Non-Perturbative Measurements
using
Minimum Photon Approaches

- **Perturbation Limits**
  - General physics of x-ray interactions (e.g. cross-sections)
  - Perturbation limits of soft and hard matter
  - Imaging resolution versus dose
- **Extracting maximum information from each photon**
  - Better algorithms
  - Improved optics
  - Advanced detectors
- **Integrated approaches to solving scientific problems**
  - X-ray measurements
  - Theory and large scale simulation
  - Other probes (e.g. TEM, optical spectroscopy)

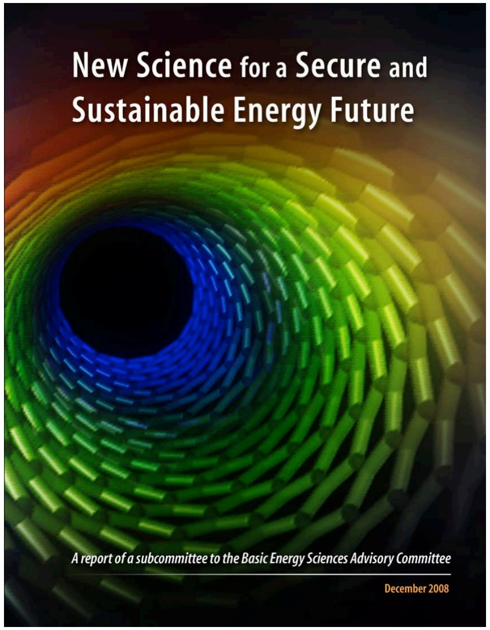
Fundamental Questions in Materials Science

What materials are present?

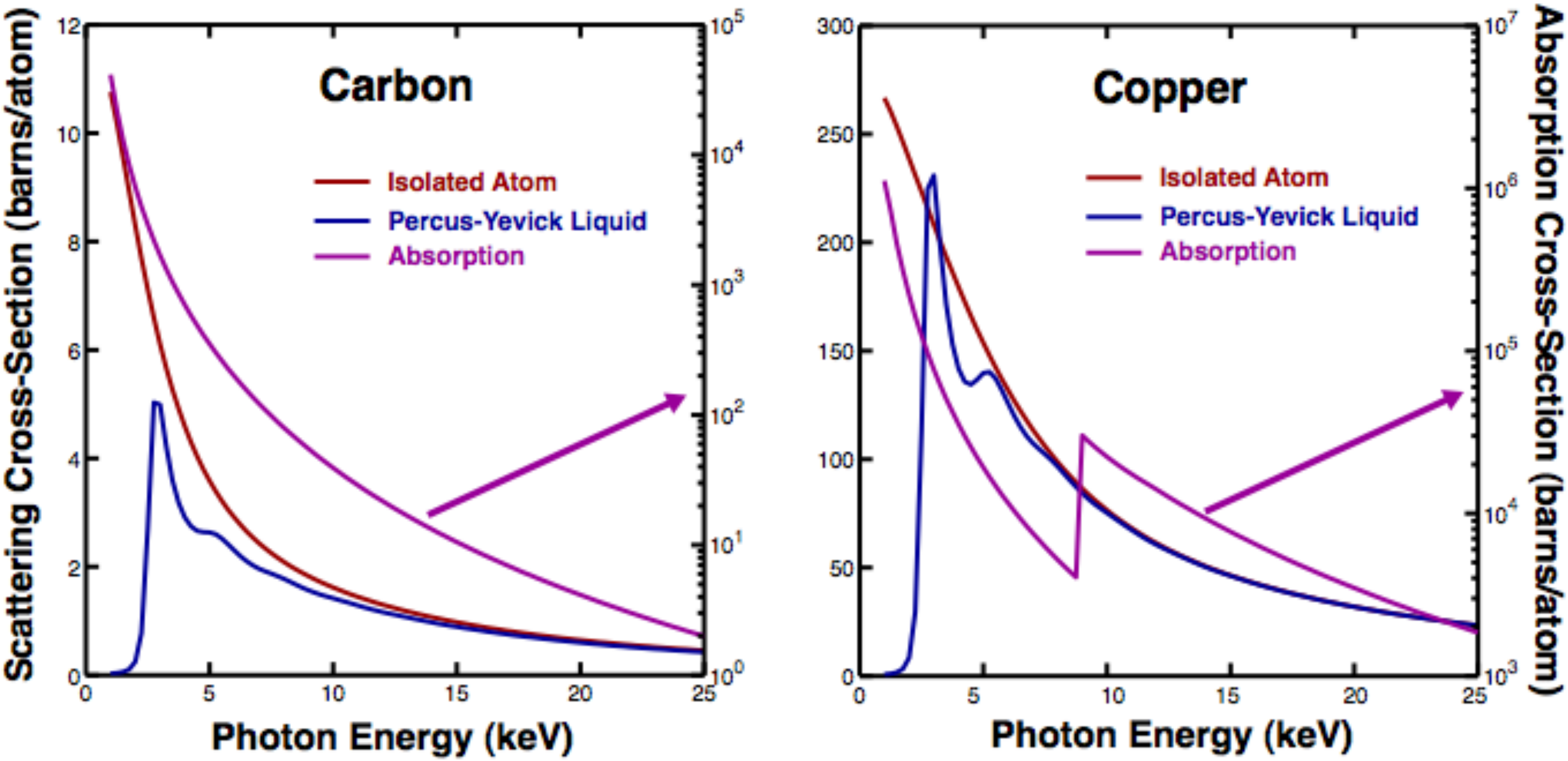
Where are the materials located?

When do crucial transformations and processes occur?

Why does a material have its structure and properties?

