Filigree with a Sledge Hammer

Self-organized Nanostructures from Ion-Beam Irradiation

R. Kree

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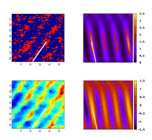
Oldenburg, July 9th 2012

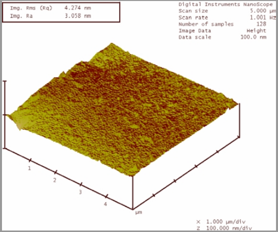


Today's menu

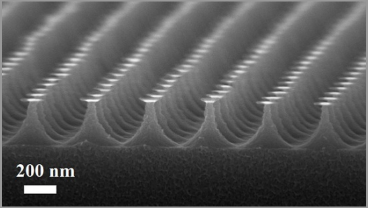
1. A failure to begin with
2. A deceptively general explanation
3. Wishful thinking: experiment and theory on the wrong track
4. Unexpected triumph, wrong interpretation
5. Complete failure, the doom of the old is the advent of the new
6. The power of dirt and other surprises
7. Anchors aweigh! New shores ahead!

A holy grail of solid surfaces

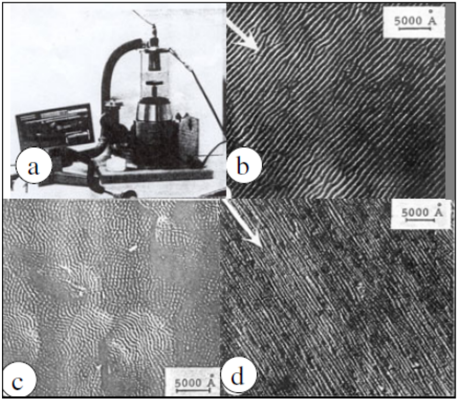
Before the advent of nanoscience:
A perfectly smooth surface



after the advent:
A surface with perfect nanostructures

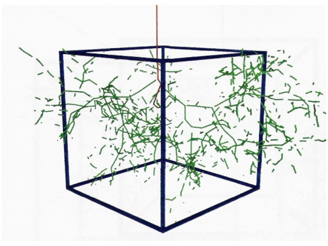


How one fails to polish glass surfaces with an ion beam



M.Navez, et.al. (1962) C. R. Acad. Sci Paris 254, p 240
"Ion sandblasting effect".

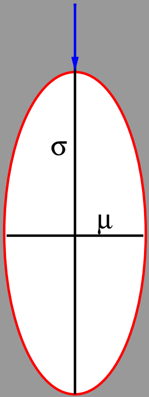
The basics



Energy of ion "keV sledge hammer" is distributed in cascades.

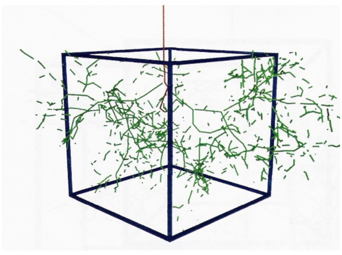
(Feix, Hartmann, RK, Muñoz-Garcia, Cuerno, PRB, 2005)

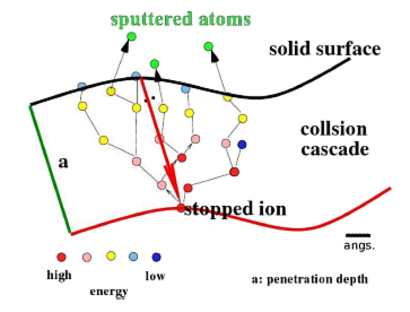
Statistics $\Rightarrow$



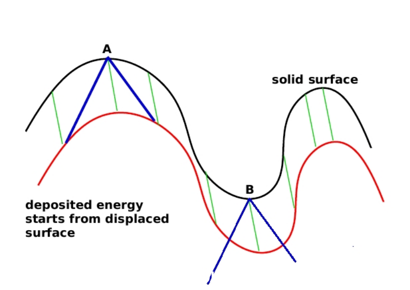
Average over deposited energy

The deceptively general explanation





Generic curvature instability:
Energy of ion "keV sledge hammer" is distributed in cascades. Valleys (B) get more energy/time than hilltops (A) and are thus eroded faster.. M. Bradley, J. Harper (1988) J. Vac. Sci. Technol. A6, 2390



The deceptively general explanation, contd.

