XPCS and Materials Synthesis

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APS-U Forum

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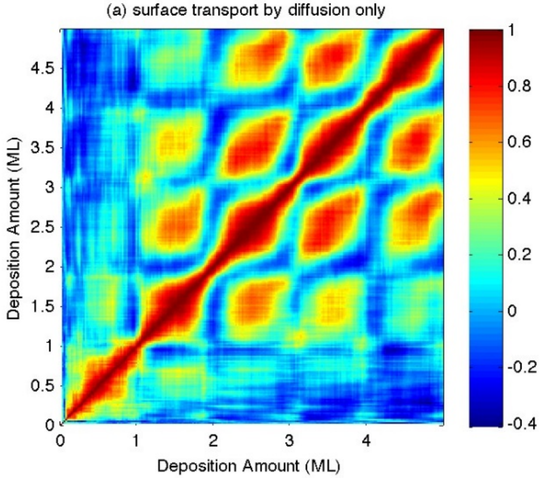
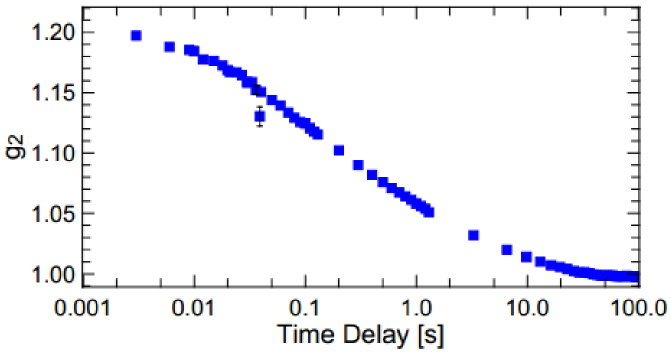


Coherent x-rays reveal atomic dynamics and function

- **XPCS signal ~ (coherent flux)^2**
- Improvements from APS upgrade directly: 10,000 – 1,000,000

APS Today:

X-ray photon correlation spectroscopy (XPCS) reveals equilibrium dynamics in strongly-scattering systems, e.g. 100 nm fluctuations of particles, membranes, soft materials, etc.

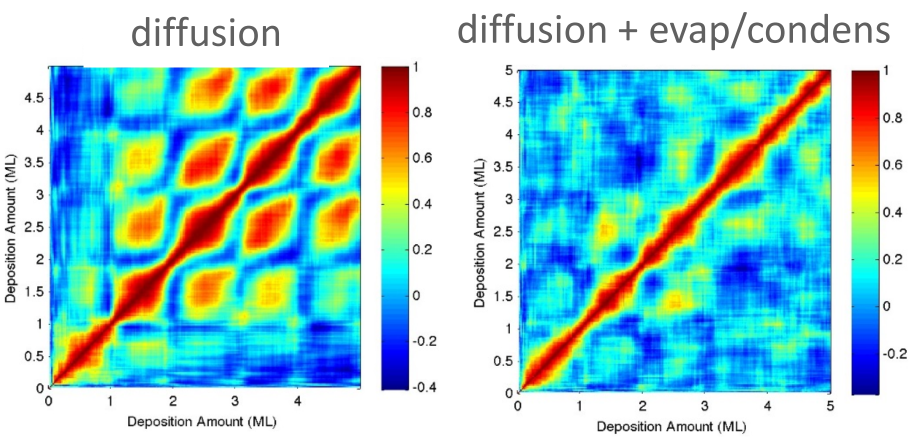


Today: XPCS autocorrelation g_2 of oil emulsion, millisecond dynamics of sub-micron droplets.

With APS-U: *4 orders of magnitude gain !!!*

Coherent flux of APS-U opens uncharted territory:

- nanosecond dynamics, atomic-scale fluctuations
- two-time correlations in non-equilibrium processes
  - mechanisms of materials synthesis
  - molecular motors e.g. mitochondria
- space-time and higher order correlations, inaccessible today
  - deformation in materials under extreme conditions
  - microfluidics for sensors, medicine



APS-U: Simulated two-time correlation functions from surface islands during layer-by-layer crystal growth, will reveal nature of atomic dynamics, enable synthesis of advanced materials, e.g. high-voltage electronic materials for a smart power grid

XPCS with more complex correlations

- "Classical" XPCS: equilibrium fluctuations, single q:

$$C(q,\Delta t)=\frac{\left\langle I(q,t)I(q,t+\Delta t)\right\rangle_t-\left\langle I^2(q,t)\right\rangle_t}{\left\langle I^2(q,t)\right\rangle_t}$$

- Equilibrium or steady-state, two-q correlations:

$$C(q_1,q_2,\Delta t)=\frac{\left\langle I(q_1,t)I(q_2,t+\Delta t)\right\rangle_t-\left\langle I(q_1,t)\right\rangle_t\left\langle I(q_2,t)\right\rangle_t}{\left[\left(\left\langle I^2(q_1,t)\right\rangle_t-\left\langle I(q_1,t)\right\rangle_t^2\right)\left(\left\langle I^2(q_2,t)\right\rangle_t-\left\langle I(q_2,t)\right\rangle_t^2\right)\right]^{1/2}}$$

- Non-equilibrium two-time, single-q correlations:

$$C(q,t_1,t_2)=\frac{\left\langle I(q,t_1)I(q,t_2)\right\rangle_{\Delta q}-\left\langle I(q,t_1)\right\rangle_{\Delta q}\left\langle I(q,t_2)\right\rangle_{\Delta q}}{\left[\left(\left\langle I^2(q,t_1)\right\rangle_{\Delta q}-\left\langle I(q,t_1)\right\rangle_{\Delta q}^2\right)\left(\left\langle I^2(q,t_2)\right\rangle_{\Delta q}-\left\langle I(q,t_2)\right\rangle_{\Delta q}^2\right)\right]^{1/2}}$$

Materials deformation revealed with coherent x-rays

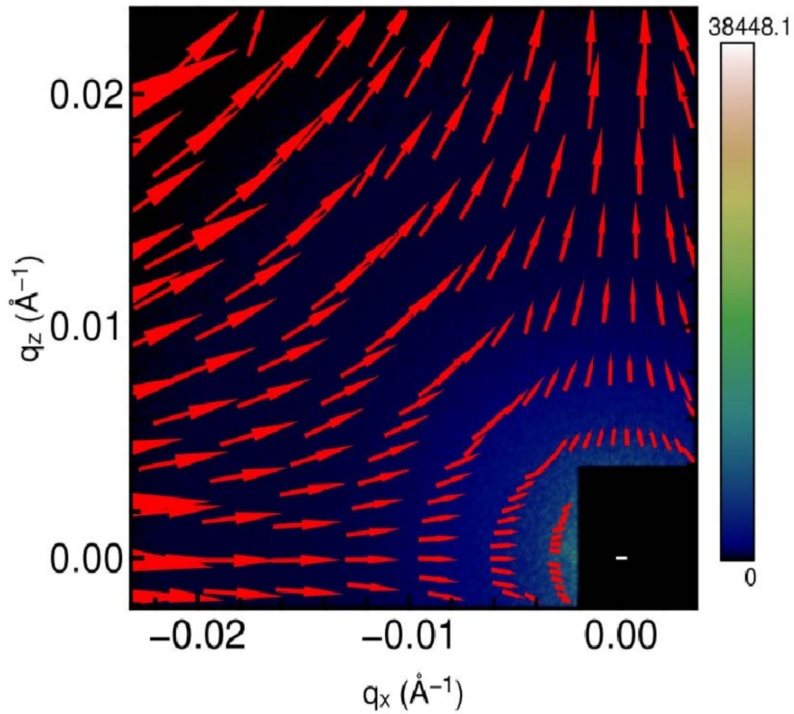
Steady-state, two-q correlations

Opportunity

- Strain tensor mapping inside of deforming material, including fluids and glasses, by using space-time cross-correlation analysis of x-ray speckle (XPCS)
- 3-D variation of full strain and stress tensors inside materials evolving in real time under loading

