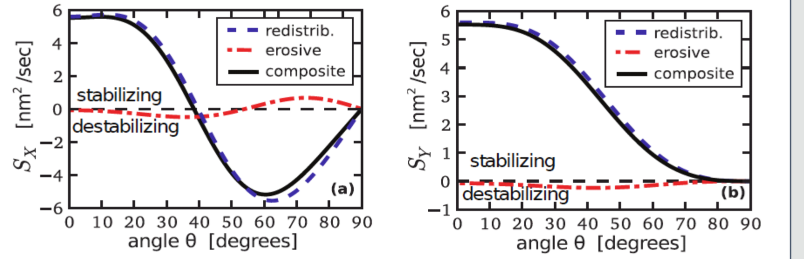
Parameter-Free Theory vs. Experiment

MD Si(001) under 250 eV Ar^+; Room temperature (amorphous); low dose (linear regime)



$$\frac{\partial h}{\partial t} = -F(b) + S_x(b)\frac{\partial^2 h}{\partial x^2} + S_y(b)\frac{\partial^2 h}{\partial y^2} - B\nabla^4 h$$

B is taken from Vauth & Mayr, *PRB*, **75**, 224107 (2007): MD of 1 keV Si→Si, Room Temp, viscous flow



Norris, Samela, Bukonte, Backman, Djurabekova, Nordlund, Madi, Brenner, Aziz, *Nature Commun.* **2**, 276 (2011).

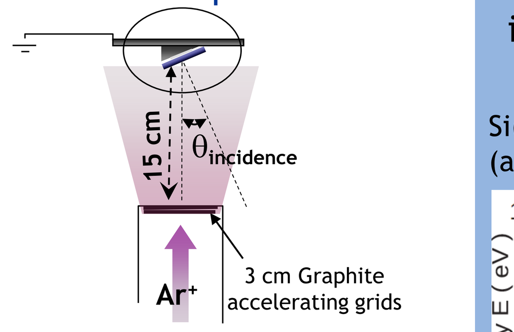
Experimental

In a collaboration with Karl Ludwig of Boston University to measure the linear dispersion relation *in situ* in real time using Grazing Incidence Small Angle X-Ray Scattering (GISAXS) at the National Synchrotron Light Source at Brookhaven National Laboratory, we measure the real-time diffusely-scattered intensity corresponding to topographic correlations at the sample surface. We observe its amplification into ripples or its decay into ultrasmooth surfaces and are able to identify the behavior for each spatial frequency. This is a direct measurement in Fourier space of the partial differential equation governing morphology evolution. We have confined our attention to the linear regime of exponential amplification and decay. The long-time, nonlinear regime will be experimentally accessible when our new system comes online.

Ion Bombardment Setup

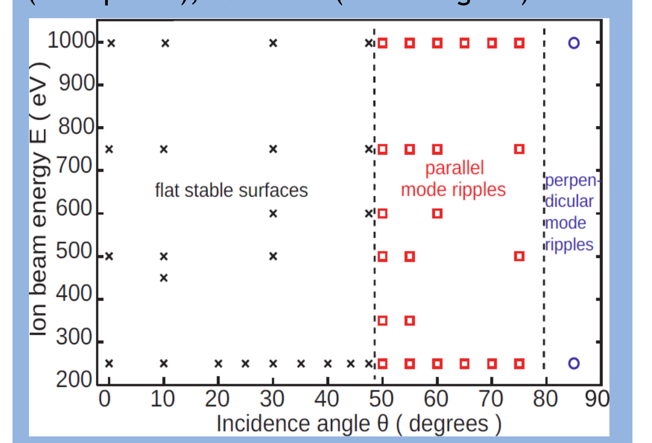
Accessible conditions

150 -1200 eV Ar^+
base pressure= 1×10^{-9} Torr
T = 30 - 1000 °C
θ_{ion}= 0° - 90 °
V_{beam}=250 V; V_{acc}=-550 V
j ~ 0.54 mA cm^{-2}
$\theta_{divergence}$= 4.5°



Phase Diagram for Si(001) Rippling in the Linear Regime (exponential amplification)

Si(001) under 250 eV Ar^+; Room temperature (amorphous); low dose (linear regime)

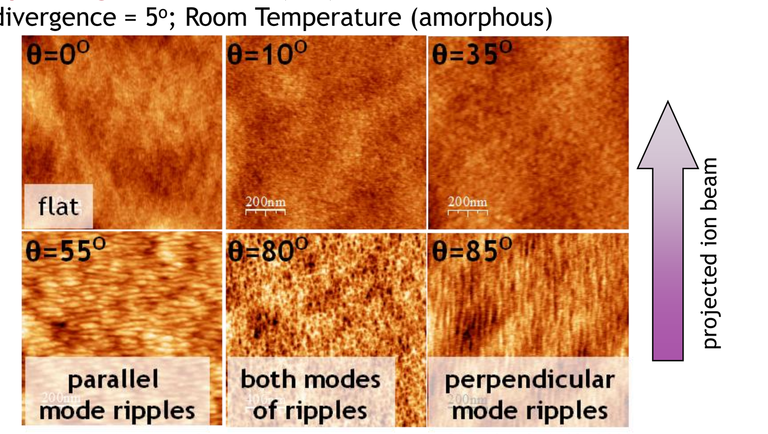


Madi, Davidovitch, George, Norris, Brenner, Aziz, *PRL* **101**, 246102 (2008).