Continuum description

Mass conservation

$\frac{\partial h}{\partial t} = Y(\theta; h)$ - div$\vec{j}$

change in surface height =

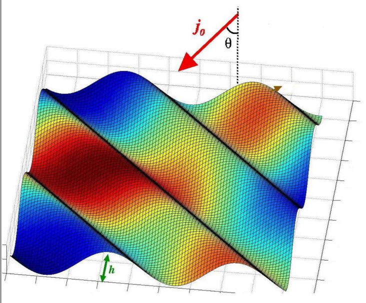
Sputter yield + surface current

$Y \rightarrow$ roughening

thermal surface current

div $\vec{j} = -K\nabla^4 h \rightarrow$ smoothing

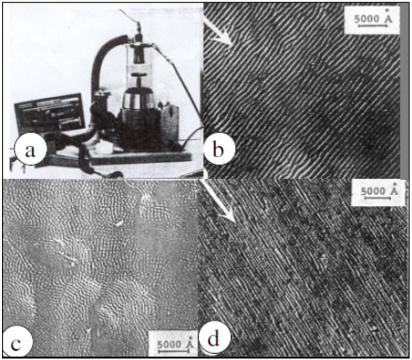
result: universal ripples



The cornerstone of Bradley-Harper Theory

Input

Erosion velocity $v(x, y) \propto$ deposited cascade energy/time $P(x, y)$.
P available from kinetic theory P. Sigmund (1969) PR 84, 383.
Then linearize in height profile.



Prediction: Ripple crests $\perp$ to ion beam direction close to normal incidence, and $||$ close to grazing incidence. Angle of 90° rotation can be calculated for different materials and ion beam parameters!

How to get on the wrong track

Is the method a player in bottom-up production processes of nanostructures? NO! Mainly because

1. patterns are too blurred
2. nothing but ripples
3. on semiconductors (Si), ripple quality appears worse than on glass

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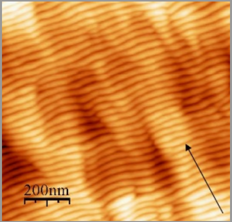

the ion-beam people's nanostructures in 1990s H.Hofsäß, K. Zhang, 1997

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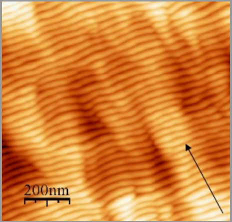

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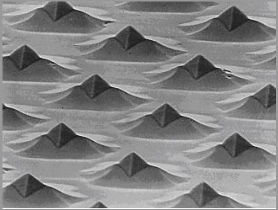

... and some from the shop next door (MBE) from Anupam Madhukar's homepage

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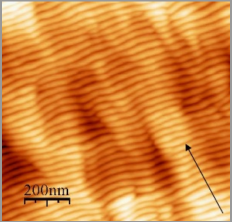

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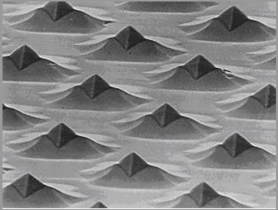

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But at least, we have a theory. Let's put it to work and try to improve.

Plenty of room for improvement

1. Non-linear effects?
2. Ion beam parameters?
3. Other materials?
4. Several beam directions, rotated samples?

Theorist's point of view

Do we understand what's going on?