Gains from APS MBA Lattice

- Open up studies into ns range
- Sub-micron spatial resolution



Speckle shifts superimposed on scattering from a 20 micron region of a rubber sample undergoing flow in a stress-strain cell. Shifts are scaled by 200. (M. Sutton, unpublished)

Now: New coherence-based techniques being developed with coarse resolution

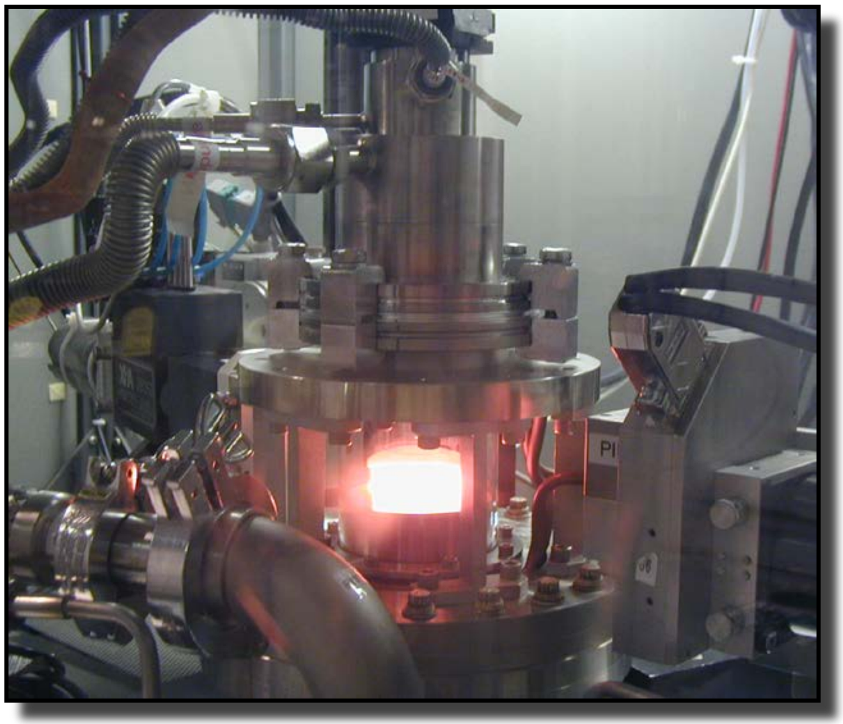
APS MBA upgrade: First direct view of molecular flow will be enabled by **factor of 10,000 to 1,000,000 improvement**

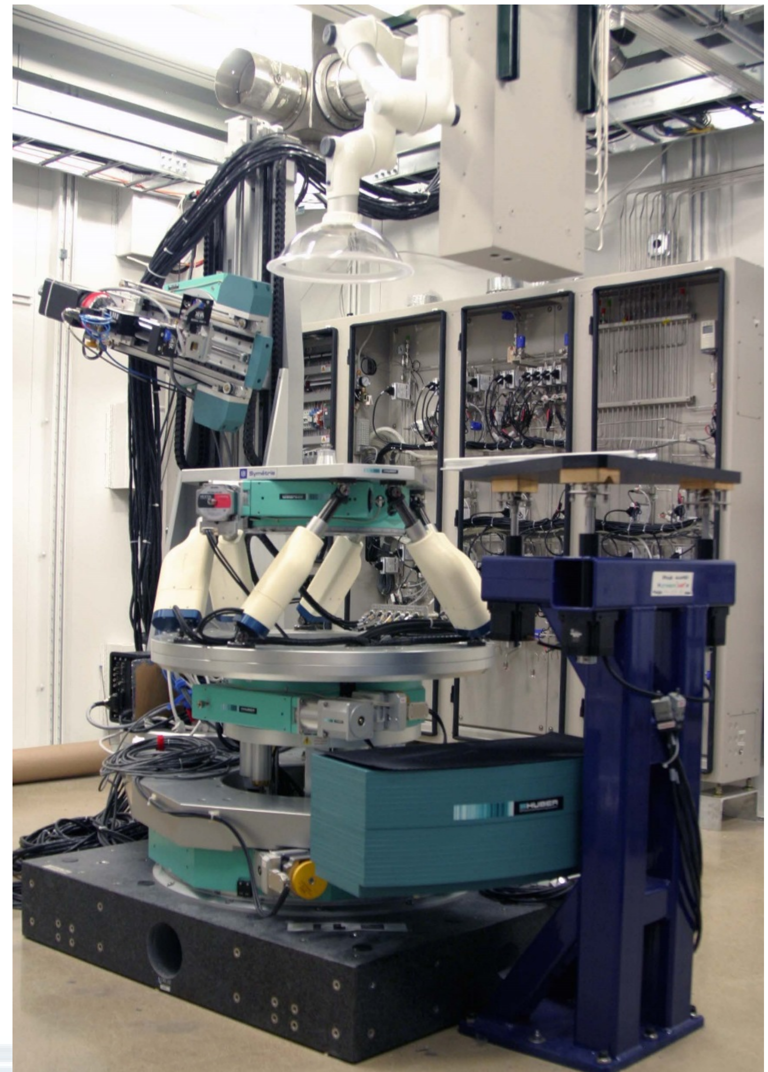
From recent APS-U science workshops: Materials and heterostructure synthesis and stability

- Challenge: Control synthesis, defect structure, and (meta-)stability in operating environments of single- and multi-phase materials and heterostructures
- Hard X-ray techniques allow in situ, real-time studies of atomic-scale mechanisms during processing
- APS-U enables coherent X-ray imaging and XPCS studies of dynamics
- Examples of "first experiments":
  - Characterize an individual point defect
  - Observe dopant interactions with dislocations, step edges during growth
  - Observe nucleation of a misfit dislocation
  - Correlations in island nucleation during layer-by-layer growth
  - Domain dynamics in strained heterostructures
  - Mass transport by flow vs. diffusion