Morphological Stability of Flat Surfaces

Control Parameters: Angle from normal incidence θ; ion energy *E*; temperature *T*

Operating Conditions: Si(001) under 250 eV Ar^+; beam divergence = 5°; Room Temperature (amorphous)

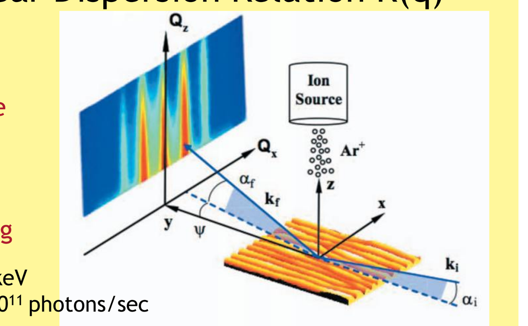


Madi, Davidovitch, George, Norris, Brenner, Aziz, *PRL* **101**, 246102 (2008).

Madi, George, Aziz, *J. Phys. Cond. Matt.* **21**, 224010 (2009).

Direct Measurement of Linear Dispersion Relation R(q)

Grazing-Incidence Small Angle X-ray Scattering



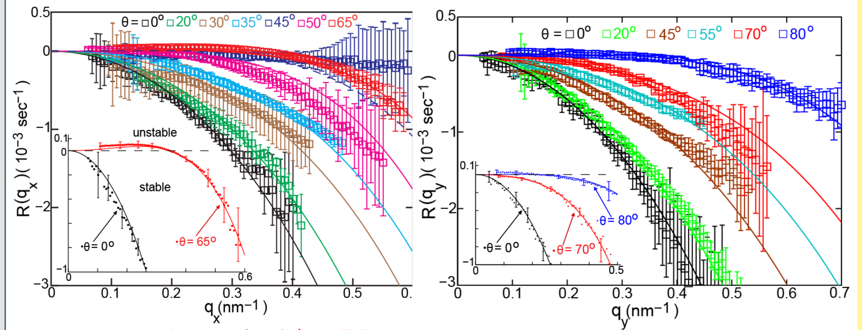
$E_{x\text{-}ray}$= 10 keV

Flux = 3×10^{11} photons/sec

Illustration: Zhou, Zhou, Ozaydin, Ludwig, Headrick, *PRB* **78**, 165404 (2008).

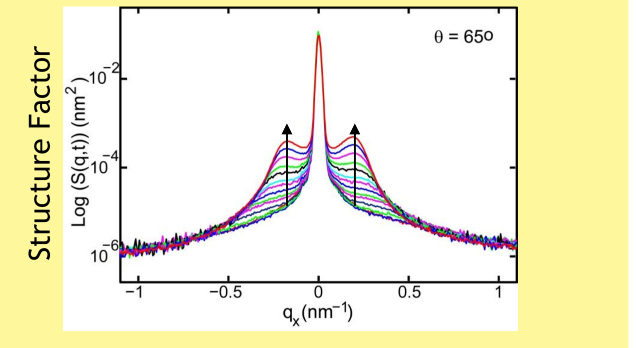
Angular Variation of Linear Dispersion Relations $R(q_x)$ and $R(q_y)$

$R(q_x) = -S_x(\theta)\,q_x^2 - B\,q_x^4$ $\qquad$ $R(q_y) = S_y(\theta)\,q_y^2 - B\,q_y^4$



Transition angle: $\theta_c^{\,*}$ ~ 47.5° $\qquad$ Transition angle: $\theta_{perp}^{\,*}$ ~ 75°

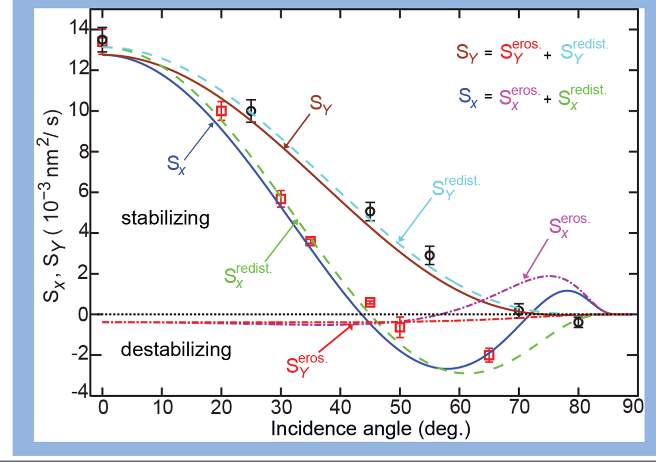
Madi, Anzenberg, Ludwig, Aziz, *PRL* **106**, 066101 (2011).



When we include noise $\alpha(x,t)$ in the linear stability analysis,

$$\frac{d\left|h(\vec{q},t)\right|^2}{dt} = 2R(\vec{q})\left|h(\vec{q},t)\right|^2 + \alpha(\vec{q},t)$$

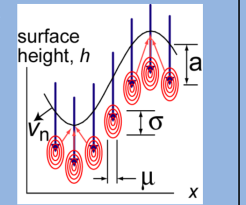
Ion Impact-Induced Mass Redistribution: Origin of linear STABILITY & INSTABILITY



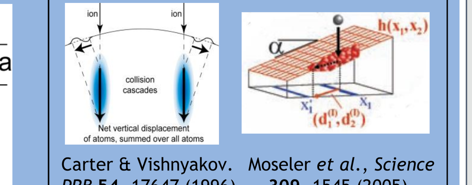
Bradley-Harper erosion-based theory is both the wrong sign and an order of magnitude too small to be relevant.

P. Sigmund, J. Mater. Sci. **8**, 1545 (1973).

R.M. Bradley, J.M.E. Harper, JVST A **6**, 2390 (1988).



Redistributive effects explain stability at low angles as well as instability at high angles.



Carter & Vishnyakov. *PRB* **54**, 17647 (1996). $\qquad$ Moseler et al., *Science* **309**, 1545 (2005).