

Real-Time X-ray Studies of Self-Organized Nanostructure Formation During Nitride Growth and Ion Bombardment

YESS – nano 2009 – Nov. 16-18, 2009

Karl Ludwig, Eitan Anzenberg, Leyla Colakerol, Ahmet Özcan,
Gözde Ozaydin, Yiyi Wang, Nathalie Bouet
Dept. of Physics; Boston University

Ted Moustakas and Anirban Bhattacharya
Dept. of Electrical and Computer Engineering; Boston University

Randy Headrick, Hua Zhou and Lan Zhou
Dept. of Physics; University of Vermont

Peter Siddons
National Synchrotron Light Source; Brookhaven National Laboratory



Overview:

- Why Real-Time Studies?
- Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)
- Facility for Real-Time Studies of Surface and Thin-Film Processes at NSLS X21
- Studies:
 - *Growth of III-Nitride Nanodots by Droplet Epitaxy*
 - *Nanoscale Surface Morphology/Nanostructure Development During Ion Bombardment*

The Big Picture –

Real-time studies:

- Complete temporal record
- No worries about sample changes before *post facto* measurement
- Consistent kinetics data all from one experimental run



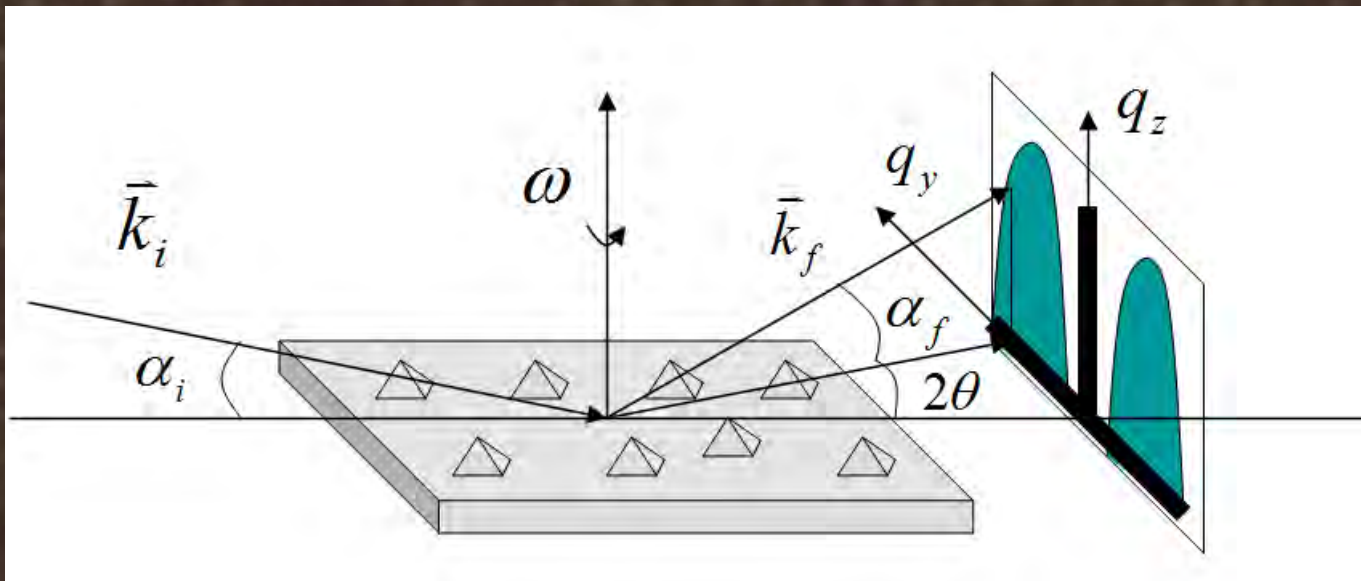
X-ray studies:

- Probe length-scales from 10^{-3} – 10^3 nm
- Control bulk/surface probe depth by varying angle of incidence/exit
- Penetrate ambient environment

Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)

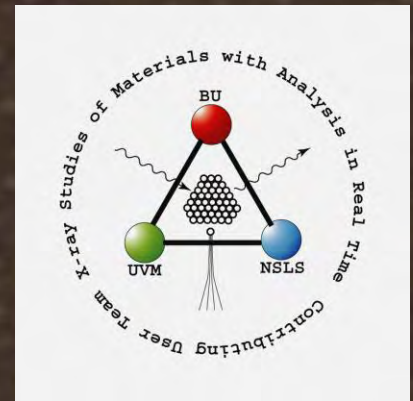
Analogous to conventional small-angle x-ray scattering:

Examine surface morphology on length scales of 1 - 200 nm

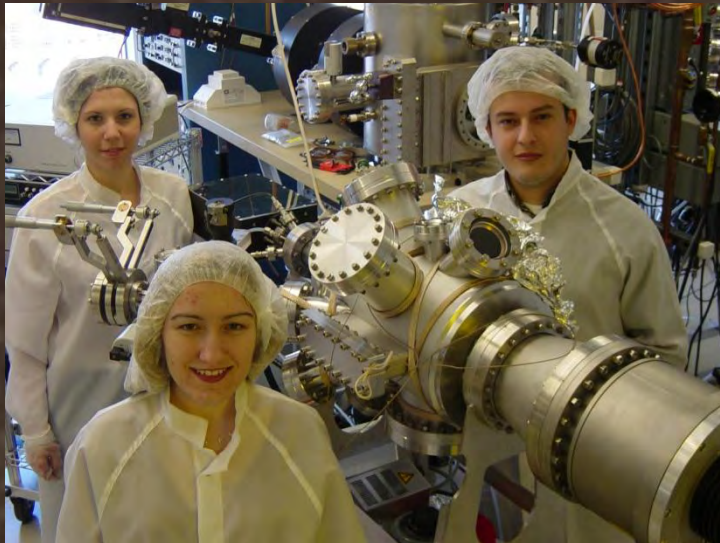


X-ray Studies of Materials with Analysis in Real Time (XSMART) Facility

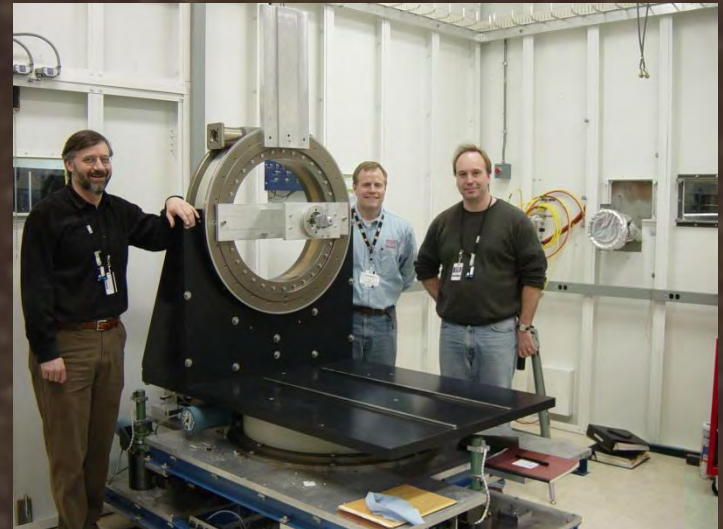
NSLS – Beamline X21



Experimental conditions can be optimized in chambers at the home laboratory ...



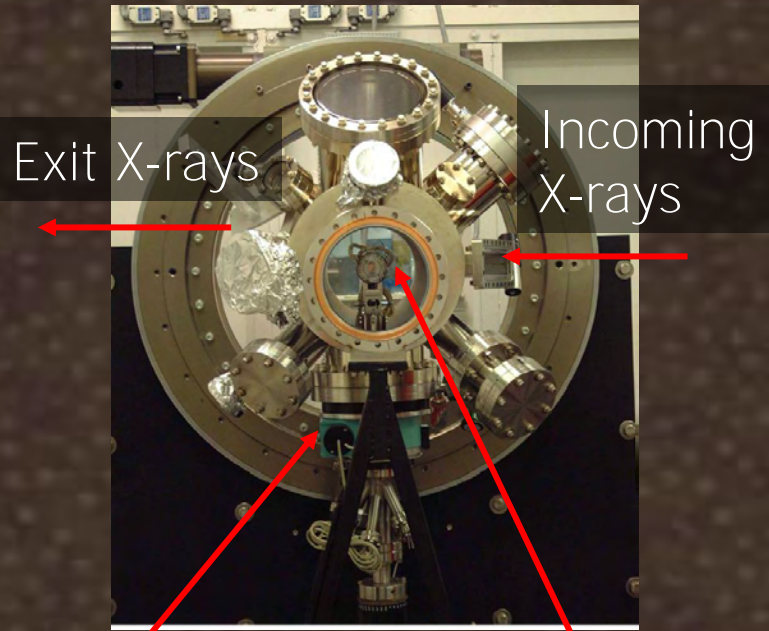
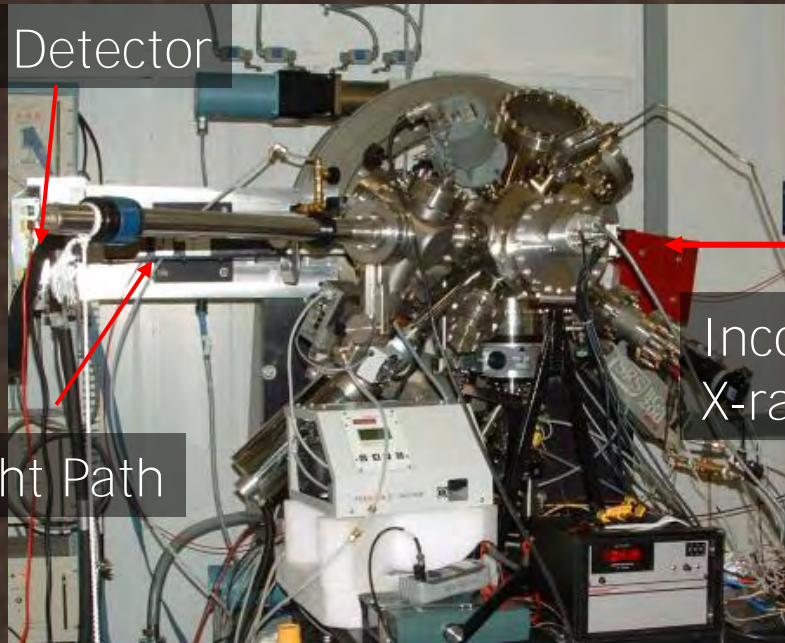
... the chambers can then be rolled onto the base diffractometer permanently installed at NSLS