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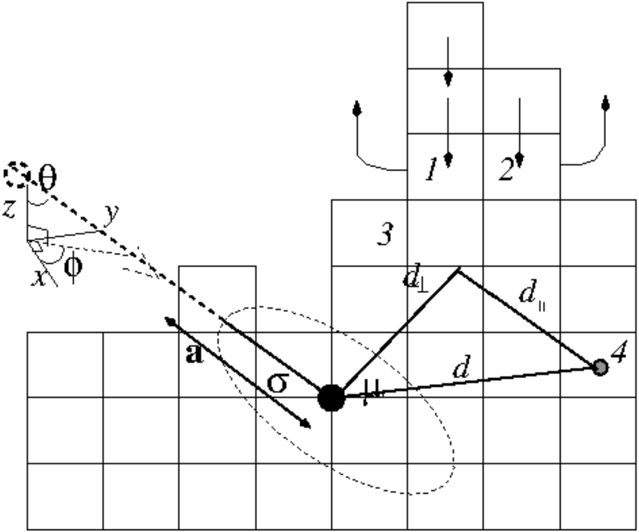
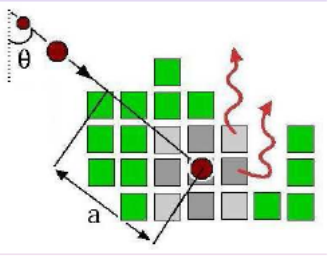
Monte Carlo Model

Model the current wisdom, see what it gives us.

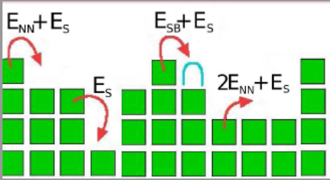


The Algorithm



N_e erosion steps

+



N_d Surface diffusion steps

Adjust N_e/N_d to physical time scales.

Hartmann, Geyer, Kölbel, R.K. ,PR B, 2002

What can be studied

1. non-linear effects

   Hartmann, Geyer, Kölbel, R.K. ,PR B, 2002

2. ion-beam parameters

   Yewande, R.K., Hartmann, PR B 2006

3. noise in ion beam, penetration depths, deposited energy

   R.K. Yasseri, Hartmann NIMB (2009), R.K. T. Yasseri, 2012

4. different single element materials

   R. K., T. Yasseri 2012

5. geometries like dual beams and rotated samples

   Yewande, Hartmann, R.K PRB 2006; Yasseri, R.K., NIMB 2010

BH works

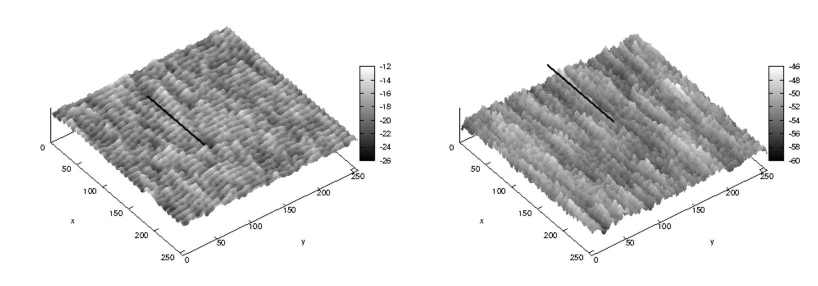


Figure: Typical morphologies of ripples obtained from the basic MC model. (a) For smaller θ (50^0) ripple wave vectors are parallel (b) for larger θ (80^0) they are perpendicular R. K. T. Yasseri, 2012

First Lessons

1. Yes, we get ripples in accordance with "BH-rotation"
2. No, they are not "nice"
3. and they are surprisingly hard to find in parameter space
4. for Si parameters we (and others) didn't find any!!!

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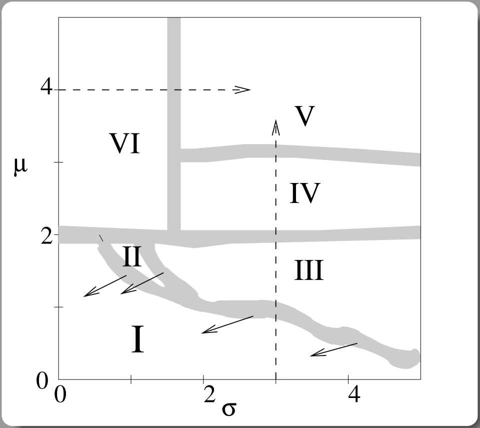
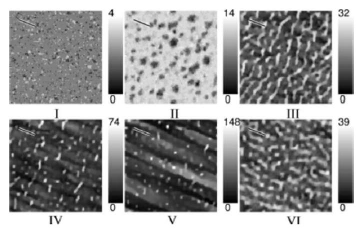
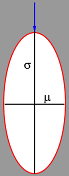
Dependence on average cascade shape