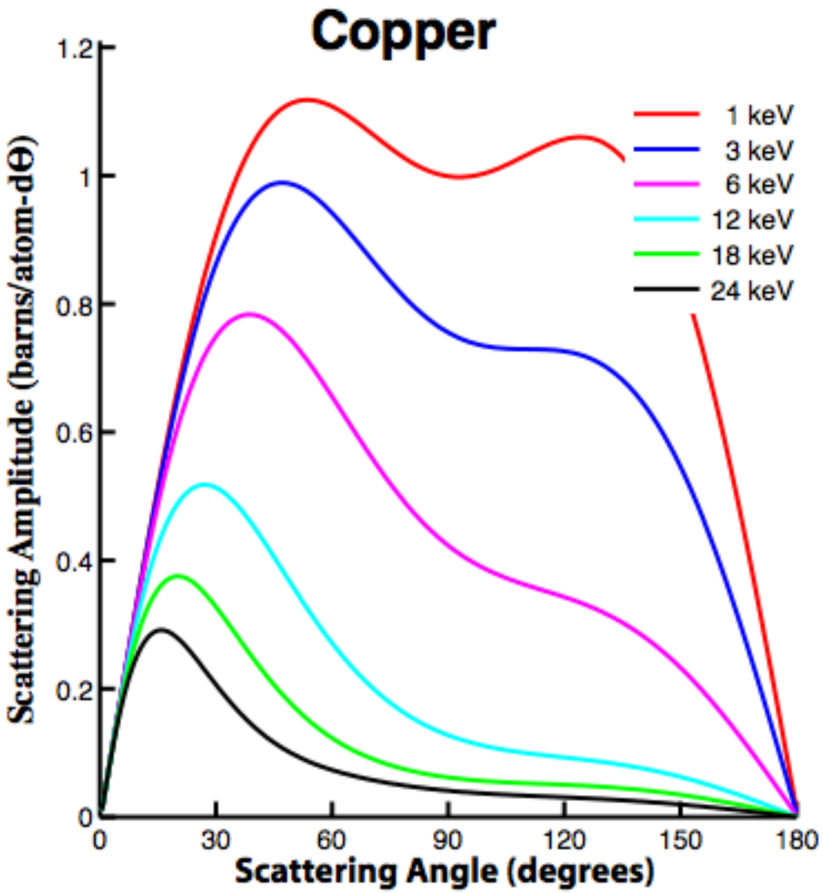


Scattering Calculations: Cross-Sections versus



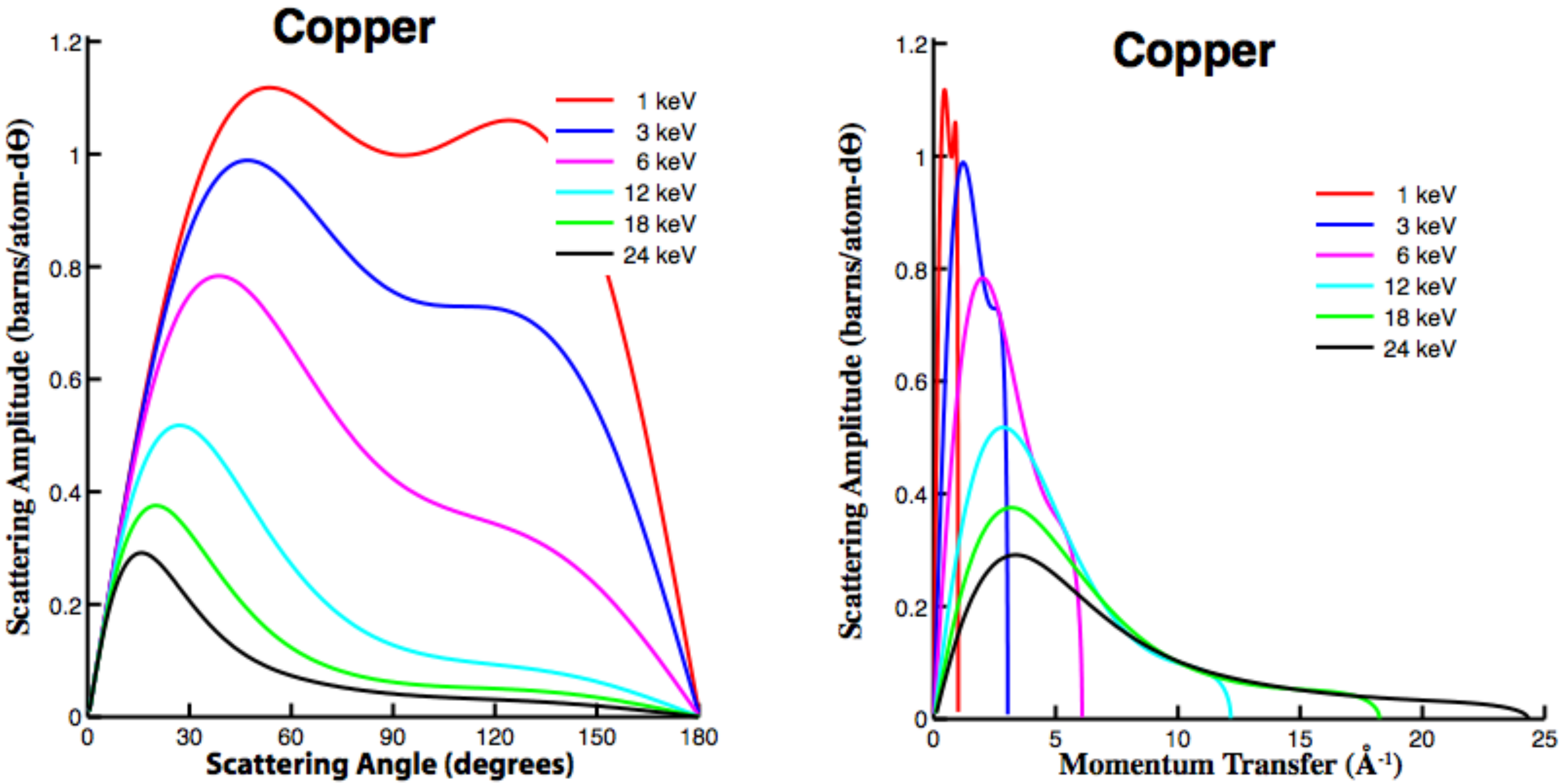
Note that the absorption cross-section is always much larger than the scattering cross-section