Diffractometer rail configuration compatible with CHESS G-line

YESS – nano 2009 – Nov. 16-18, 2009

Diffractometer Geometry



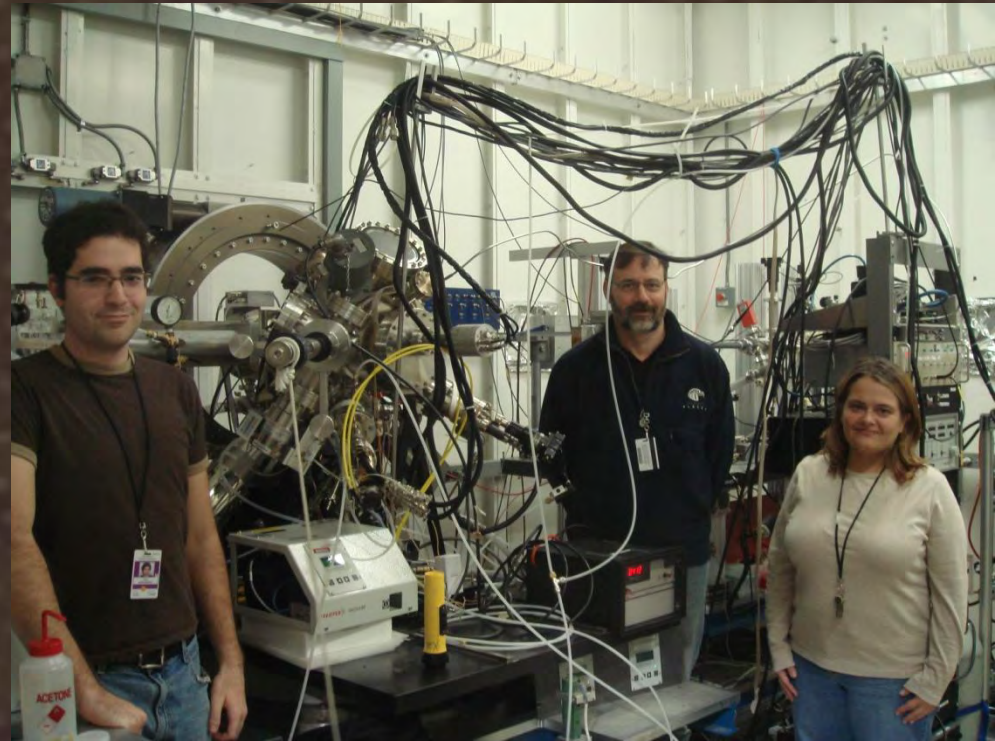
Surface Modification and Characterization Instrumentation

Current Facility Equipment:

- Thermionics sample manipulator with BN heating element capable of heating samples to $\sim 800\text{ }^{\circ}\text{C}$
- Oxford Scientific OSPrey ECR plasma source
- Applied Epi UNI-bulb RF plasma source
- Applied Epi SUMO effusion cells
- US Inc. sputter deposition source
- Balzers mass spectrometer
- Staib RHEED system
- Iacon infrared pyrometer

~ 50 access in-plane scans

$\sim 22^{\circ}$ access out-of-plane scans



Two Examples of Recent Research Areas:

- Growth of III-Nitride Nanodots by Droplet Epitaxy

APL **88**, 181915 (2006); JAP **100**, 084307 (2006); PRB **74**, 235304 (2006); JAP **102**, 073522 (2007); JAP **103**, 103538 (2008)

- Nanoscale Surface Morphology/Nanostructure Development During Ion Bombardment

APL **81**, 2770 (2002); APL **87**, 163104 (2005); NIM B **264**, 47 (2007), JAP **103**, 033512 (2008); JVST B **26**, 551 (2008)



Example 1:

III-V Nitride Nanodot Growth

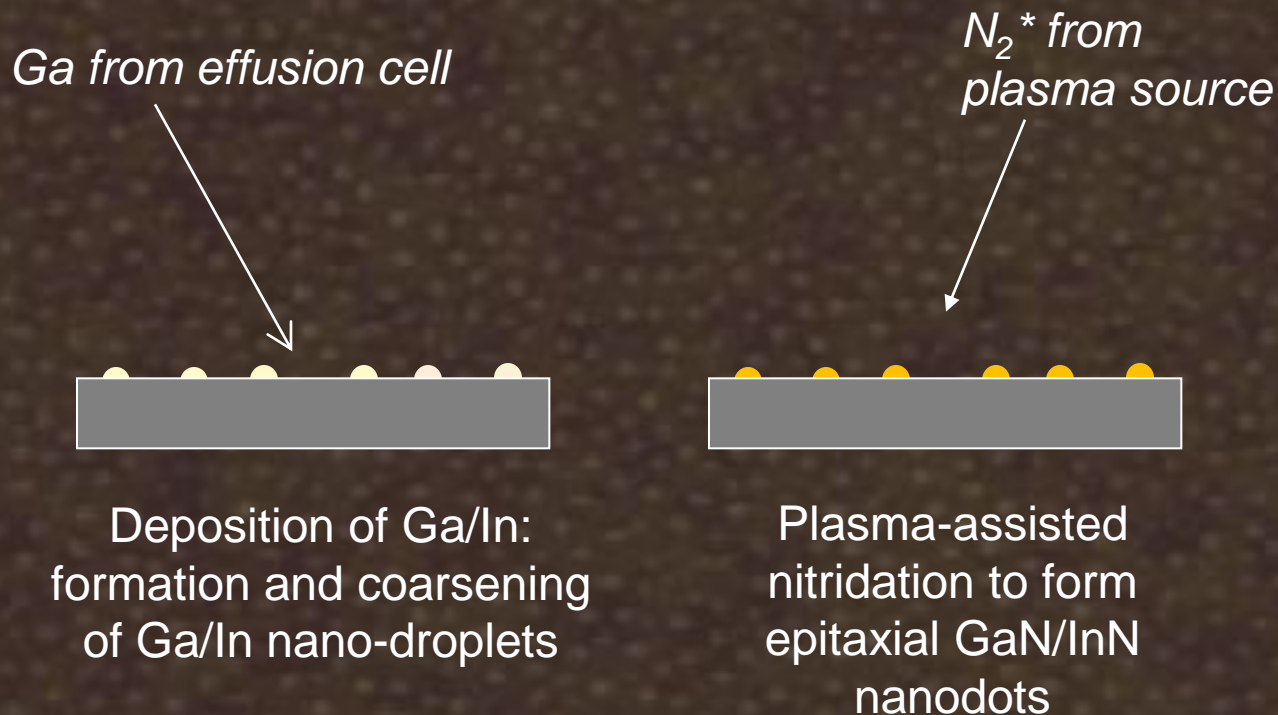
Group III-nitrides under intense development for optoelectronics, lighting and photovoltaic applications

Two Topics:

- 1) GaN nanodot growth by droplet epitaxy on sapphire
- 2) InN nanodot growth on GaN

GaN Nanodot Growth by Droplet Epitaxy

Lack of appropriate group-III nitride substrates so most films grown heteroepitaxially: sapphire is most popular substrate



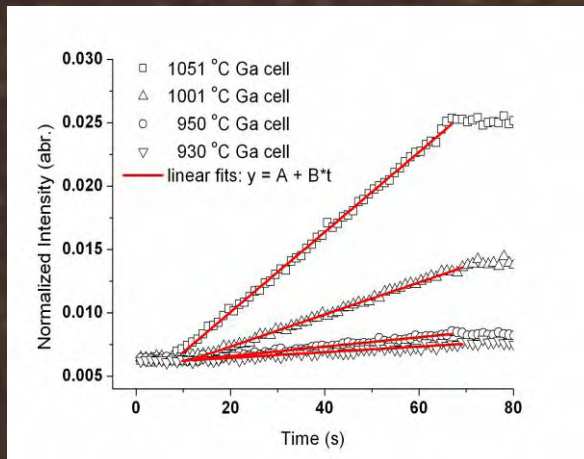
Ga Adsorption/Desorption Kinetics on Sapphire (0001)

Measure adsorption/desorption rates using Ga fluorescence

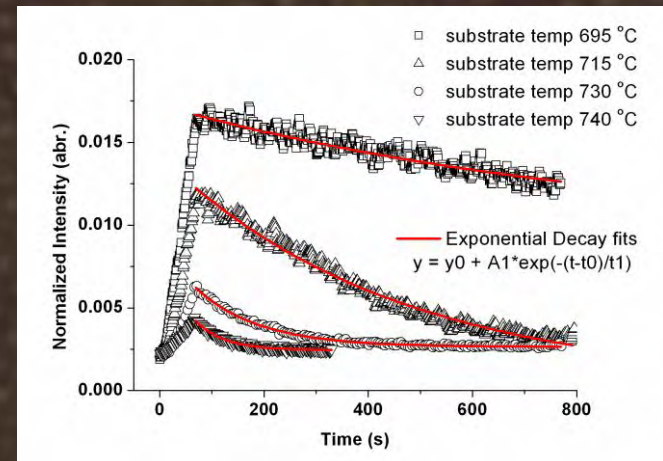
Measure rates as a function of:

- effusion cell temperature (Ga flux)
- substrate temperature

Fits to linear adsorption rate
(following initial transient)