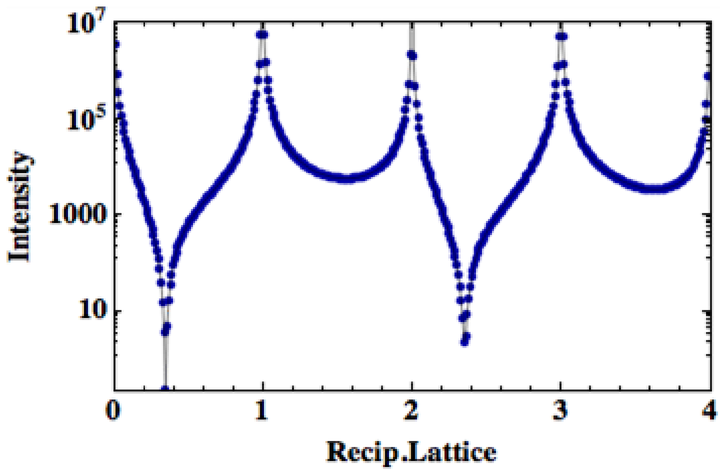
In situ studies of synthesis using hard x-rays

- Hard x-rays penetrate chamber and harsh environment to allow *in situ* studies
- New diffractometer design enables *in situ* **coherent** x-ray studies of growth
  - Long sample-to-detector length
  - High stability hexapod
  - Fully automated nitride MOCVD system

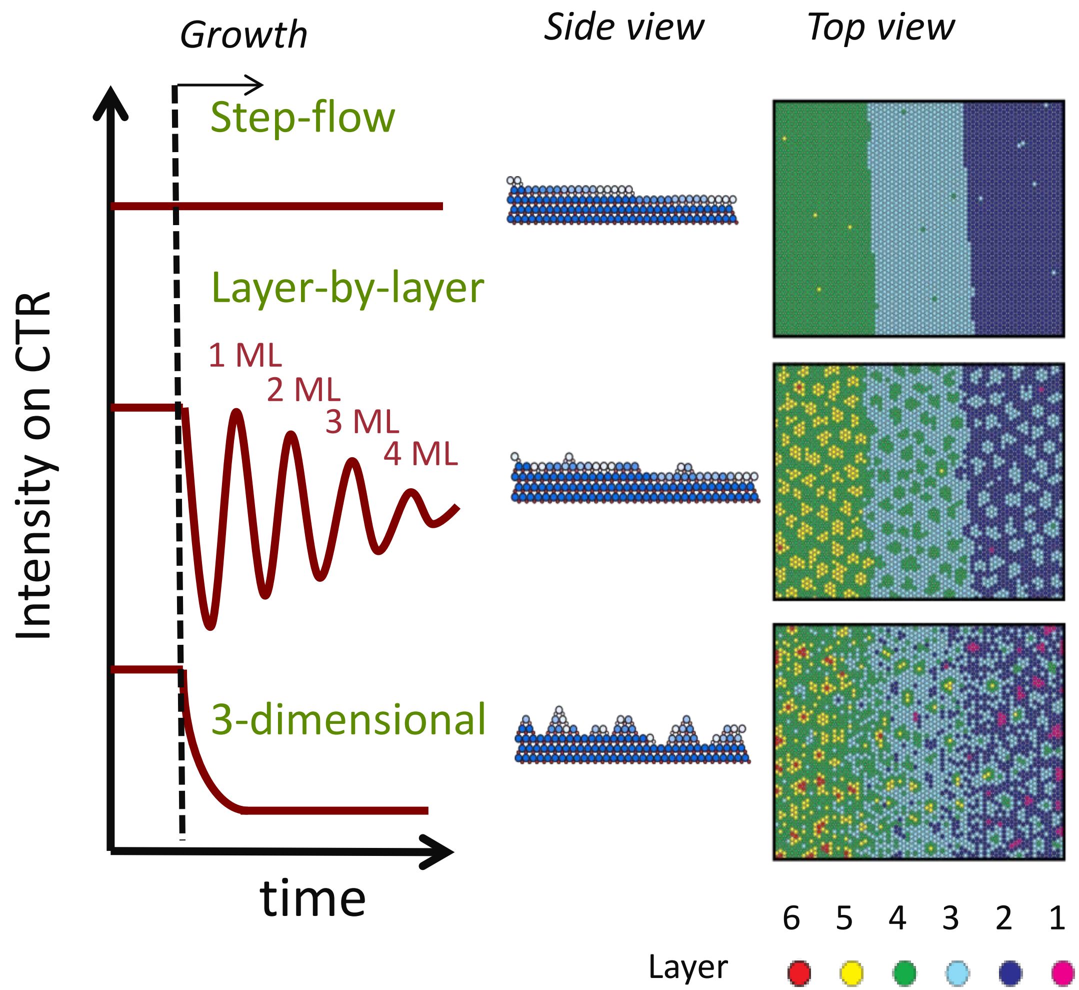




CTRs and growth modes

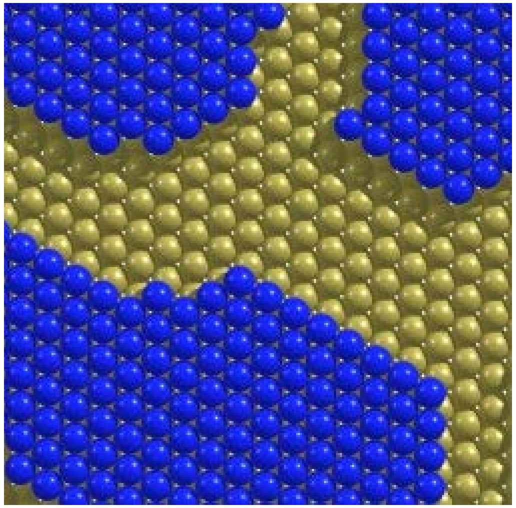


- Anti-Bragg positions on Crystal Truncation Rods (CTRs) highly sensitive to surface morphology
- Intensity evolution shows growth mode, indicates balance between deposition, surface transport, attachment at steps