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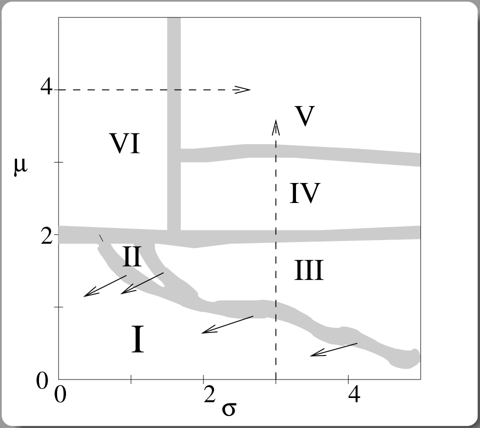
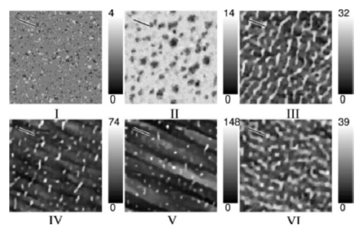
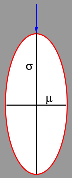
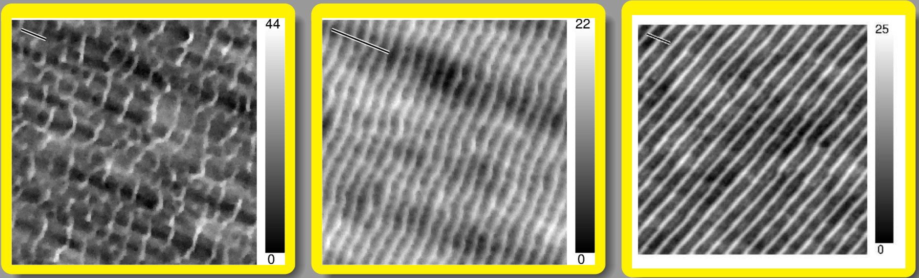






Lots of different pattern types (ripples, dots, holes, ...), but none of them "nice".

Non-linear effects depend on surface diffusion

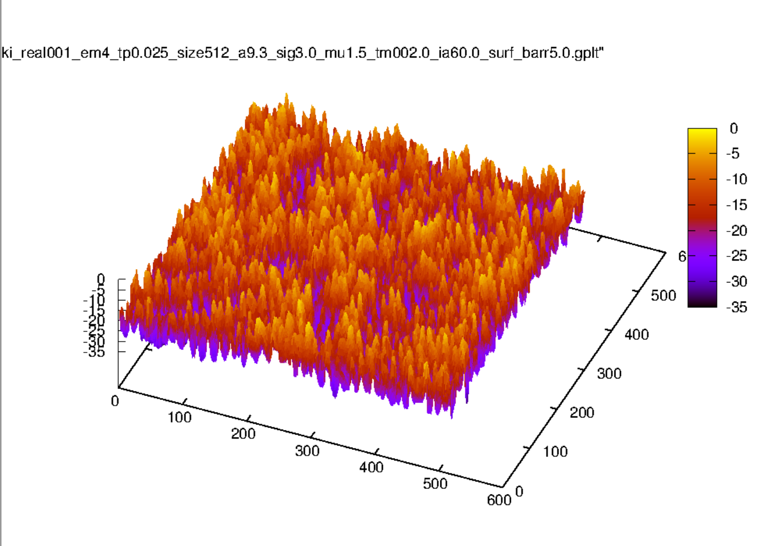


Three long-time snapshots. Only difference is surface diffusion mechanism
Left: based on height differences, Middle: based on path dependent barriers, Right: Wolff-Villain irreversible downhill relaxation. Continuum theory predicts spatio-temporal chaos (Kuramoto-Sivashinski type) as asymptotic behaviour.