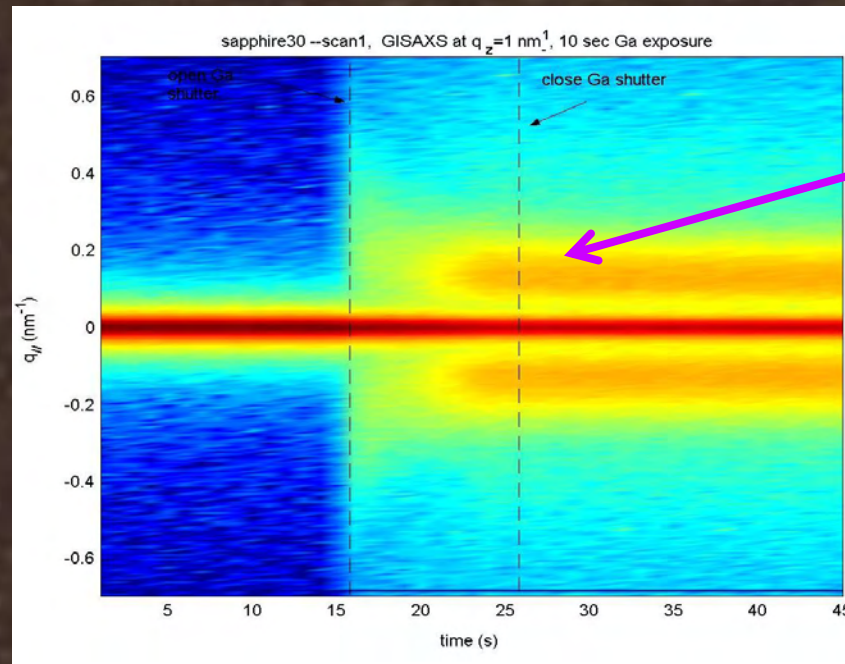
Fits to exponential desorption rate



III-V Nitride Nanodot Growth by Droplet Epitaxy

Evolution of GISAXS pattern during Ga exposure
from effusion cell:

c-plane
sapphire
@ 780 C



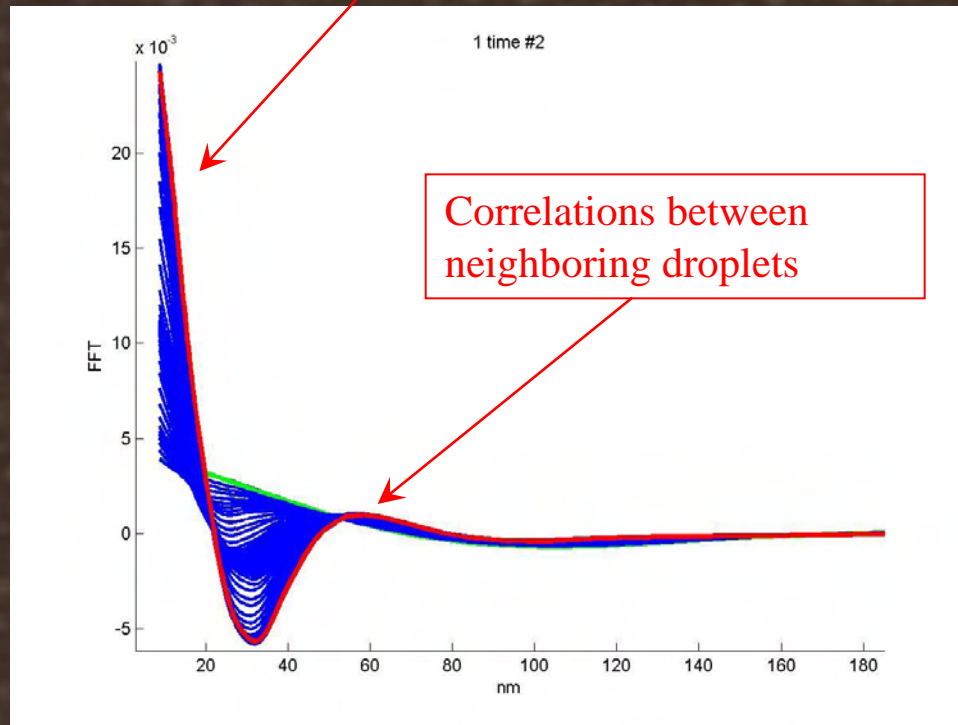
Growth of peaks
shows formation
of correlated
nanodroplets on
surface

↔ 10 sec Ga exposure

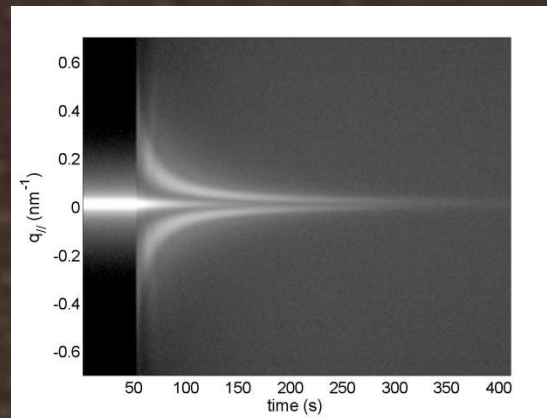
Ga Droplets: Real-Space Correlation Function

Fourier Transform GISAXS $S(q)$ to get real-space pair correlation function:

Correlations within a single droplet



Ga Droplet Coarsening during Continuous Deposition



PHYSICAL REVIEW A

VOLUME 40, NUMBER 7

OCTOBER 1, 1989

Kinetics of droplet growth processes: Simulations, theory, and experiments

Fereydoon Family

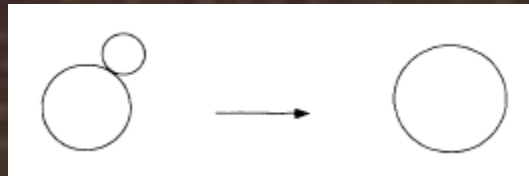
Department of Physics, Emory University, Atlanta, Georgia 30322

Paul Meakin

Central Research and Development Department, E.I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0356

(Received 19 April 1989)

Main mechanisms: *Nucleation, growth and coalescence*

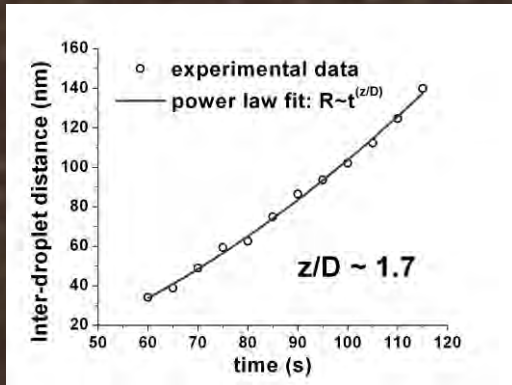
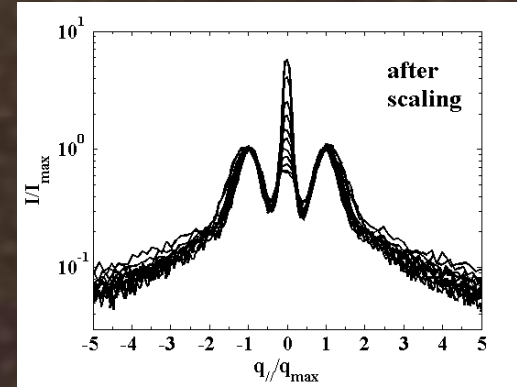
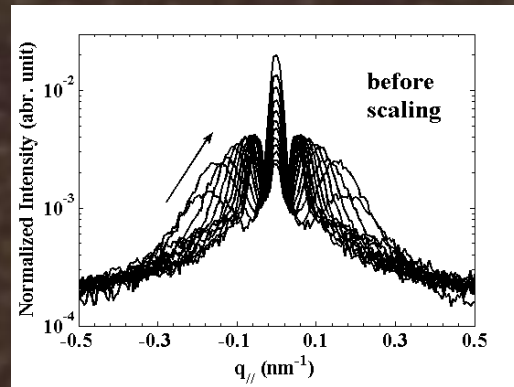


$$r = (r_1^D + r_2^D)^{1/D}$$

Growth and coalescence lead to scaling of droplet size distribution:

Ga Droplet Coarsening during Continuous Deposition

Theory and simulation predict scaling of droplet size distribution:

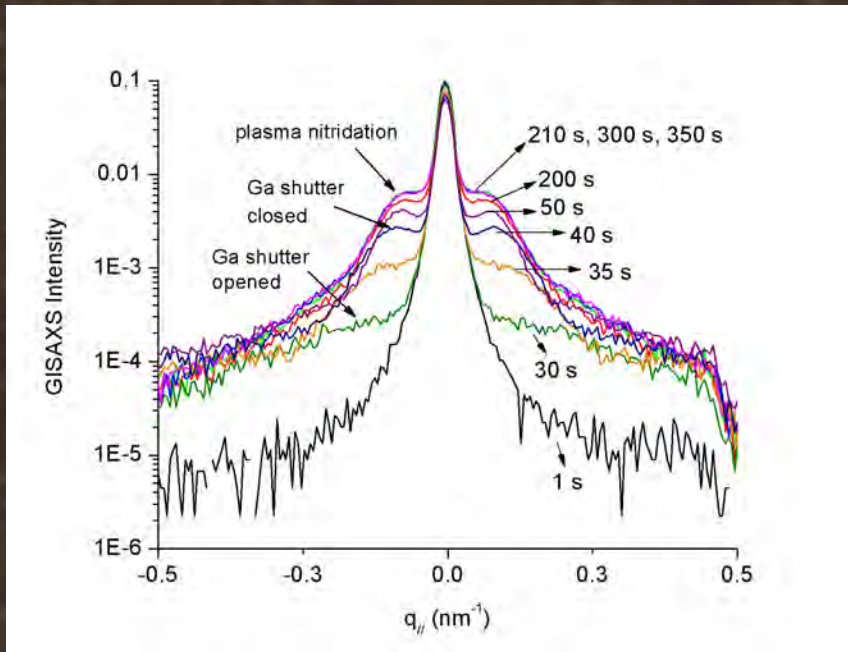


$R(t) \sim t^{z/D}$ where D is the dimensionality of the droplet and $z = D/(D-2)$.

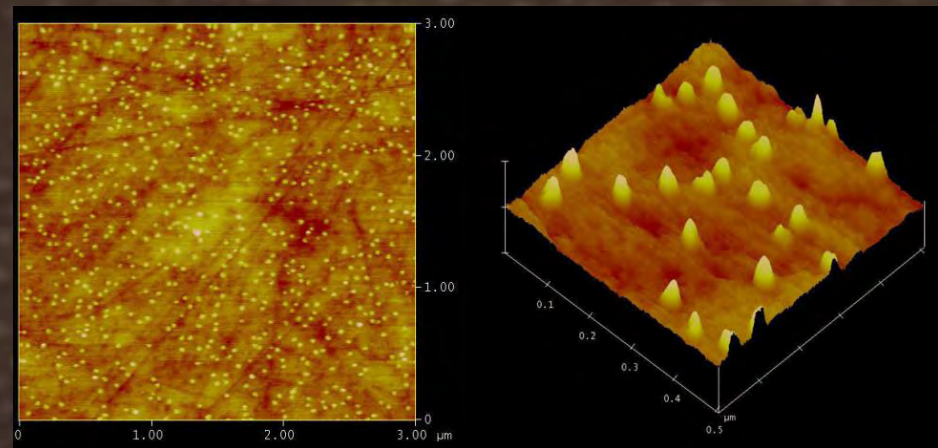
This gives a droplet dimensionality of $D=2.6$, which is between the limits expected for 2- and 3-dimensional growth. This is consistent with the fact that the droplets are relatively flat.