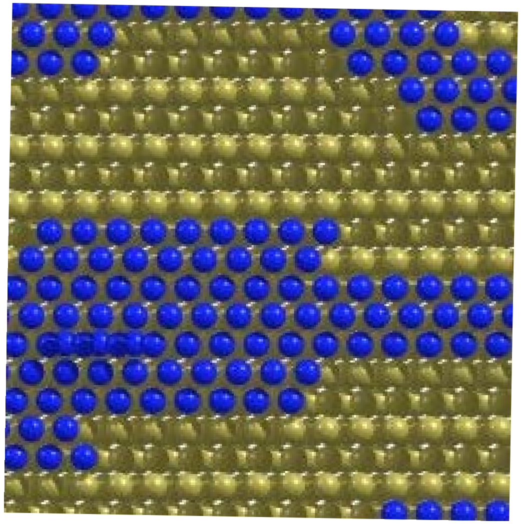


Effects of surface orientation on atomic-scale mechanisms of crystal growth

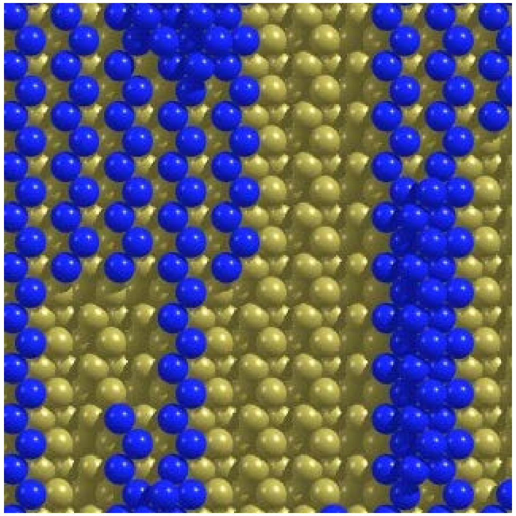
c-plane surface
[0001] out of plane



m-plane surface
[0001] vertical



a-plane surface
[0001] vertical

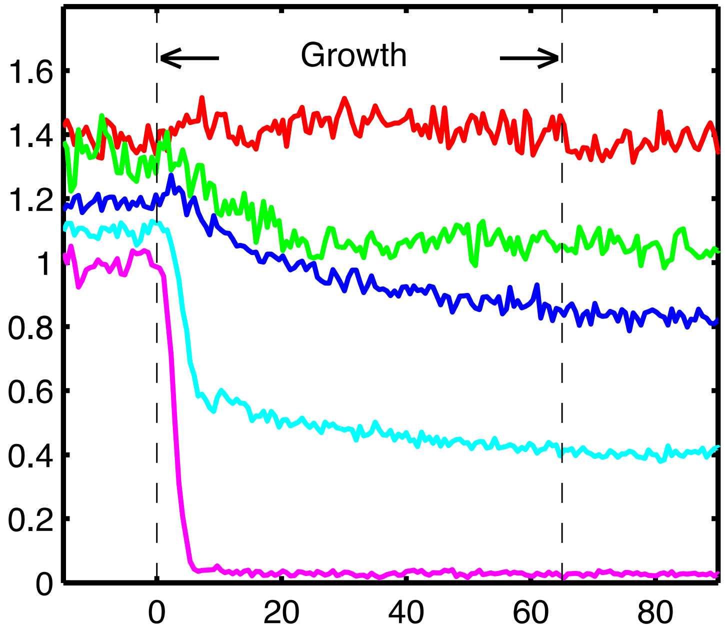


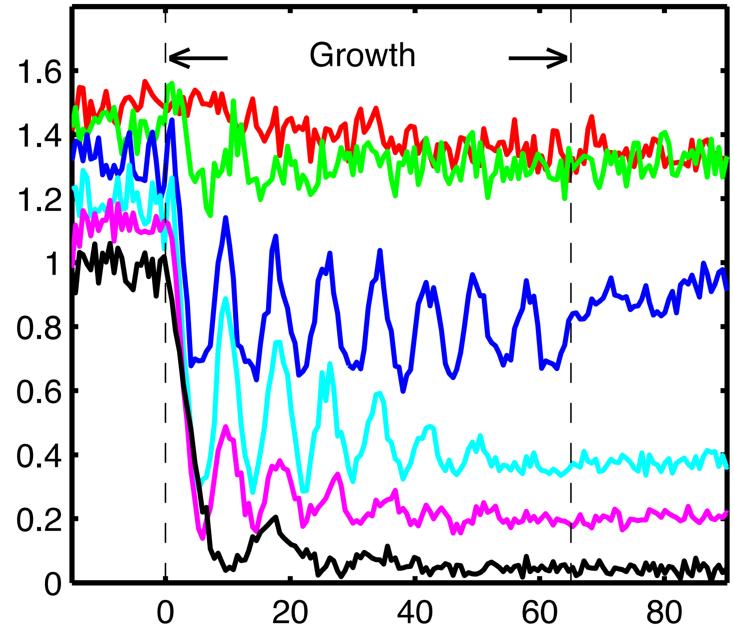
Ga sites in wurtzite GaN structure; blue shows islands at 50% coverage

- Step energies, adatom diffusivities are expected to be highly anisotropic on m- and a-plane surfaces of GaN
- What effects does this have on growth mechanisms?

Growth modes vs T on c-plane and m-plane GaN

Growth of 22 Å of GaN at 0.3 Å/s





c-plane:

No layer-by-layer growth region

- high Ehrlich-Schwoebel barrier for diffusion over island edges?

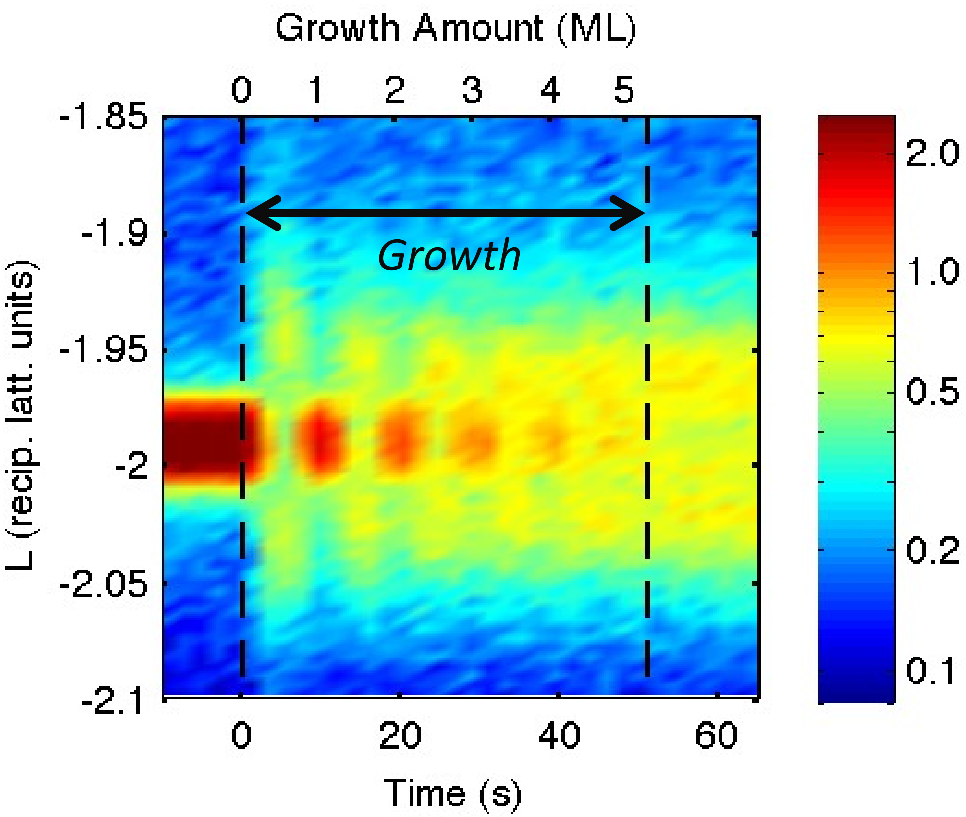
m-plane:

See all 3 growth modes:
step-flow, layer-by-layer, 3-D

E. Perret et al., APL 105, 051602 (2014)

Incoherent scattering gives average island spacing

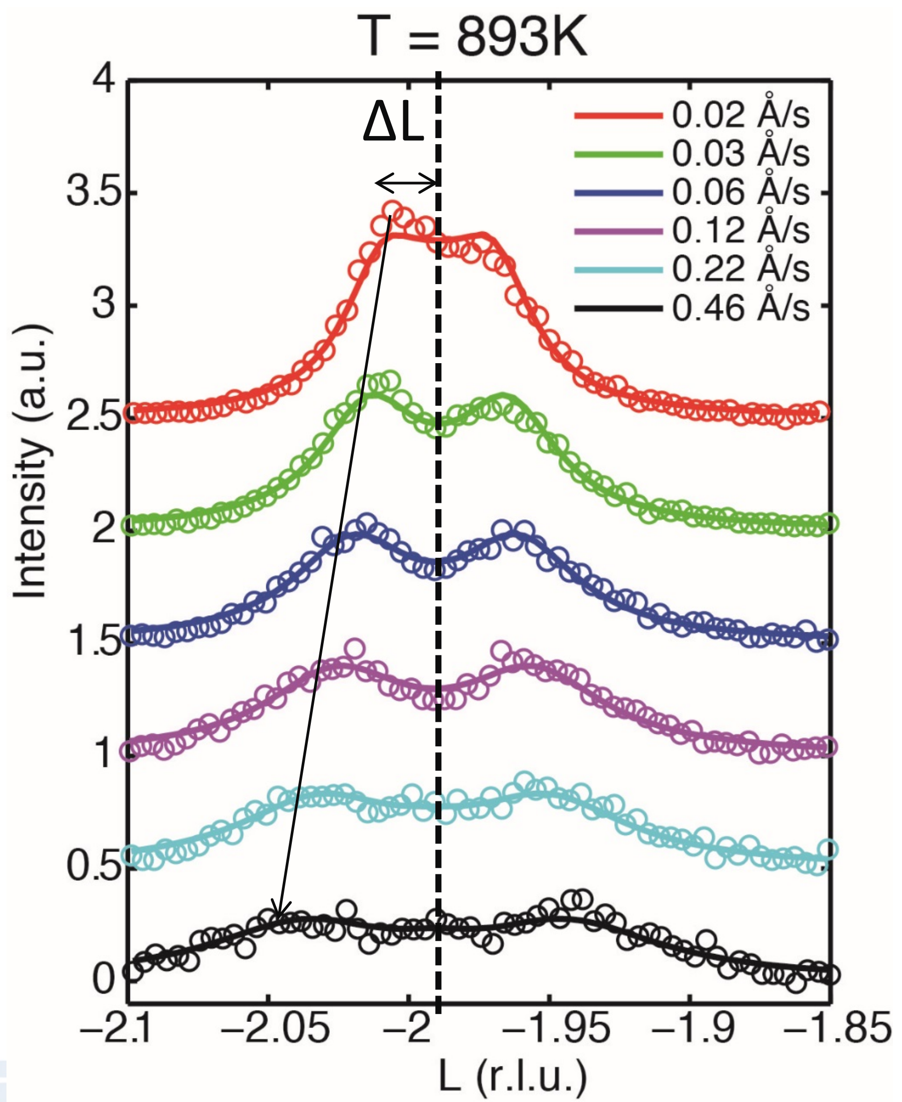
Intensity map versus time for the
(0.5 0 -0.5 -2) CTR position, GaN m-plane



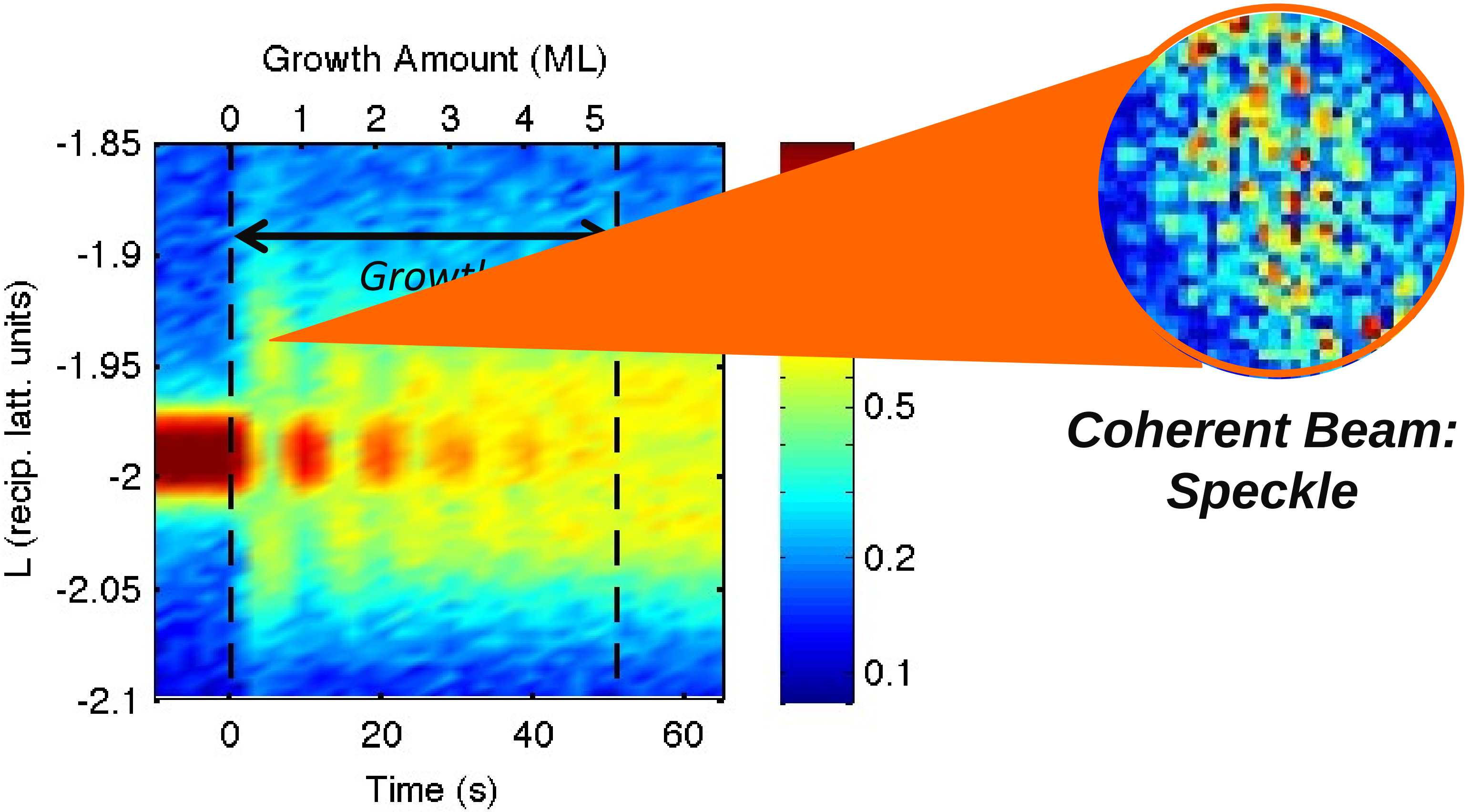
1 ML oscillation period = 2.76 Å of growth

E. Perret et al., unpublished (2015)

Diffuse scattering at 0.5 ML
Peak position gives island spacing $S = c_0 / \Delta L$