Scattering Cross Section

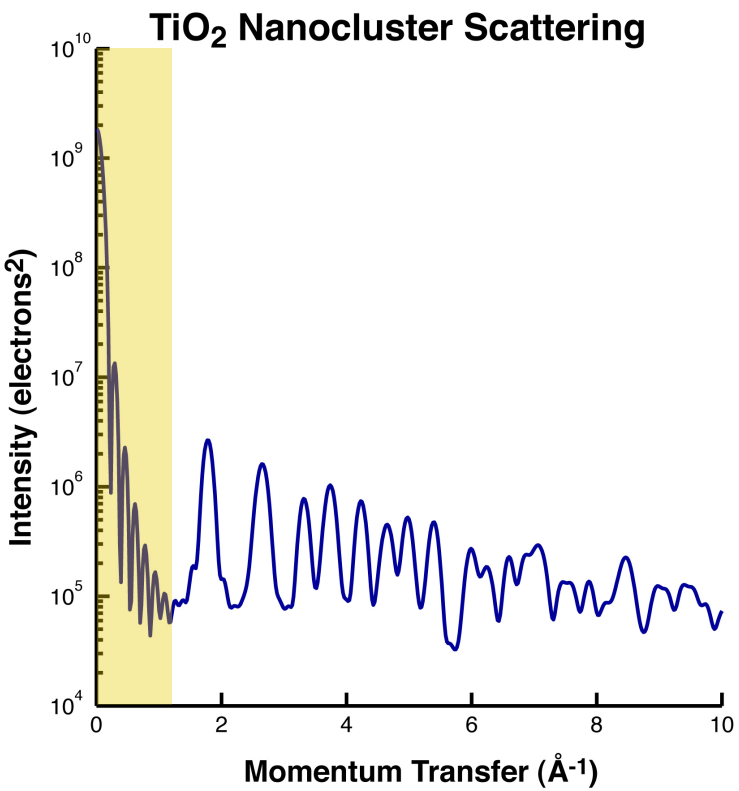


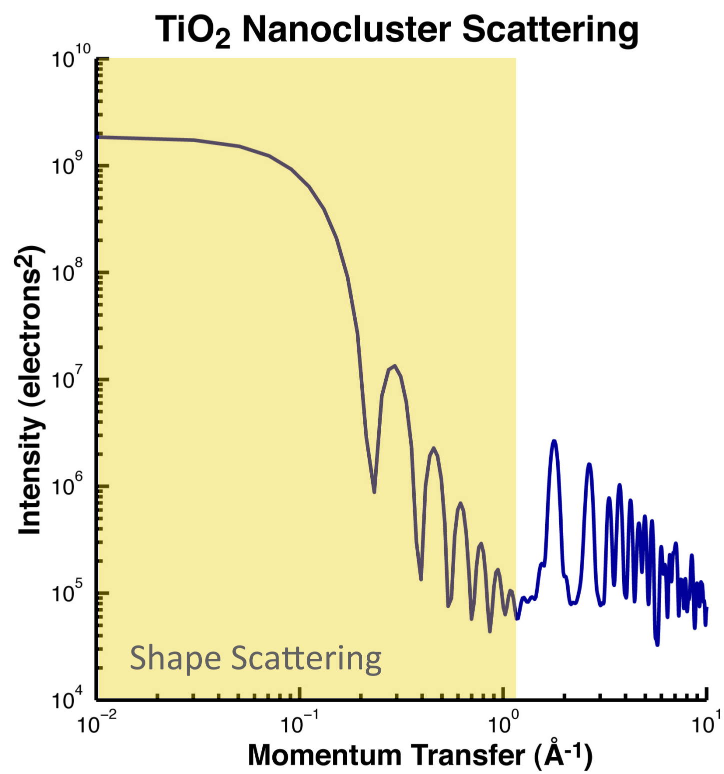
The strong scattering over all of angle space is why crystallographers often prefer to work at lower photon energy (i.e. the scattered intensity is spread out of a large angle space and the integrated intensities are much higher.

Scattering Cross Section



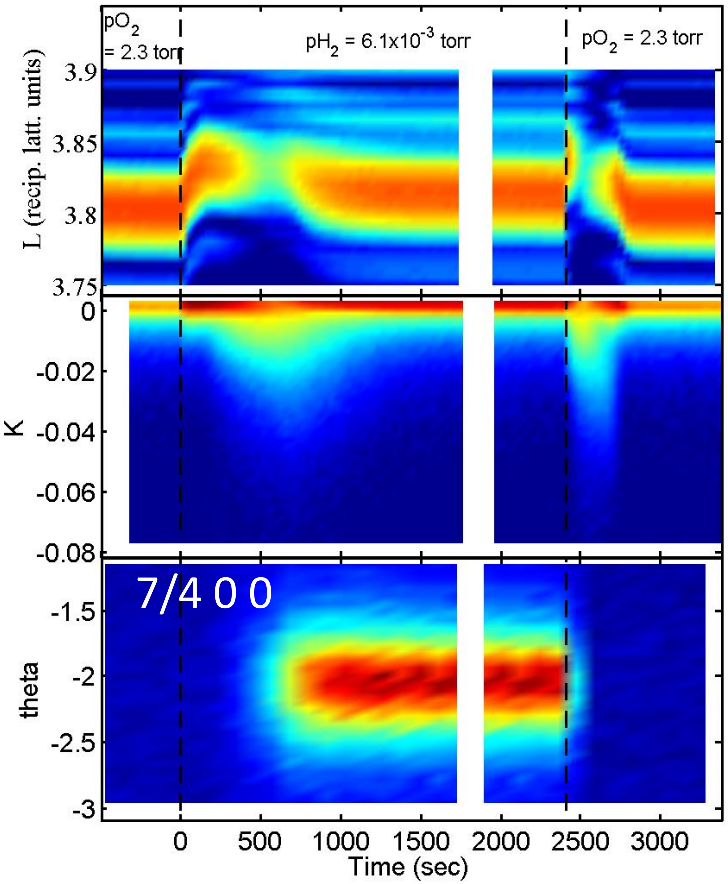
Scattering Calculations: Include Atomic Correlations

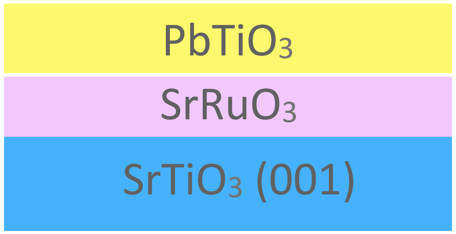




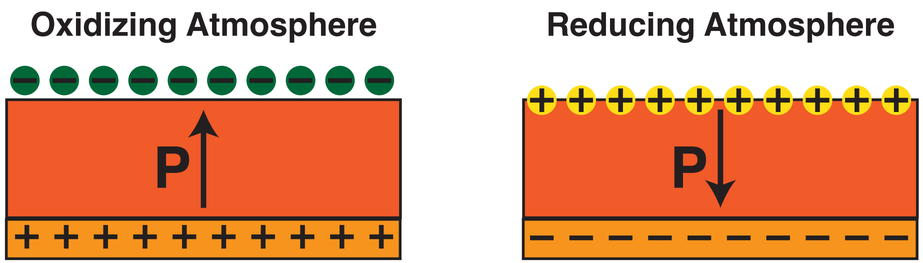
Polarization Switching in Ferroelectric Oxides

The ferroelectric polarity of a thin $PbTiO_3$ film can be switched by changing the boundary conditions through gas phase chemistry.