General failure

None of the trials lead to substantially improved quality of patterns (both in Theory and Experiment)

The Si ripple desaster

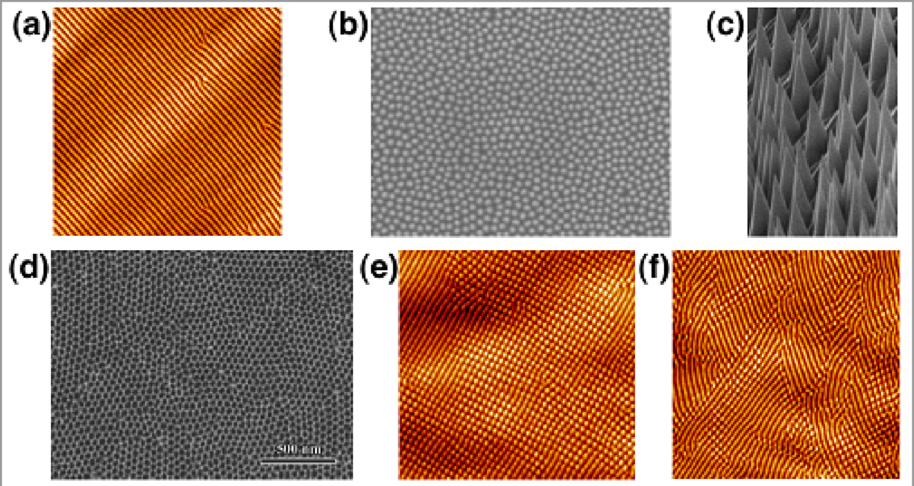


R. K., T. Yasseri 2012

“So, we’ve come to the end of this pretty lousy show. ” “ I must say, I’m glad it’s over.”

But then! SURPRISE!!!

Unexpected triumphs



(a) Ripples on Si B. Ziberi et al. 2009. (b) An array of nanodots on GaSb S. Facsko et al. 1999. (c) Cones on copper Reiche and W. Hauffe 2000. (d) Hexagonal array of nanoholes on Ge Q. Wei et al. 2009. (e) Square array of nanodots on Si B. Ziberi et al. 2009. (f) Ripples of two different wave vectors on Si at a 25 degree angle of incidence B. Ziberi et al. 2009.

But Why ???

1. because we do it so well controlled
2. because we have special beam parameters
3. because we use special materials (GeSb, GaSb, InP)
4. why did other labs fail to reproduce the results?

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A really clean experiment on Si

Köln/Leipzig/Dresden-Rossendorf/: Macko et al (2010), Nanotechnology, 21, 085301

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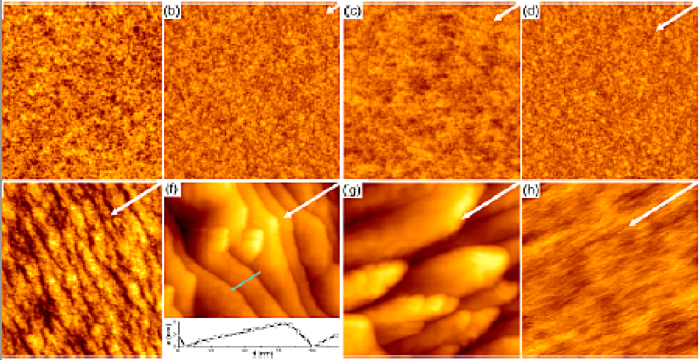