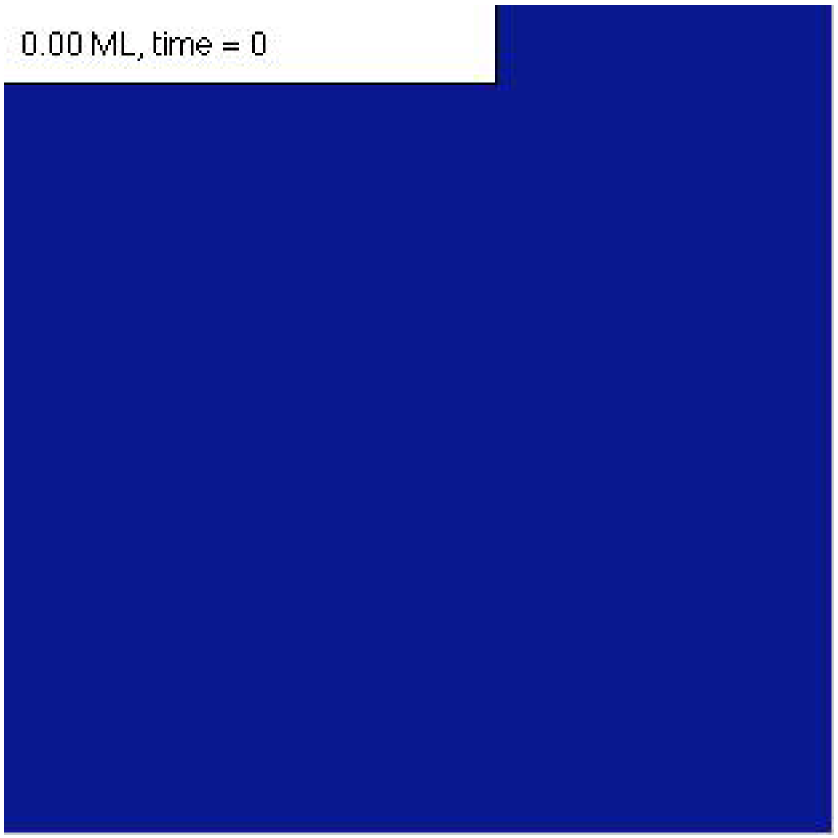
Impact of coherent x-ray studies



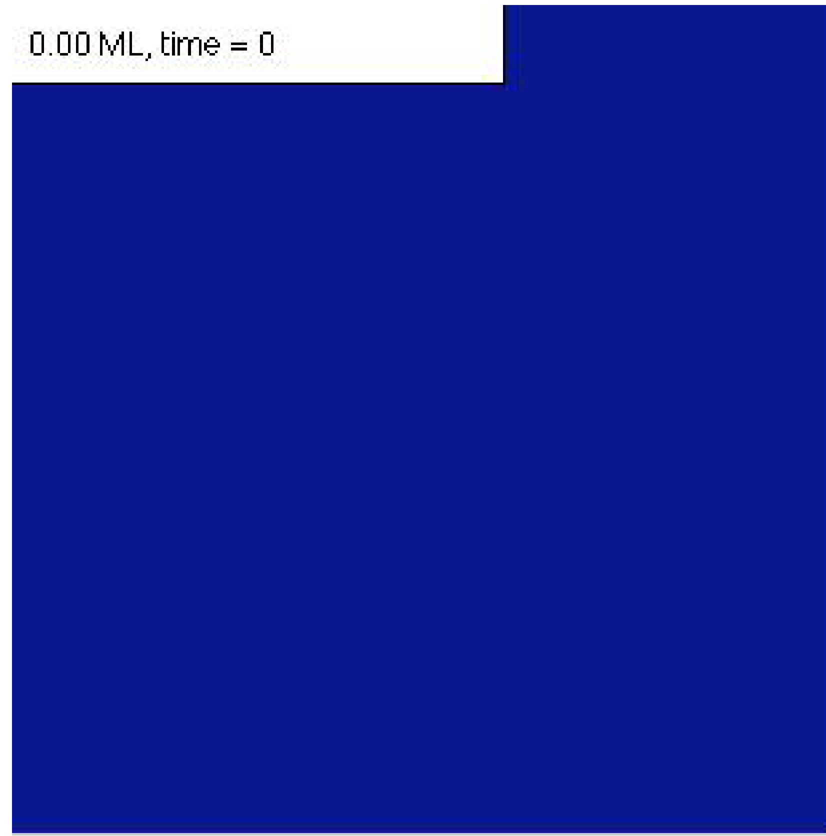
- Coherent x-ray studies will reveal island arrangements and equilibrium dynamics
- X-ray Photon Correlation Spectroscopy (XPCS) studies of island dynamics may be feasible with current source in favorable cases
- Bragg Coherent Diffraction Imaging (BCDI) of static islands may be feasible now; real-time BCDI studies of dynamics will require the APS Upgrade