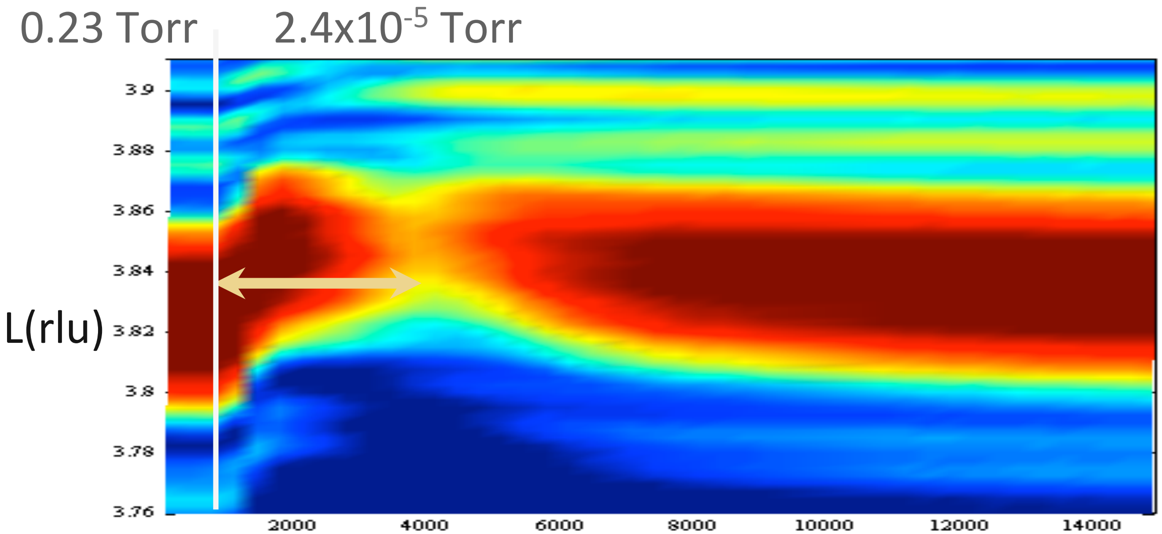


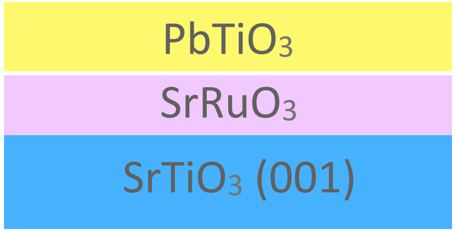


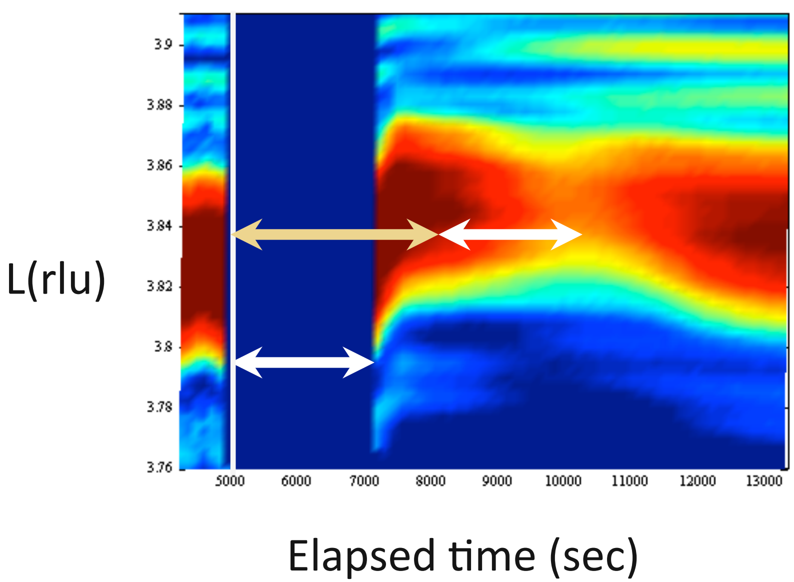
Switching Schematic



X-rays "improve" kinetics of chemical switching





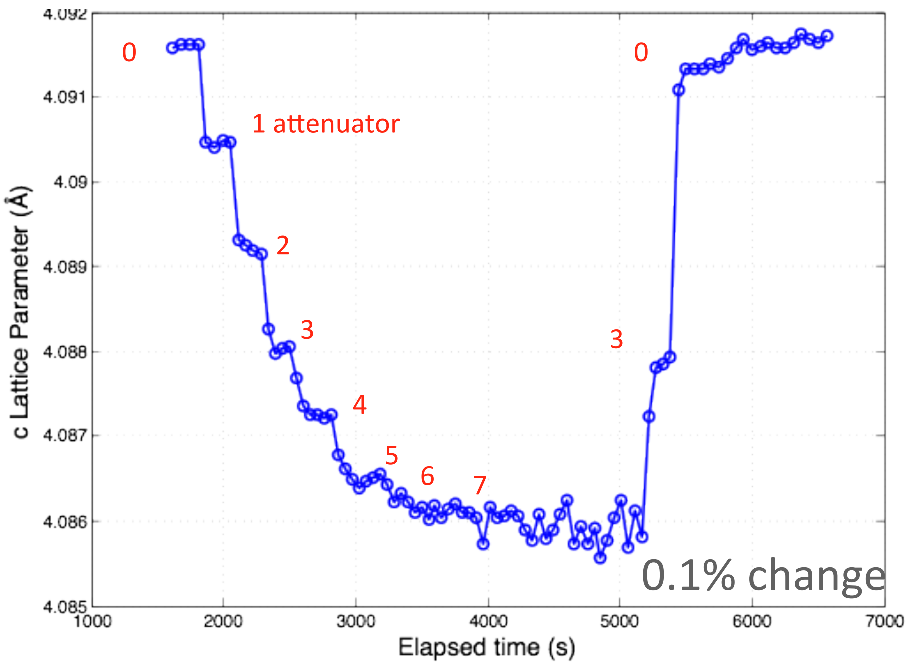


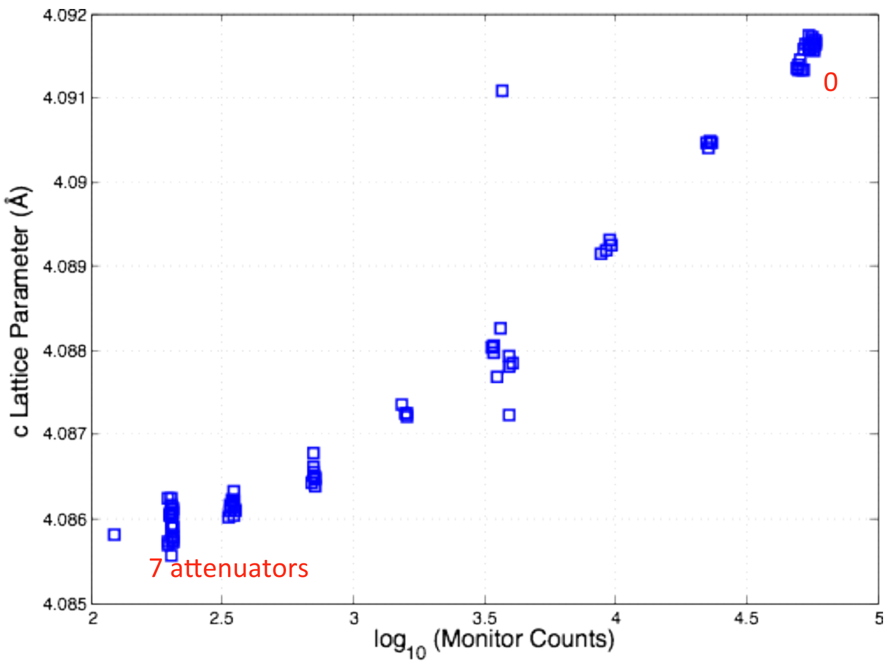
10 nm PTO/SRO/STO at 500C

- up to down switch is the "slow switch" (~2800 sec)
  - ➙ 0.23 to 2.4×10^{-5} Torr
- time delay in up to down switch ≈ time x-rays are off sample

Effect of x-rays on c lattice parameter (monodomain up)