Nitridation of nanodroplets to form single crystal nanodots – Droplet Epitaxy

GISAXS during nanodroplet formation and subsequent nitridation

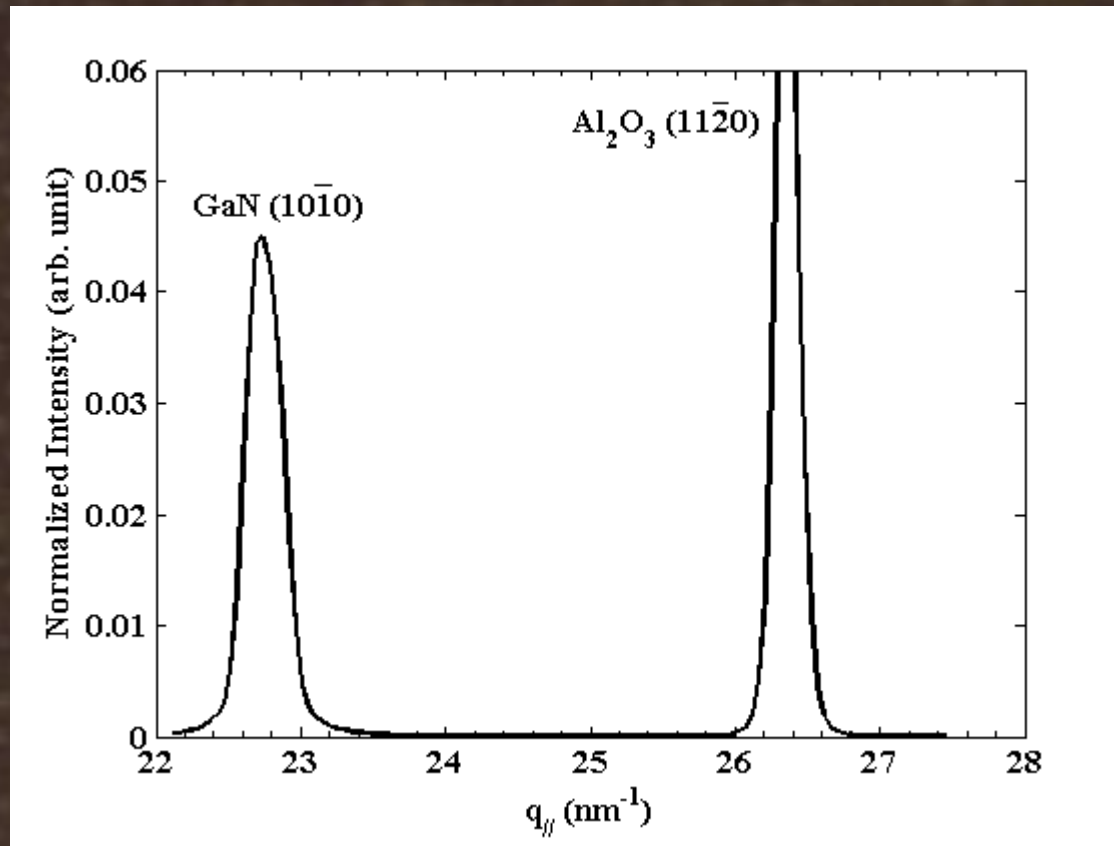


AFM topograph of resulting nanodots



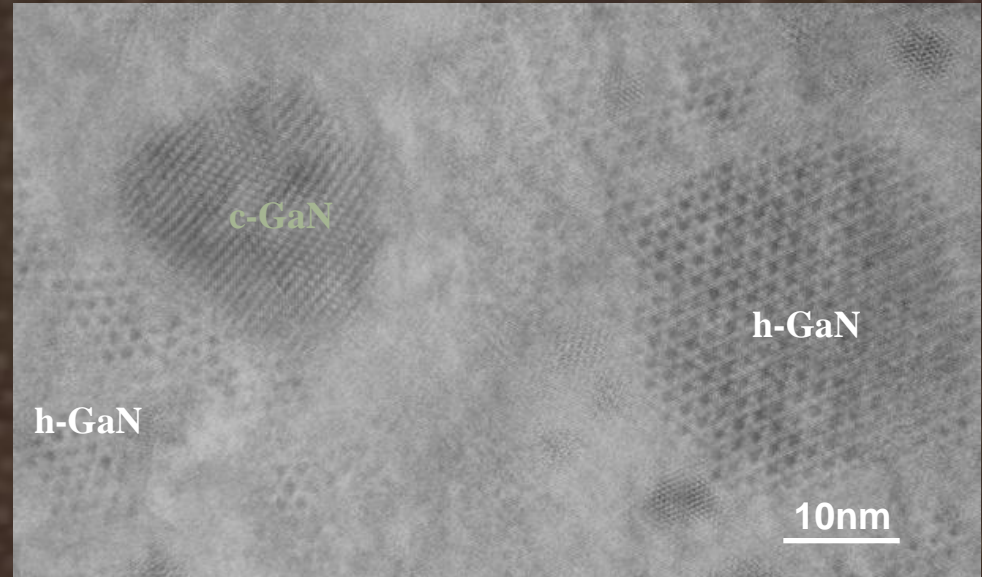
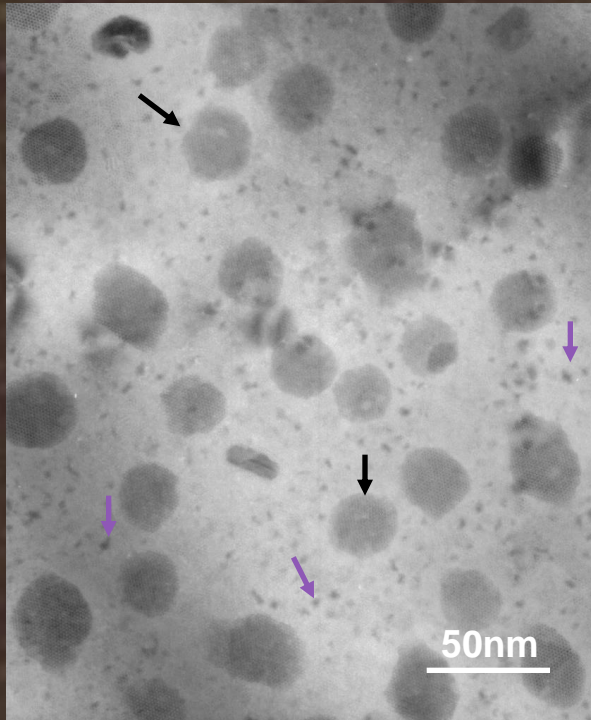
GaN Nanodots: Grazing-Incidence Diffraction

GID scans show that the GaN nanodots are fully strain relaxed



TEM Plan View of GaN Nanodots

TEM work of collaborators Lin Zhou and David Smith – Arizona State University



- Two sizes of GaN nanodots on sapphire surface
- Existence of both cubic and hexagonal GaN nanodots
- Hexagonal array of fringes—moiré fringes caused by overlapping of GaN and sapphire lattice

Kinetics of droplet growth processes: Simulations, theory, and experiments

Fereydoon Family

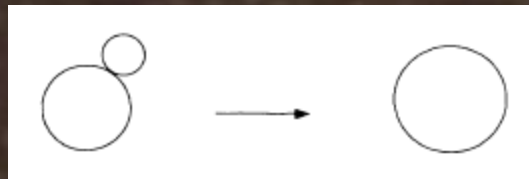
Department of Physics, Emory University, Atlanta, Georgia 30322

Paul Meakin

Central Research and Development Department, E.I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0356

(Received 19 April 1989)

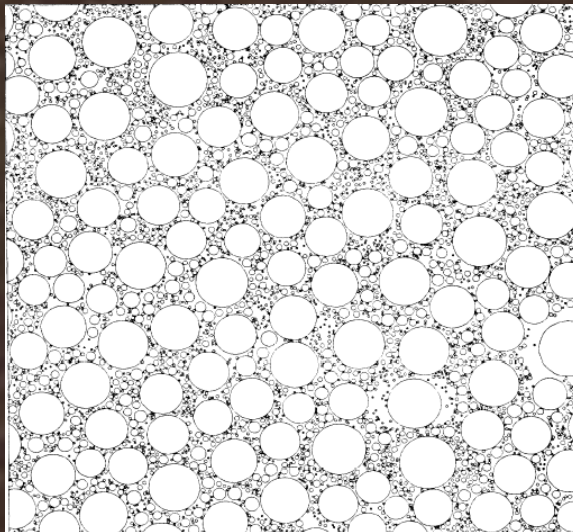
Main mechanisms: *Nucleation, growth and coalescence*



$$r = (r_1^D + r_2^D)^{1/D}$$

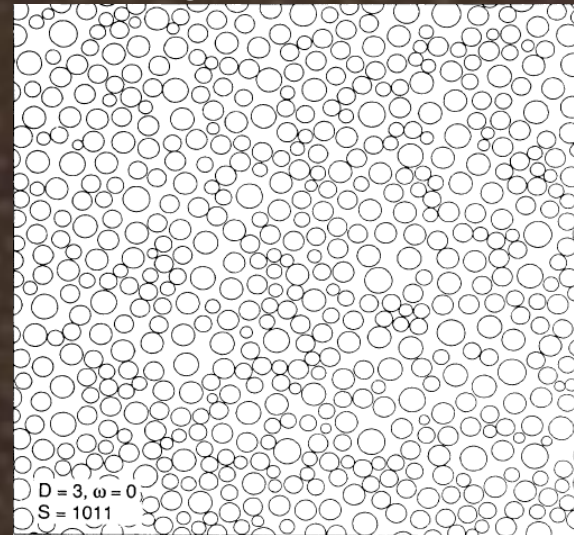
Simulation results:

Homogeneous nucleation



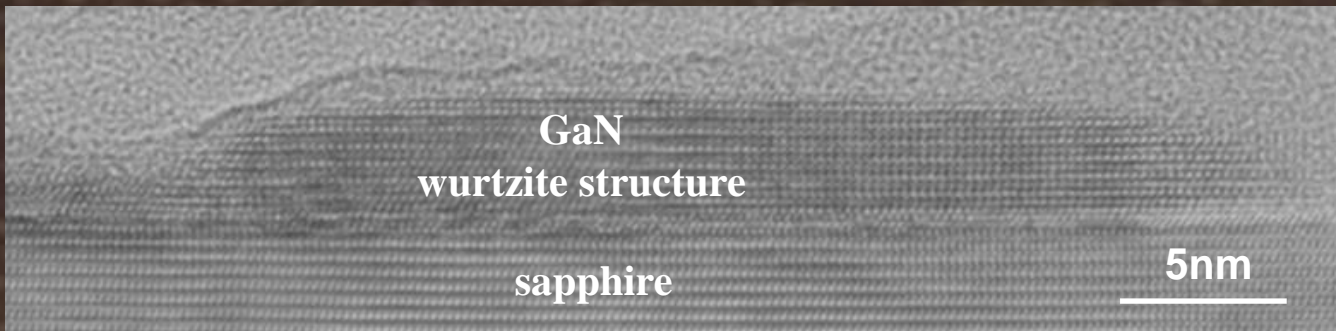
Monodispersed droplets +
smaller polydispersed droplets

Heterogeneous nucleation

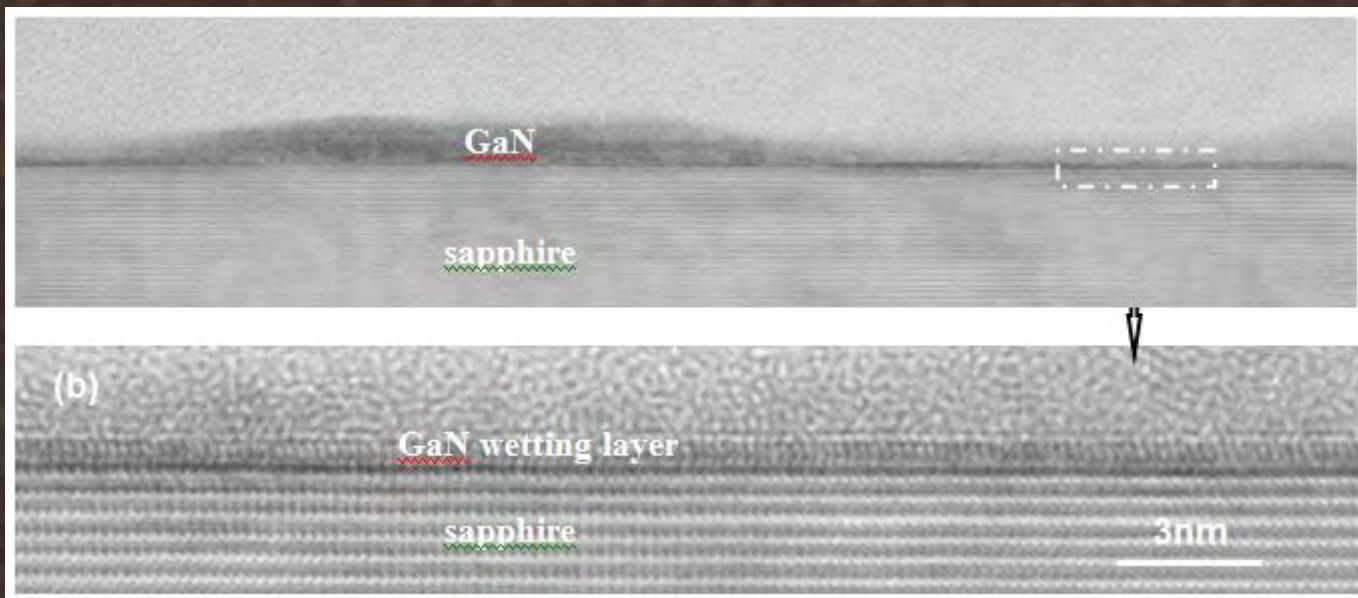


Monodispersed droplets

TEM analyses — high resolution cross-section

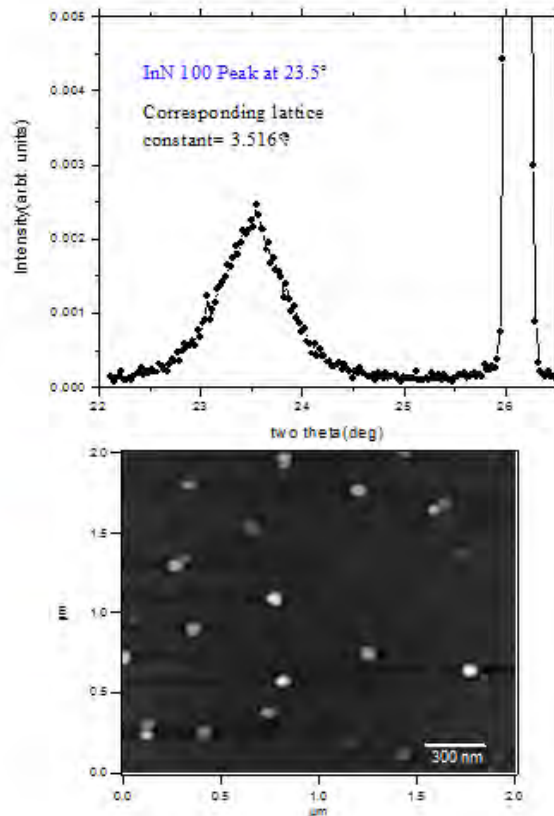
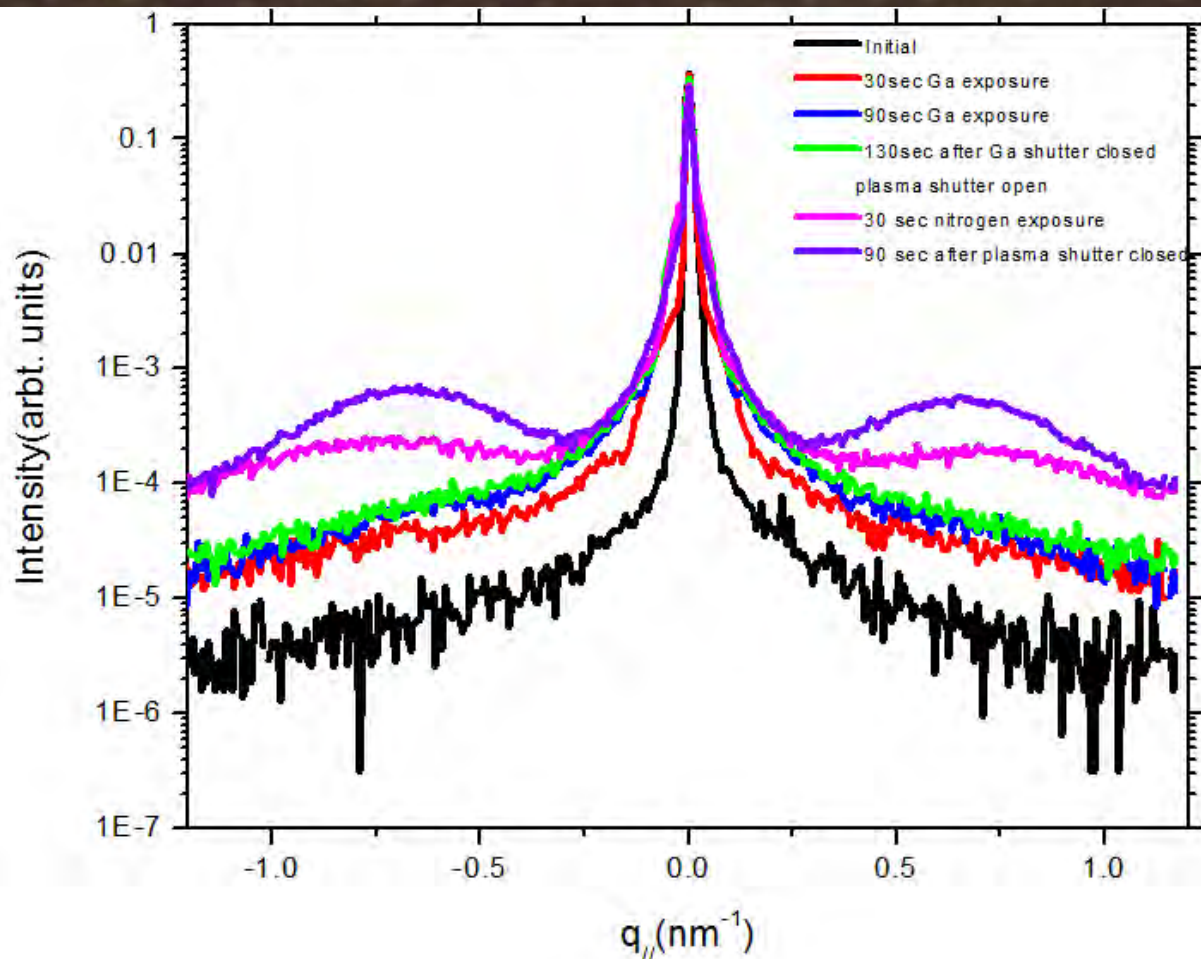


At low temperatures a GaN wetting layer forms between the dots – possibly due to reduced mobility of Ga atoms on the surface:



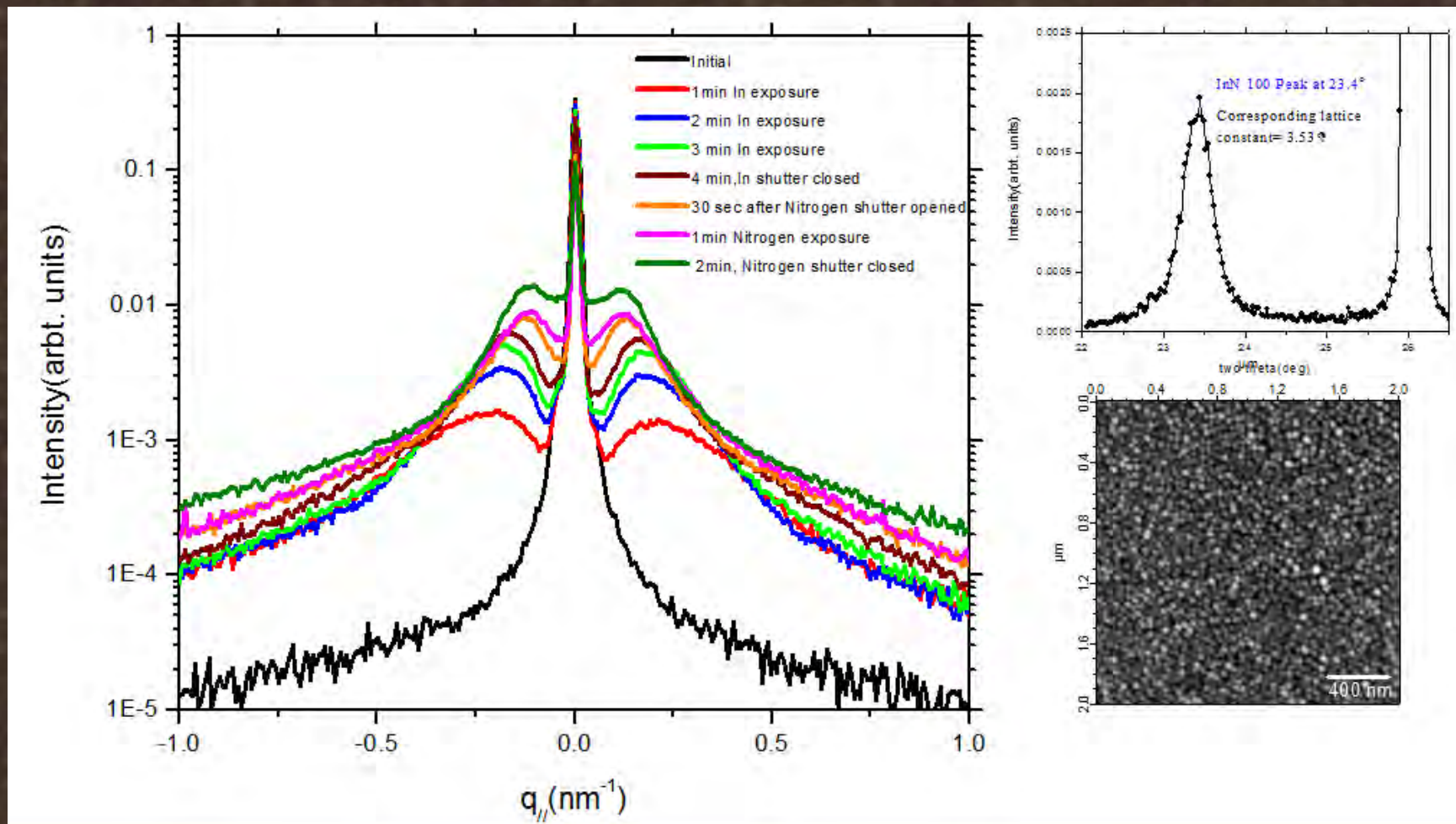
InN Nanodot Growth on GaN (0001) by Droplet Epitaxy

InN growth at 300 C



InN Nanodot Growth on GaN (0001) by Droplet Epitaxy

InN growth at 200 °C



Example 1 Conclusions...

GaN and InN Nanodot Growth by Droplet Epitaxy

- 1) We can clearly observe and quantify the kinetics of absorption/desorption with real-time GISAXS
- 2) Scaling dynamics of droplet nucleation, growth and coalescence observed in agreement with theory/simulation
- 3) Size and spacing of nanodots controlled by deposition rate and substrate temperature
- 4) Evolution of droplets/dots during plasma-assisted nitridation can be observed. Nitridation produces epitaxial nanodots.

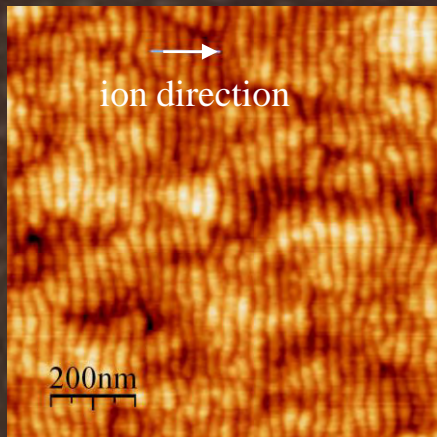


Example 2:

Self-Organized Nanostructure Formation During Low-Energy Ar⁺ Bombardment of Si (100)

Off-Axis Bombardment –

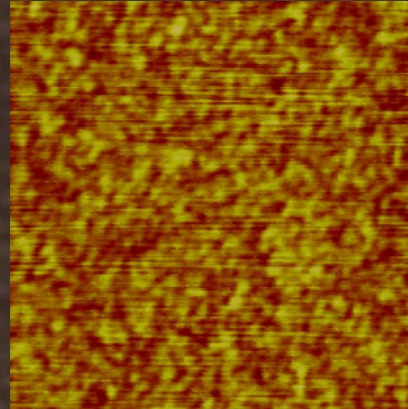
Ripples:



Si(100)

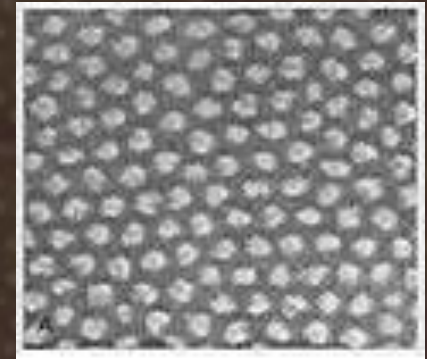
Normal Incidence Bombardment–

Smoothing:



Si(100)

Dots:



GaSb (100)

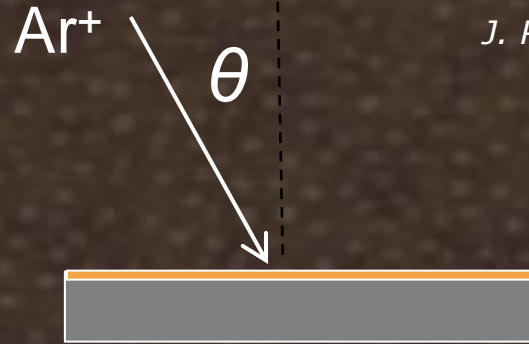
Facsko *et al.*, Science **285**,
1551 (1999)

Surface Morphology Development During Low-Energy Ar⁺ Bombardment of Si (100)

Two Topics:

- 1) “Native” evolution of surfaces during room temperature bombardment
- 2) Evolution of surfaces with Mo “seeding” to form nanodots

Nanostructuring During Ion Bombardment Topic 1: Native evolution of Si(100) during room temperature bombardment



J. Phys. Condens. Matter. 21, 224008

For 1000 eV Ar^+ ions at room temperature:

For small angles θ , the surfaces is smoothened

For larger angles θ , ripples spontaneously form

Phase Diagram with transition between smoothening/ripple regimes at $\theta \sim 45^\circ$ Madi *et al.*: PRL **101**, 246102 (2008)

How can we think about nanoscale surface morphology development during ion bombardment? (amorphous surface)

Smoothing: “Lateral Mass Redistribution”
momentum transfer from ion knocks atoms “downhill”

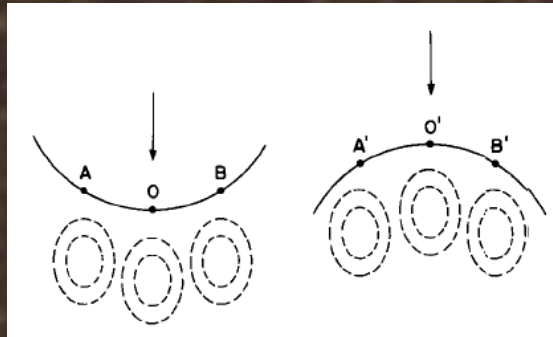
Thermal or ion-induced diffusion or viscous flow

Stochastic nature of bombardment, relaxation

$$\frac{\partial h(x,t)}{\partial t} = -V_0 + v_{LMR} + v_{BH} \nabla^2 h - B \nabla^4 h + (noise)$$

Average sputter erosion rate

Bradley-Harper roughening term



Theory of ripple topography induced by ion bombardment

R. Mark Bradley
Department of Physics, Colorado State University, Fort Collins, Colorado 80523
James M. E. Harper
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

Linear theory solution in reciprocal space:

$$S(q, t) = S(q, 0)e^{-R(q)t} + \frac{\langle \eta^2 \rangle}{R(q)} (1 - e^{-R(q)t})$$

Morphology development is governed by the amplification factor:

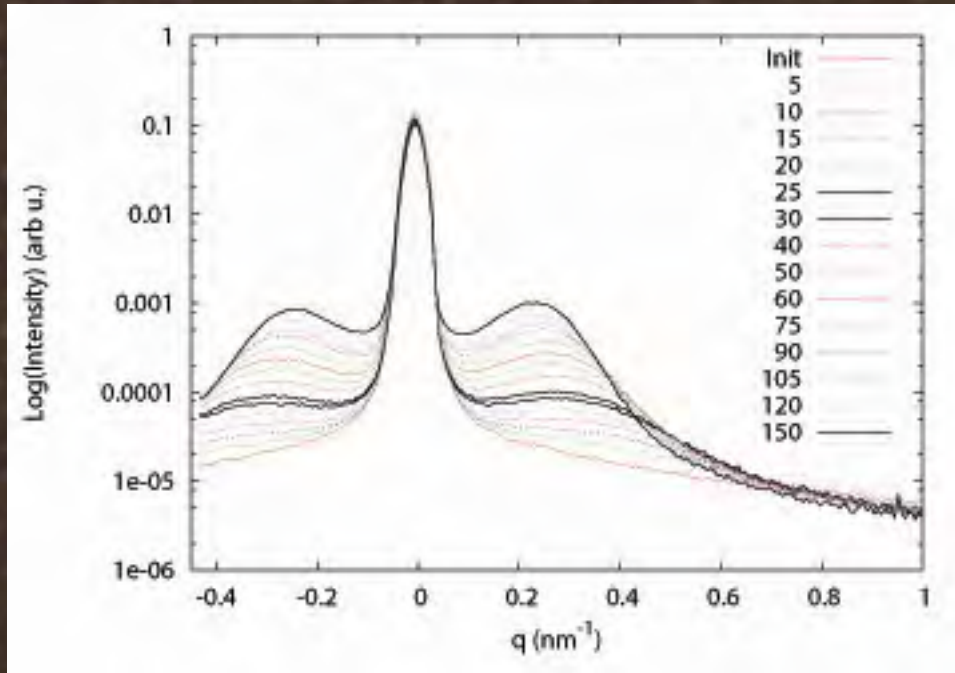
$$R(q) = A(\theta)q^2 + B(\theta)q^4$$

If $R(q) > 0$ then mode is stable

If $R(q) < 0$ then mode is unstable

Measuring $R(q)$ for different incident angles can tell us much about the physical mechanisms operating during bombardment

Use Real-Time GISAXS to Measure Evolution of $S(q)$



Growth of GISAXS peak due to formation of ripples during ion bombardment.