SOS (2D) KMC simulations of growth

(a) surface transport by diffusion only



(b) surface transport by evaporation/condensation and diffusion

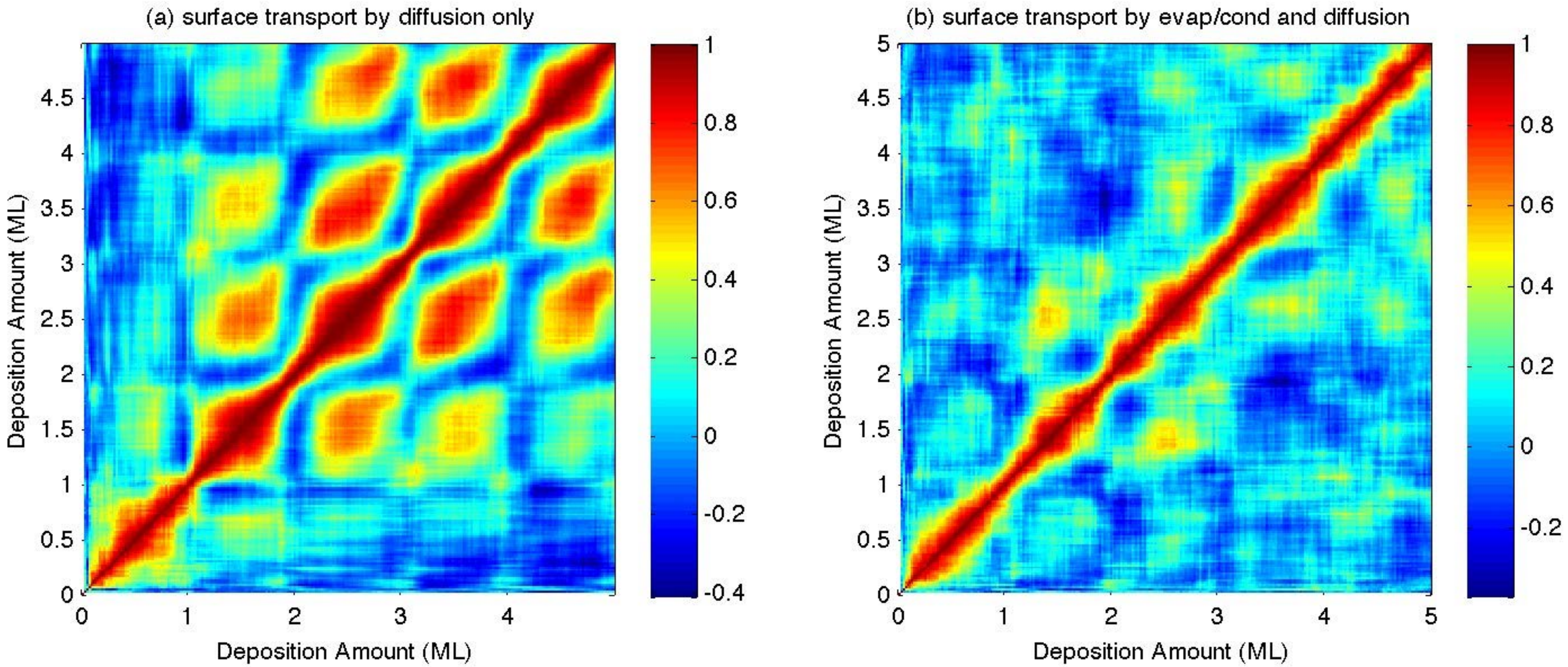


simple cubic lattice

Surface XPCS using coherent X-rays: sensitive to both transport dynamics and mechanisms

- Standard XPCS will allow observation of rates of atom transport and step fluctuations
- Two-time correlations will reveal persistence of island nucleation positions on succeeding layers, which can be related to transport mechanisms

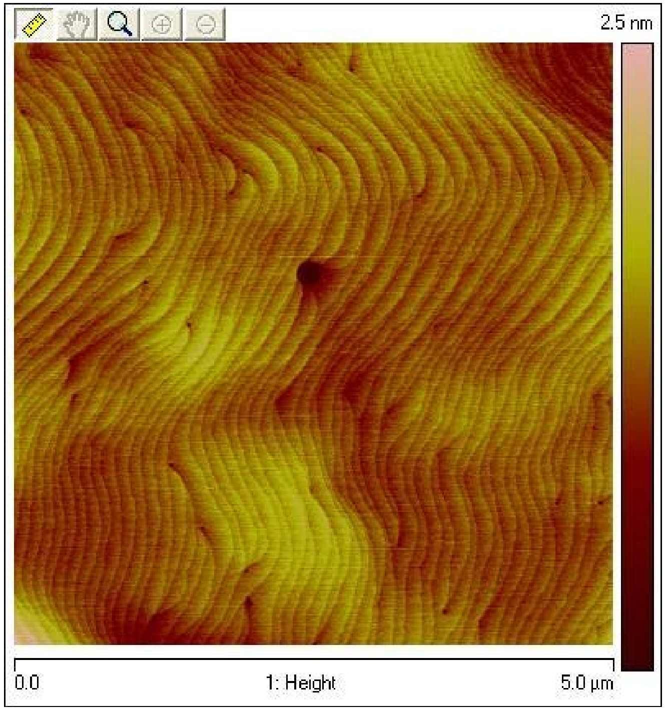
Simulated two-time correlation functions in speckle from islands during LBL growth



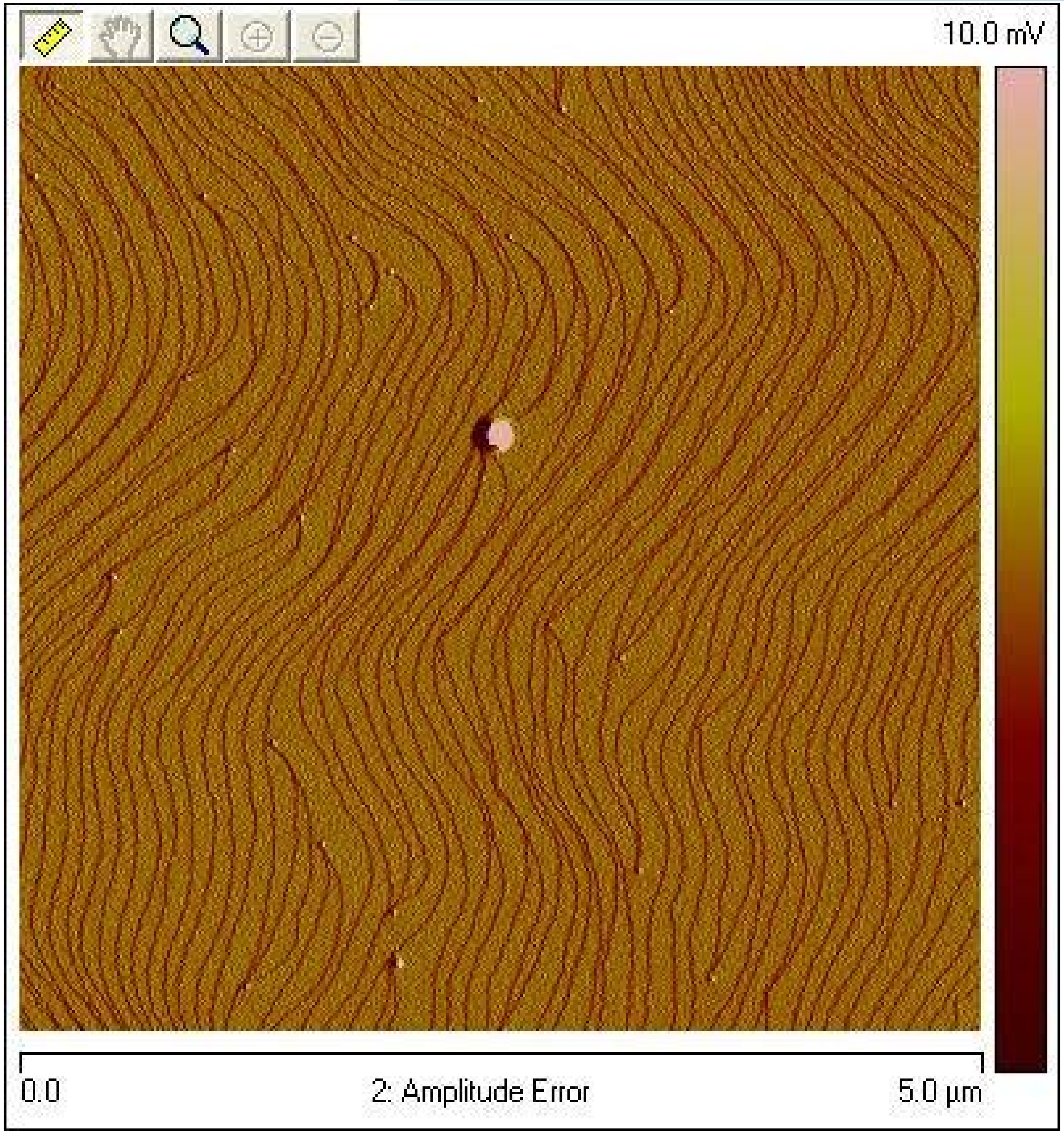
Steps on GaN c-plane

Character of monolayer (½-unit-cell-height) steps varies with orientation and alternates between layers.

What are their dynamics?