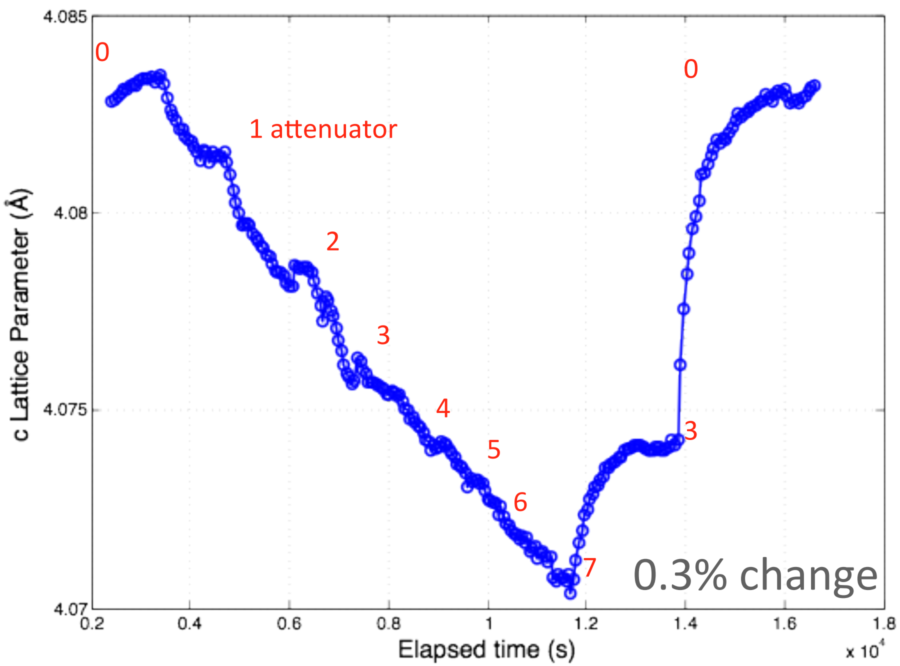
- X-rays help compensate depolarizing field (larger *c* lattice parameter)
- In the up state (10 nm PTO/SRO/STO at 500C at pO_2=2.3 Torr)
  - fast response to x-rays

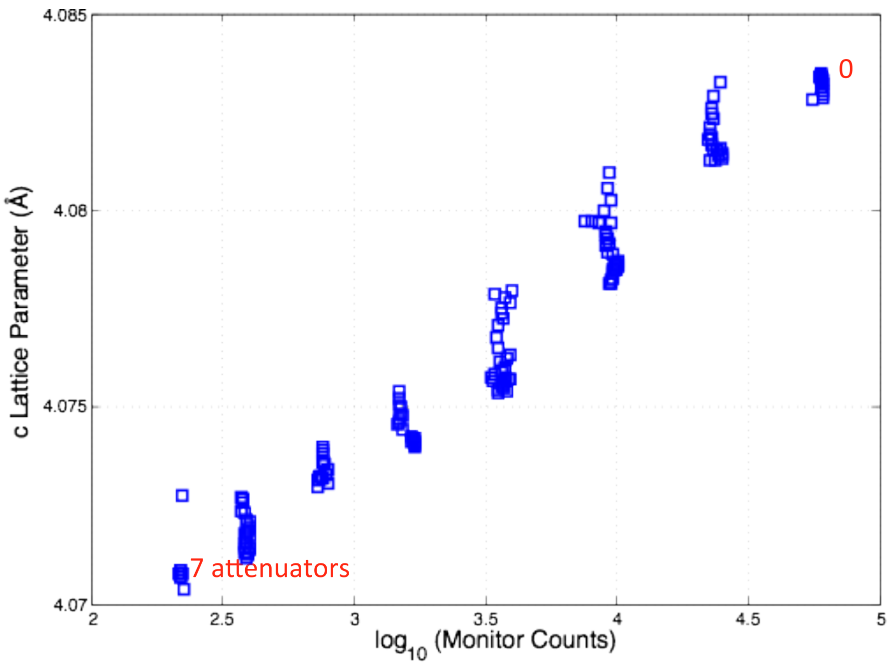




Effect of x-rays on c lattice parameter (monodomain down)

- X-rays help compensate depolarizing field (larger *c* lattice parameter)
- In the down state (10 nm PTO/SRO/STO at 500C at $pO_2=2.4x10^{-5}$ Torr)
  - slower response to x-rays