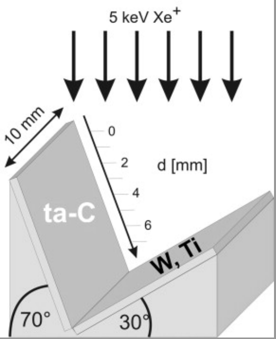
Figure 1. STM topographs of Si(100) after a fluence of $2 \approx 10^{22}$ions m^{-2} 2 keV Kr^+ at 300 K. The angle of incidence ϑ with respect to the surface normal is (a) 0°, (b) 15°, (c) 26°, (d) 45°, (e) 60°, (f) 75°, (g) 79° and (h) 83°. The image size is for (a)-(d) and (h) 316 nm $\times$ 316 nm and in (e)-(g) 625 nm $\times$ 625 nm. The white arrows in (b)-(h) indicate the ion beam azimuth. The corrugation Δz is 3 nm in (a)-(e) and (h) and 30 nm in (f) and (g). Inset in (f): height profile along line indicated in (f).

No ripples in MC for Si parameters is not a bug, — it's a feature!

New explanations: The power of dirt

Discovered by accident H. Hofsäss und K. Zhang Appl. Phys. A, 2008:

To create ripples on Si, you need dirt (i.e. a submonolayer concentration of metals like Fe or Mo at the surface)

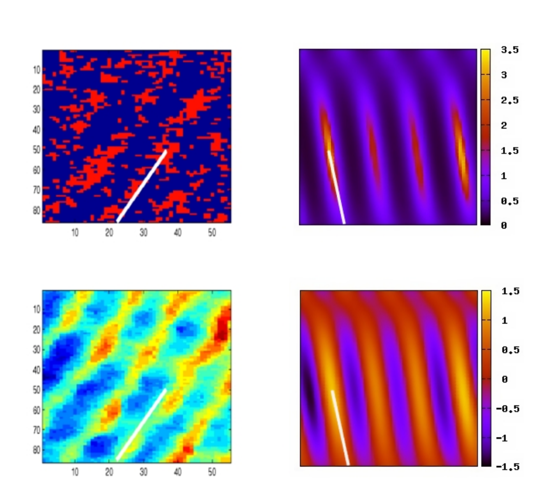


(from H. Hofsäss, K. Zhang 2009)

Surfactant sputtering: Dirt, which influences pattern formation

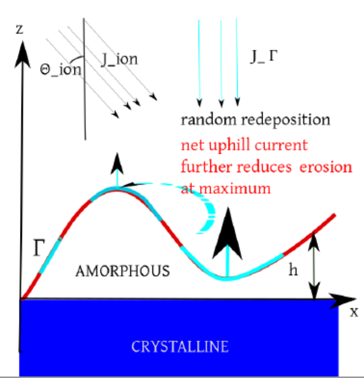
MC study of surfactant sputtering

R.K., T. Yasseri, A. Hartmann, NIMB, 2009



Left: MC, Right: Continuum theory
Up: dirt, Down: Topography

Physical mechanisms



1. Si covered by Fe/Mo has slightly reduced sputter yield.
2. more metal is sputtered from valleys than from crests (BH instability), but it is redeposited homogeneously. Thus metal concentration is enhanced on crests. Thus even less is sputtered from crests etc.

Adatoms: The overlooked major player

Now, we can get ripples on Si by dirt. But they are not “nice” Still, the physical mechanisms are missing, which make ripples “nice”. Here is the hottest candidate: the cascade particles, which reach the surface but are not sputtered off, i.e. adatoms. Adatoms make up $\sim 80 - 90$ % of cascade at surface.

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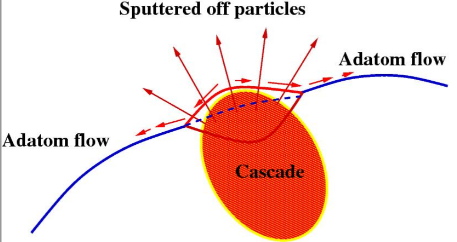


Ion induced adatom flow is random motion + drift due to remaining ion momentum

What ion-induced adatoms can do

A) Adatom drift leads to smoothing (downhill current)