Each scan is approximately 2 min apart.

Fits to exponential process at each wavenumber yield

$$R(q)$$

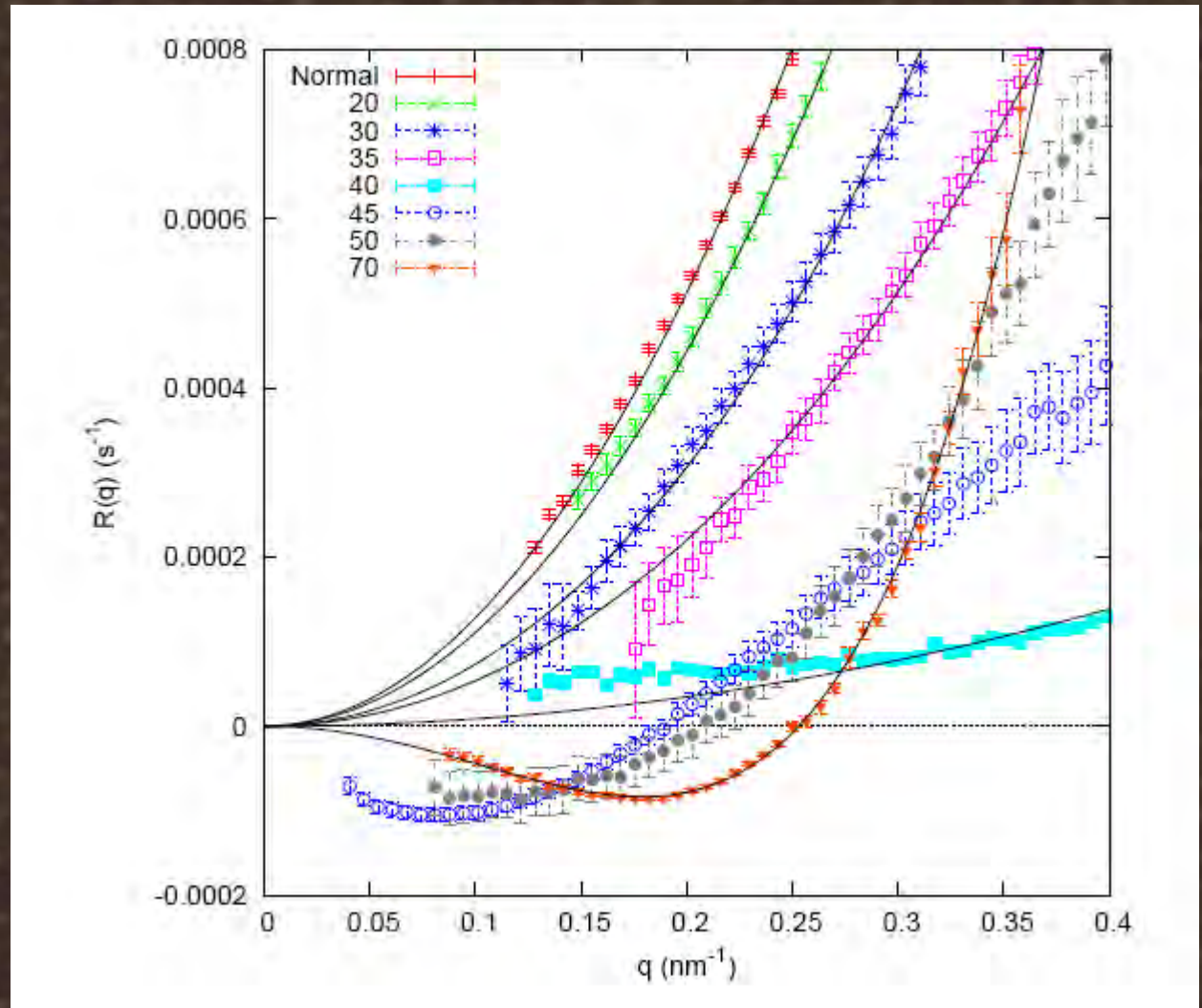
Work in collaboration with C. Madi and M. Aziz, Harvard University

Measured Amplification Factor $R(q)$

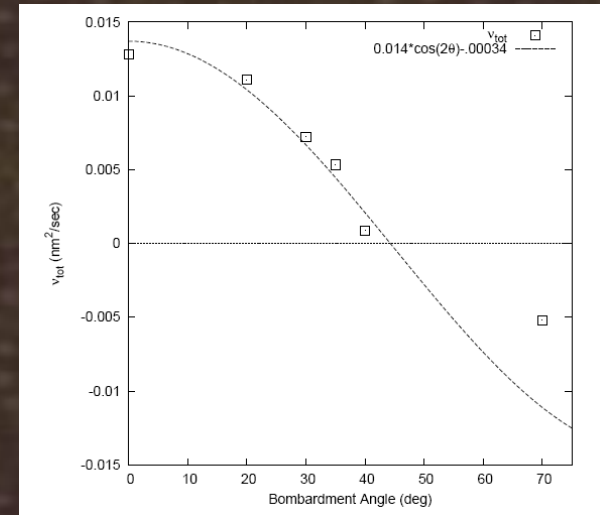
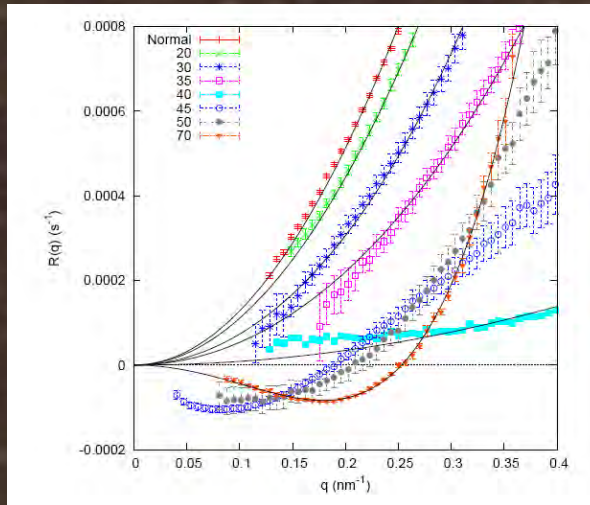
$R(q) > 0$:
“Smoothing”

$R(q) < 0$:
Instability to
Nanoripple
Growth

Phase transition
at bombardment
angle
 $\theta_c \sim 40-45^\circ$



Amplification Factor $R(q)$ – Smoothing Regime



In the smoothing regime ($\theta < \theta_c$)

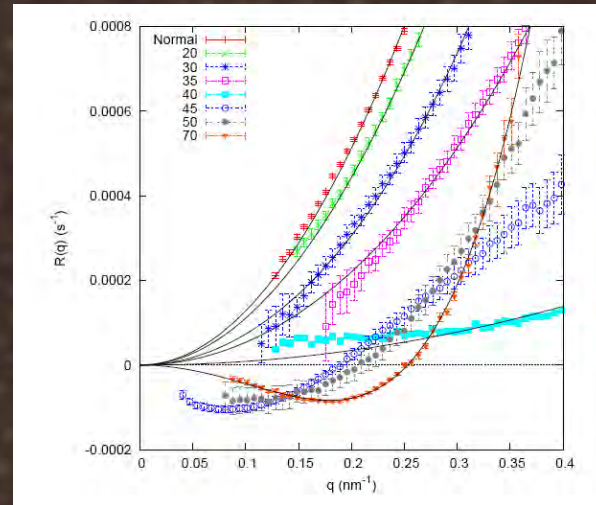
$$R_{exp}(q) \sim v_{tot} q^2$$

No (or little) evidence of q^4 diffusion/viscous flow relaxation

Dependence of $R(q)$ on ion bombardment angle θ is expected form when dominant process is Lateral Mass Redistribution (ion momentum knocking atoms downhill):

$$v_{tot} \approx v_{LMR} \sim \cos(2\theta)$$

Amplification Factor $R(q)$ – Instability Regime



Deep in the instability regime ($\theta > \theta_c$)