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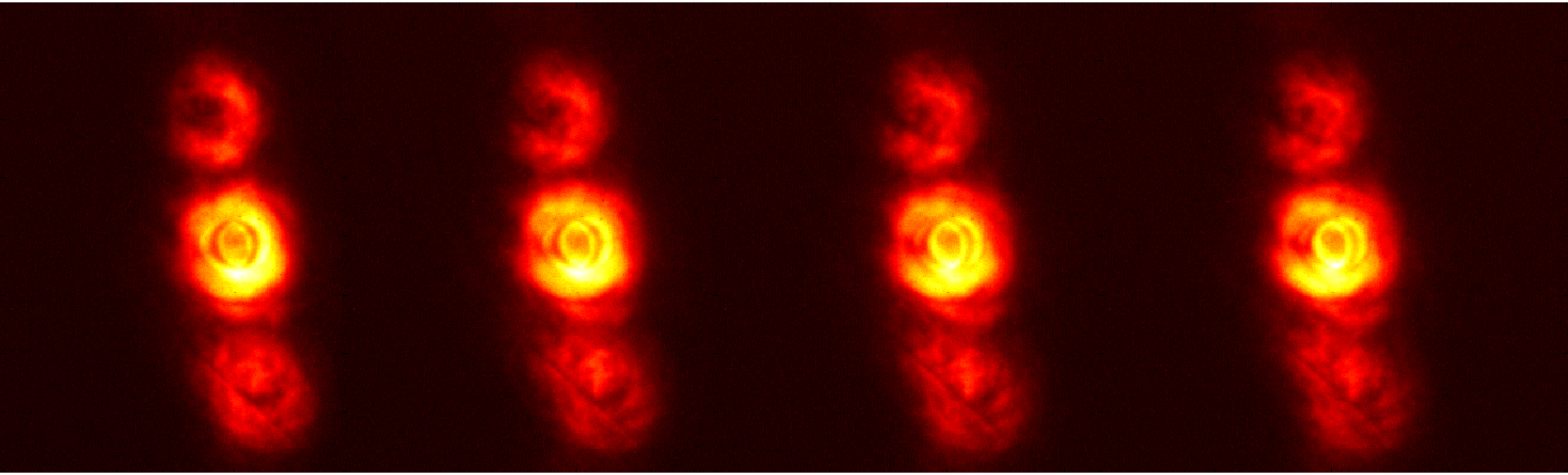
Damage to Epitaxial $PbTiO_3$ Film During Ptychography

Main Bragg peak shows partial relaxation out-of-plane lattice parameter.

Also, stripe satellite peaks diminish in intensity and sharpness as PTO stripes become more disordered.

002 PTO peak from a 40-nm diameter spot illuminated repeatedly with 10 second exposures.
After 200 sec of accumulated exposure, changes begin
After 600 sec, we see Bragg peak relaxation and stripe disorder.

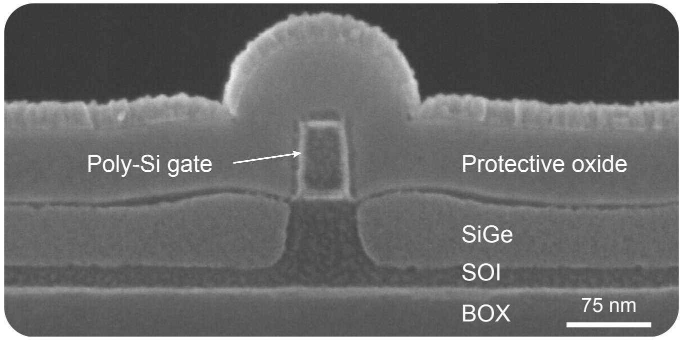
1st point 20th point 40th point 60th point



Stress and Strain are Key to Mesoscopic Behavior

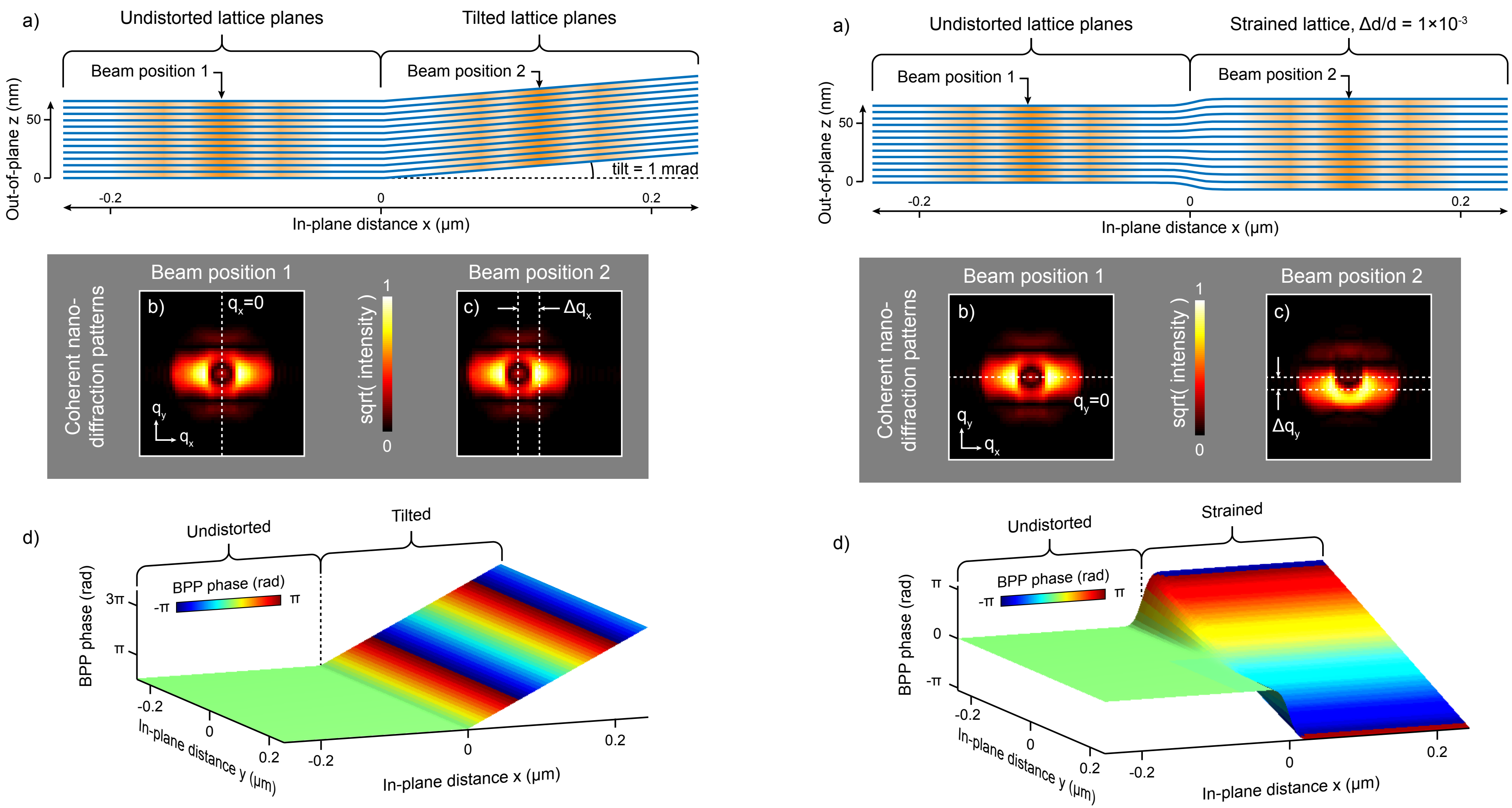
- Stress and strain are important materials parameters available to manipulate properties and performance.
- Control and prediction of lattice responses is challenging since they depend on the complete environment and processing history.
- Measurement and visualization of lattice distortions is necessary to understand the structure and performance in mesoscale systems.
- Studies must be done *in operando* to avoid changing the device boundary conditions.