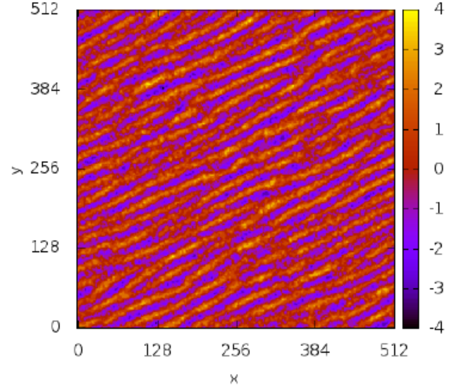
G. Carter, V. Vishnyakov, PR B 1996

What ion-induced adatoms can do

A) Adatom drift leads to smoothing (downhill current)

G. Carter, V. Vishnyakov, PR B 1996

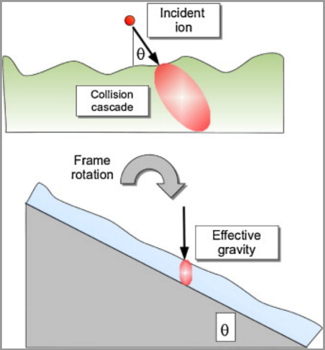
B) Adatoms is all you need to create patterns.



Sputtering yield zero !! S. Schütz, R.K. 2012

An illuminating physical picture

R. Cuerno 2011

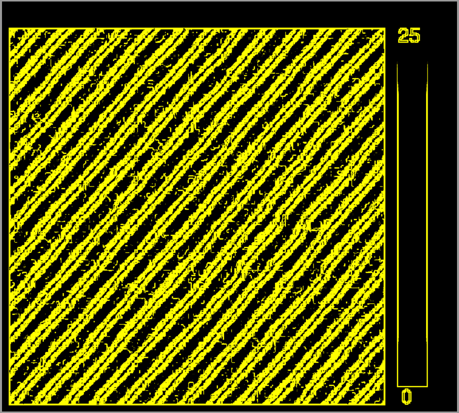


1. ion induced flow
2. analogous to flow of a fluid film on an inclined plane
3. well known ripple instability at critical angle
4. adding dirt is like adding a surfactant in the film
5. leads to Marangoni instability (nice ripples)

R. Kree, Conf. I.B.S. Bhubaneswar, India, 2011

A step closer to the holy grail

Adatoms turn ripples into nice ripples



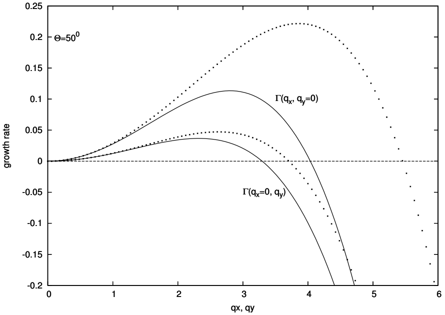
Si sputtering parameters, adatom flow parameters fitted to smooth surface stability region R.K. 2012

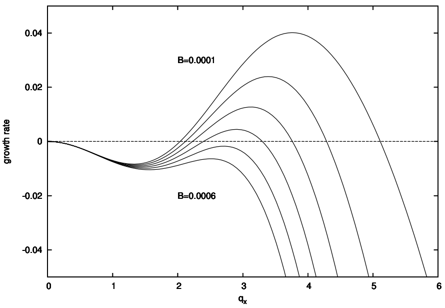
So, what makes ripples nice?

M. Bradley, PR B 2012, S. More, R. K. App. Surf. Sc. 2012

Do we understand, how adatom flow creates nice ripples?

From a theoretical point of view: Changing type II into type I instabilities





Anchors aweigh! New shores ahead!

Which combinations of adatom flow, preferential sputtering, chemical forces, ... turn the type II (sloppy ripples) instability into a type I (nice ripples, regular dot arrays) instability? This knowledge is the key to technological application.

Conclusions

1. Nanostructures (ripples, dots) appear spontaneously under ion beam irradiation
2. due to a generic curvature instability
3. on clean Si, you cannot produce clear ripple patterns in this way
4. but with dirt (Fe/Mo), you can
5. adatom flow driven by ions, chemical forces etc can turn ("sloppy ripple´´) type II instability nto ("nice ripple´´) type I instability
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