Z(height)



Amplitude error

mar132013_a.001 N130312a (ANL126A)
~130nm grown at hiT

Reciprocal space signatures of surface step structures

Opportunity for two-q correlations in equilibrium dynamics

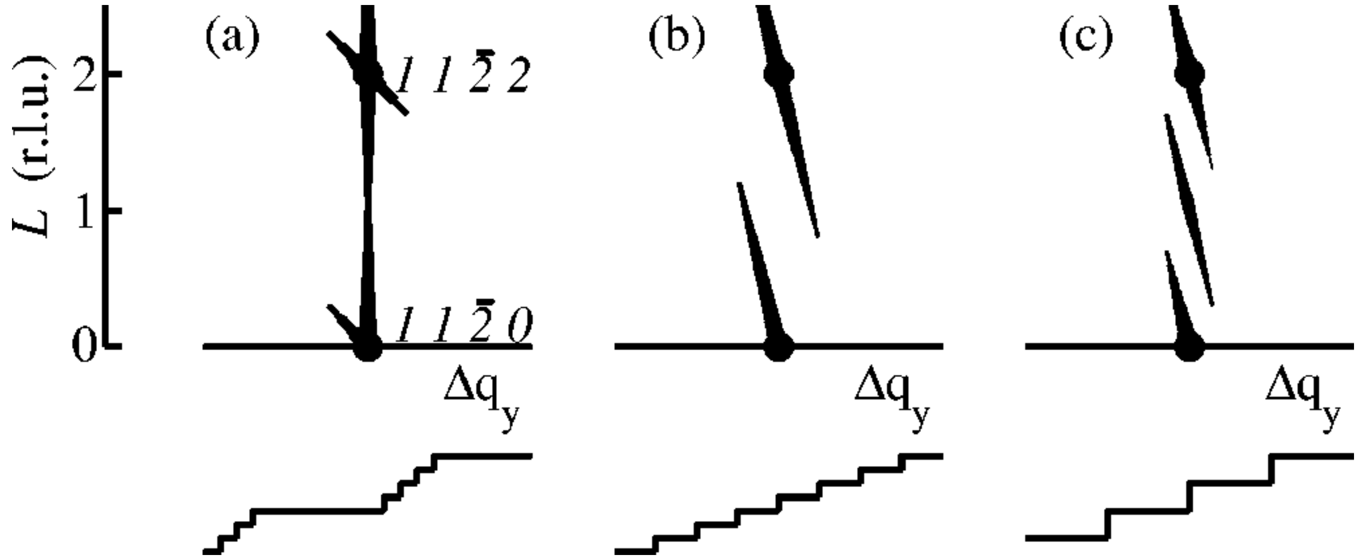
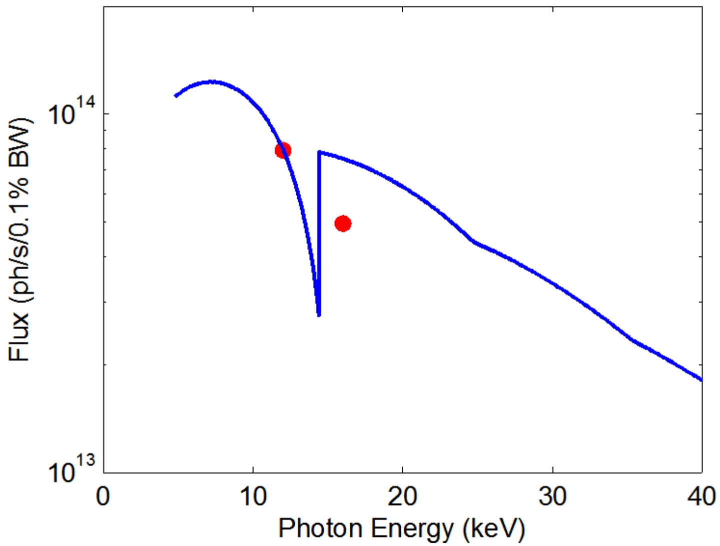


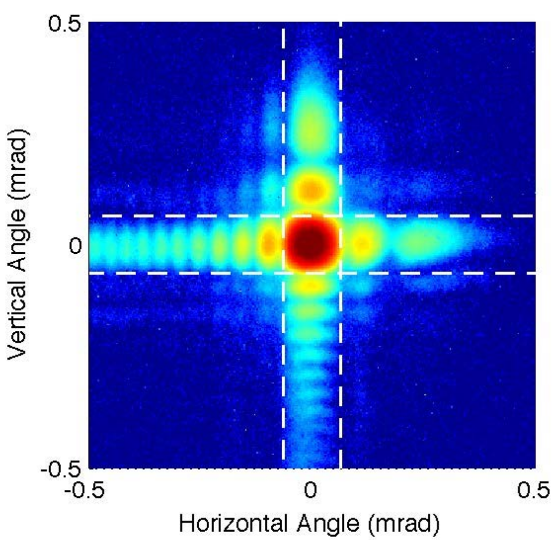
FIG. 1. Schematic of the crystal truncation rods from surfaces with (a) large (0001) facets; (b) monolayer-height steps; and (c) double-height steps. The index L is in reciprocal lattice units (r.l.u.).

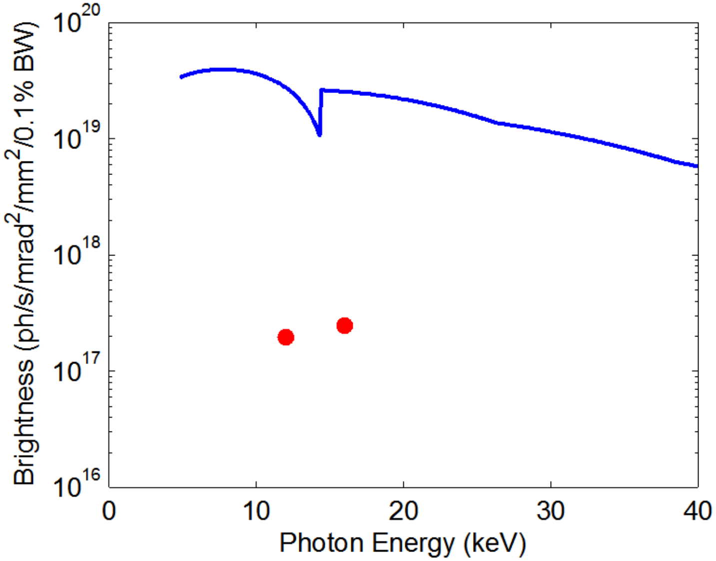
M. V. Ramana Murty et al., PRB 62, R10661 (2000)

Coherence characterization at 12ID-D

- Used diffraction from slits as function of width to characterize beam divergence
- At 12 keV:
- Horizontal: 27.4 urad (2.9 times source)
- Vertical: 18.3 urad (47.4 times source)
- Loss in brightness: factor of 140
- Likely cause: 8 unpolished Be windows
- Plan for 12ID windows/optics upgrade being implemented







Summary and outlook

- In situ XPCS studies will be a powerful technique to reveal atomic-scale mechanisms during materials synthesis
- More complex correlations (2 q, 2 t, 2 q – 2t) can be explored with increased coherent flux
- A new hexapod diffractometer and growth system are being commissioned
- Excellent opportunity for in-situ, high-energy coherent beam studies of materials synthesis and processing at a new optimized sector 28