Example: SiGe stressor layers are used to locally modify band structure and improve silicon device performance.

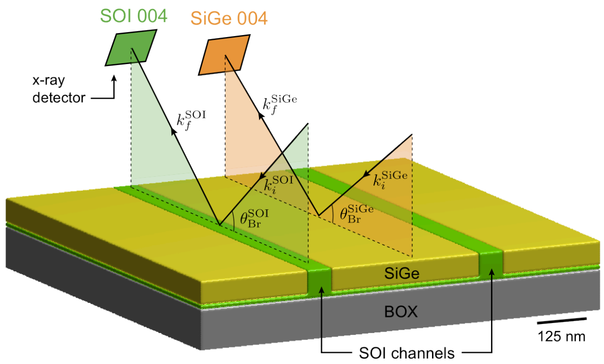


3D Bragg ptychography has great potential for *in operando* studies

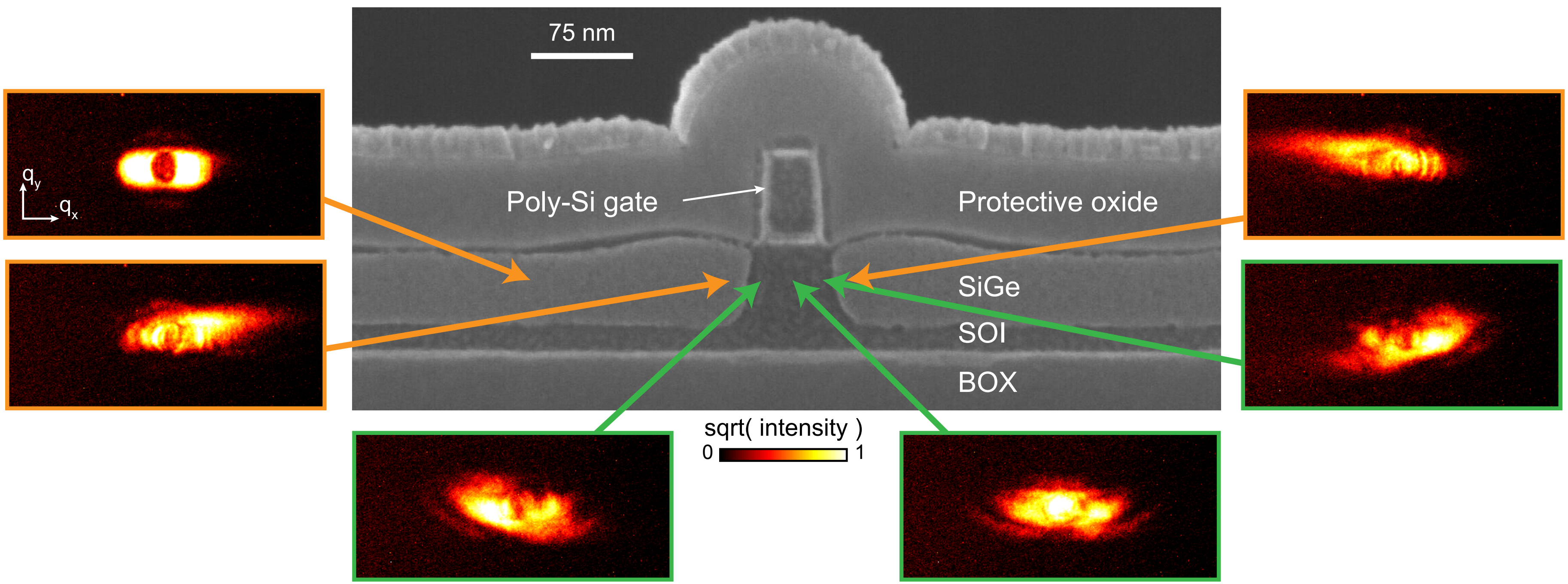
Difference between Tilt and Strain



Nanodiffraction from SiGe Device



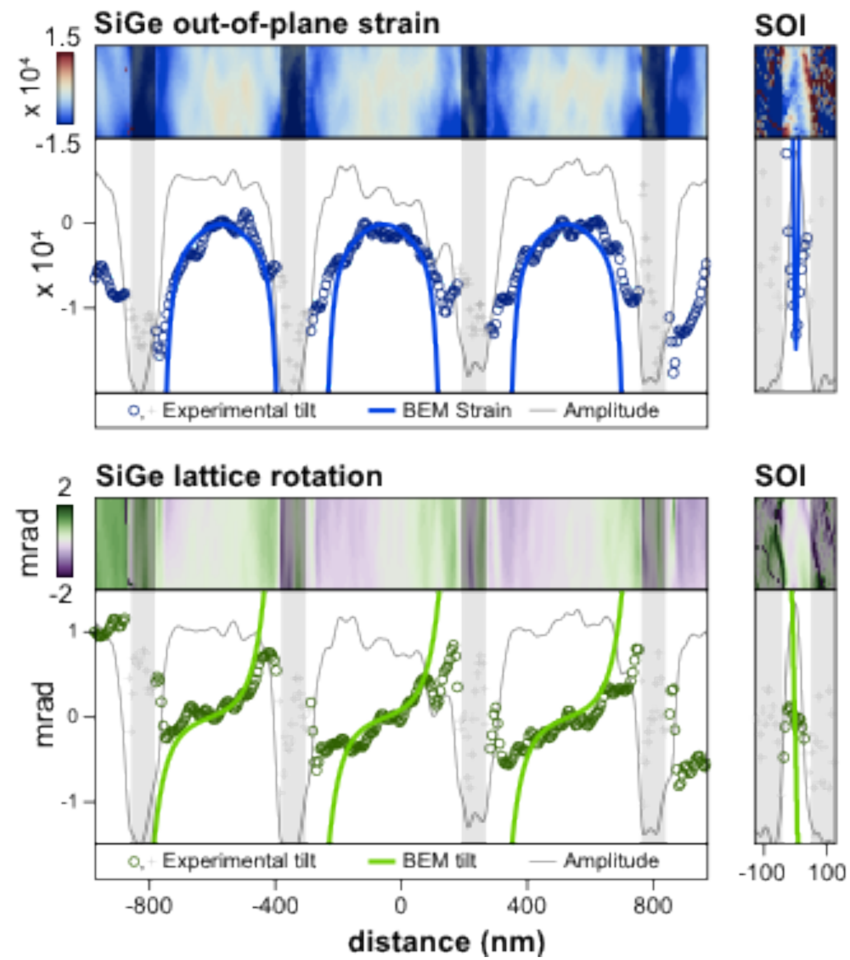
Work by Martin Holt, Stephan Hruszkewycz, Conal Murray, Judson Holt, Debbie Paskiewicz and PHF