$$R_{exp}(q) \sim \left[-|v_{tot}| q^2 + B q^4 \right]$$

Now q^4 diffusion/viscous flow relaxation seems to play an important role

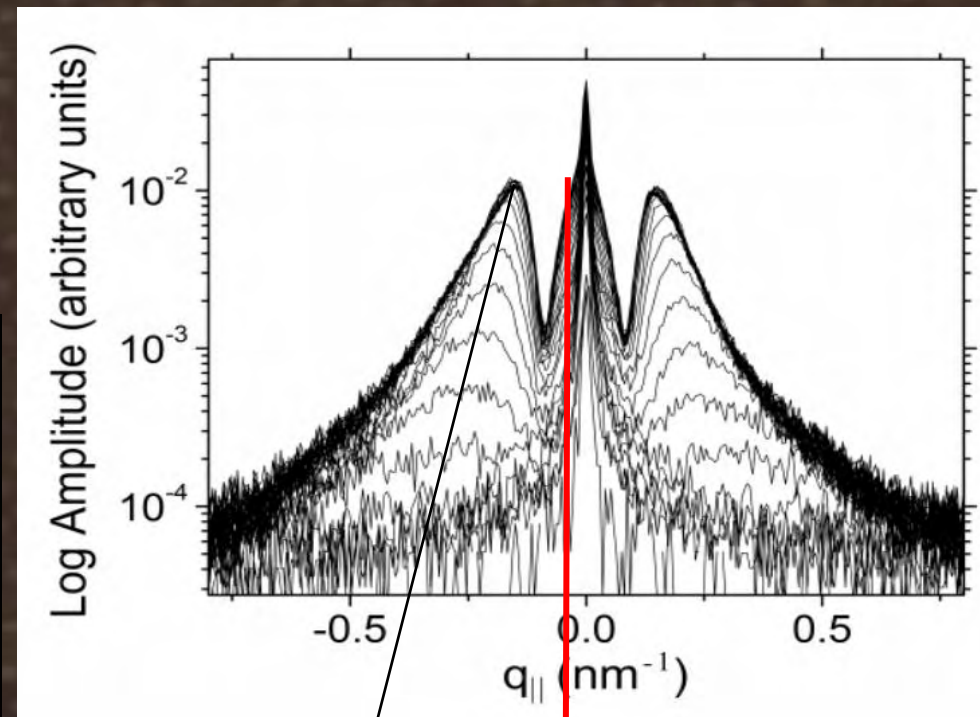
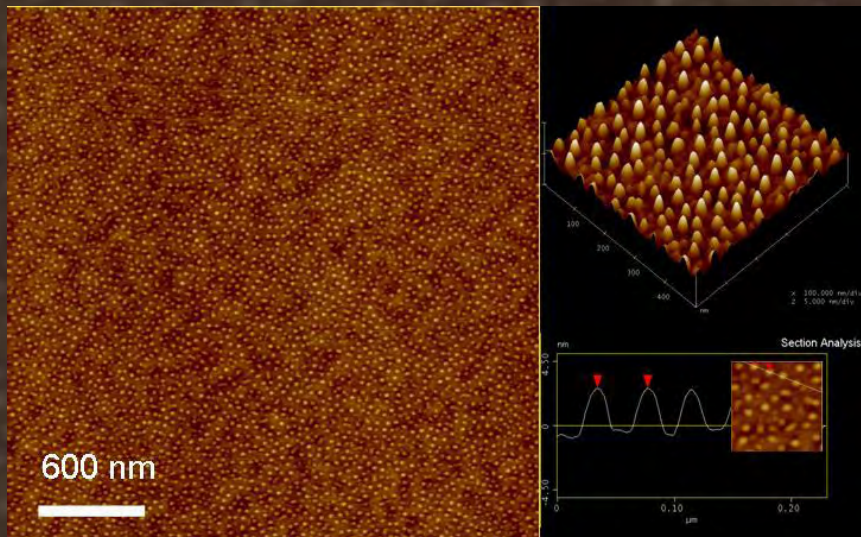
In this regime, behavior is consistent with Bradley-Harper instability playing dominant role

Nanostructuring During Ion Bombardment Topic 2: Evolution of Si Surfaces with Mo “seeding” to Form Nanodots

J. Vac. Sci. Tech. B 26, 551; *Nucl. Inst. Meth. Phys. Res. B* 264, 47; *APL* 87, 163104

Nanostructures form spontaneously with a period of ~ 30 nm and a height of ~ 3 nm.

Evolution of GISAXS scattering patterns

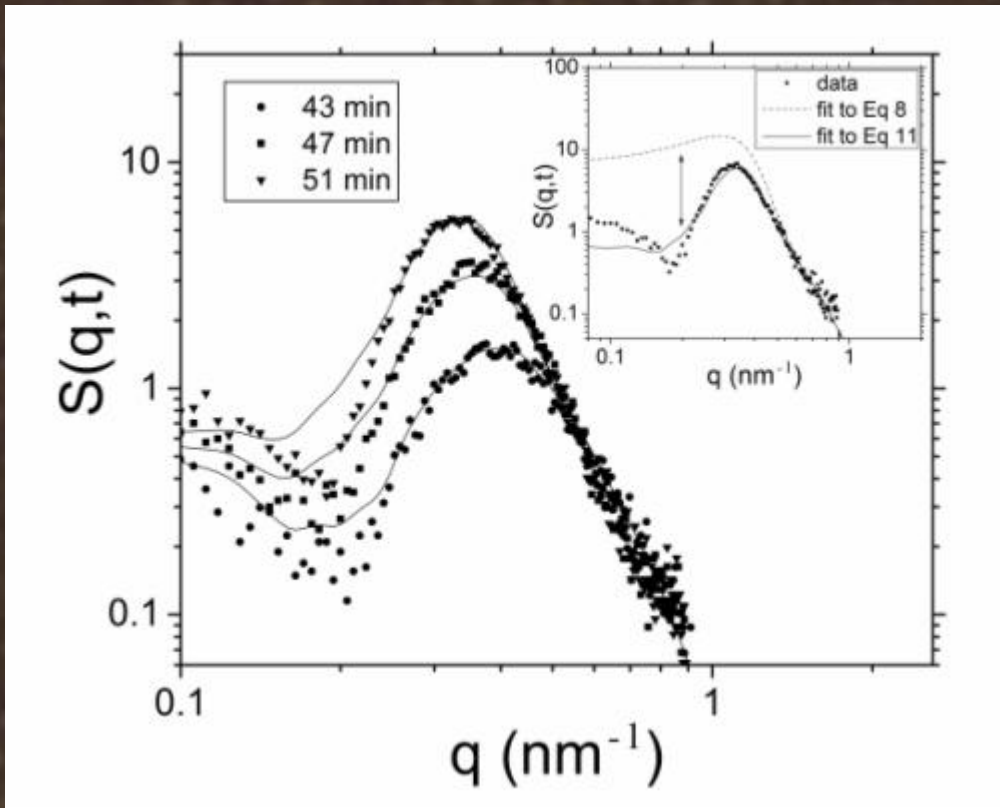


nanostructures

long-wavelength roughness

What is happening during Seeding?

Fits of the GISAXS evolution during nanodot formation can tell us much!



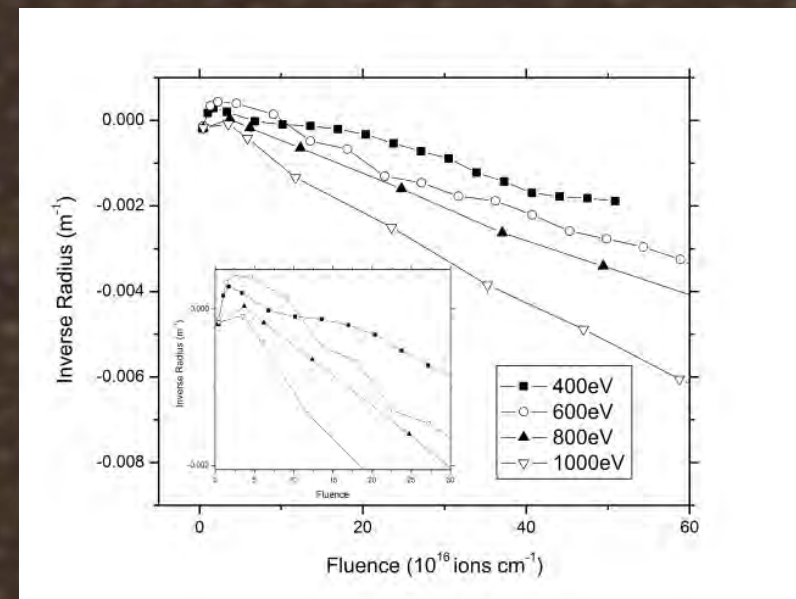
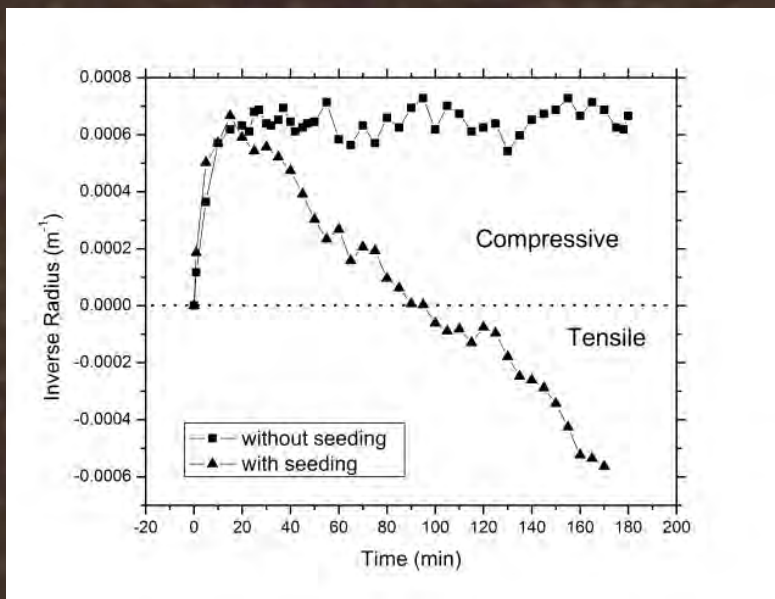
Fits of the nanodot formation process to measure coefficients in kinetics theory:

- *Actual roughening term is stronger than theoretical predictions of known roughening or smoothing terms*
- *Dominant noise is due to the stochastic nature of the ion-induced surface relaxation – Does seeding inhibit relaxation?*

What is happening during Seeding?

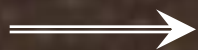
Look at the stress!

Real-time stress measurements using wafer curvature:



No Seeding – Compressive stress develops because Si surface is amorphized (lower density)

Seeding – Very large tensile stress develops because Mo silicides have higher Si density!



We believe that stress is driving Si nanodot formation!

Example 2 Conclusions...

Nanoscale Si surface morphology evolution during
low-energy Ar⁺ bombardment

1) **Native case:** Critical angle $\theta_c \approx 40\text{-}45^\circ$ separating regions of
“nanosmoothing” and self-organized growth of nanoripples

Measurement of amplification factor $R(q)$ suggests:

$\theta < \theta_c$ – surface evolution dominated by lateral mass redistribution

$\theta > \theta_c$ – surface evolution dominated by BH instability and ion-induced
diffusion/viscous flow relaxation

2) **Seeding with Mo:** Growth of nanodots during normal-
incidence bombardment

- *Possibly due to induced stress on the surface*



Conclusions...

We've seen 2 examples of the NSLS X21 real-time x-ray studies:

- III-Nitride Nanodot Growth
- Nanoscale surface morphology evolution during ion bombardment of Si (100)

Real-Time GISAXS Provides a Powerful Tool for the Investigation of Nanostructure Formation on Surfaces

We would like to acknowledge funding from
NSF-DMR and DOE-BES:



Boston University X-ray Diffraction Laboratory