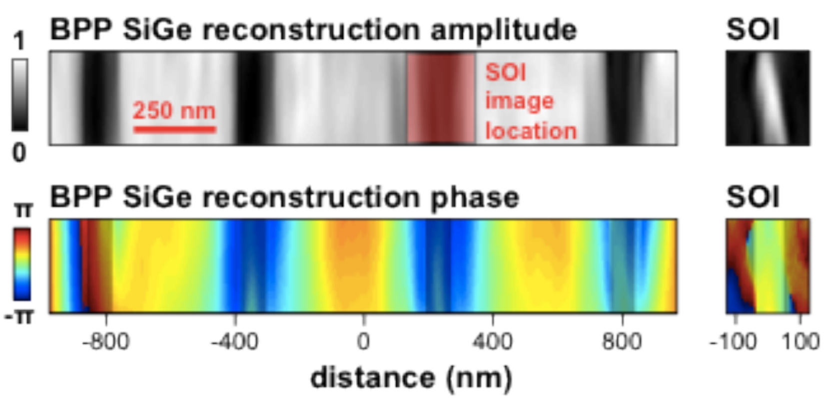


SiGe Device Strain and Deformation

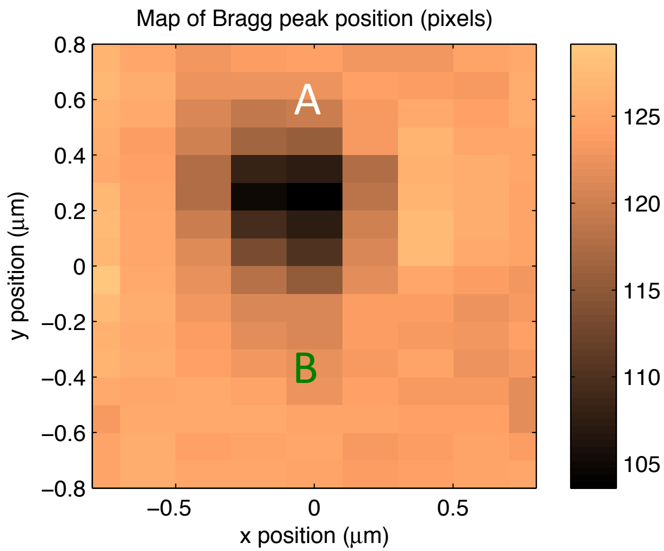
Modeling almost exactly reproduces our BPP reconstruction.

Boundary element method (BEM) calculation shows that there should be both tilts and strain near the active channel.





Damage to Epitaxial SiGe on SOI

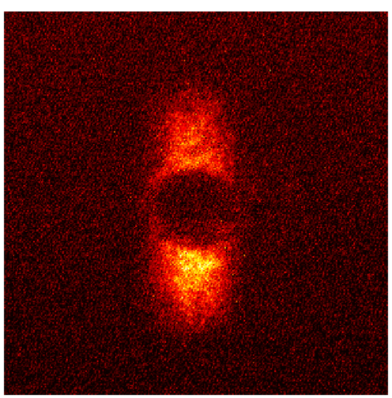


Black region is location of a ptychography spiral scan: 1000 pts, ~600nm diameter, 10 sec exposures, 40nm focused beam diameter, 13nm step size, 65% overlap.

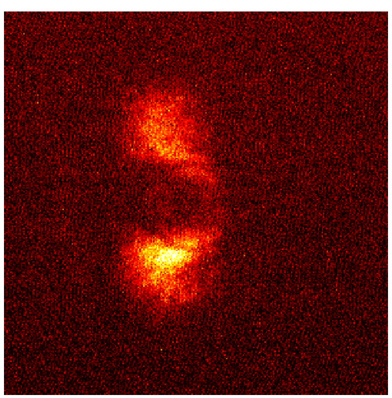
Estimate of flux, 9×10^8 in the focused spot

Scan shown taken with <1 sec exposures to assess damage, plotted as Bragg peak centroid along the 2θ direction

Position B, undisturbed



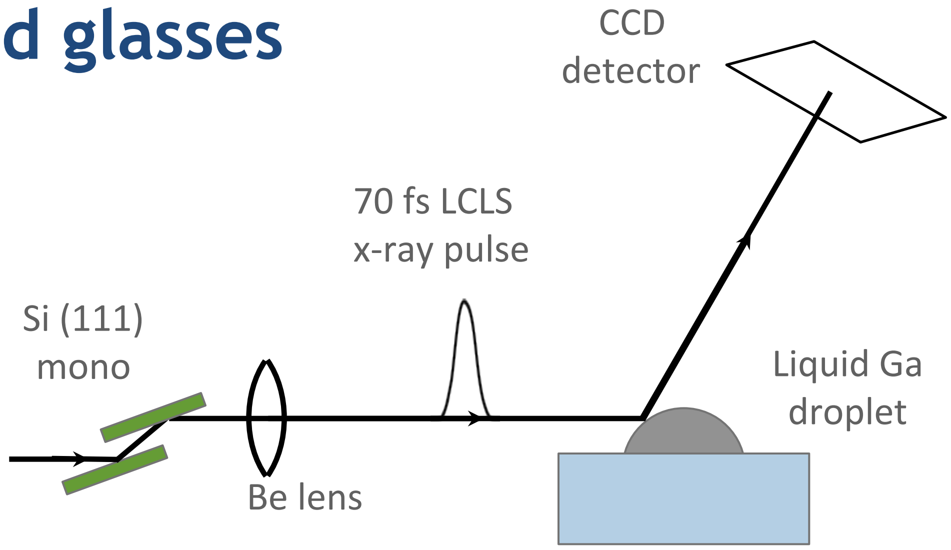
Position A, modified



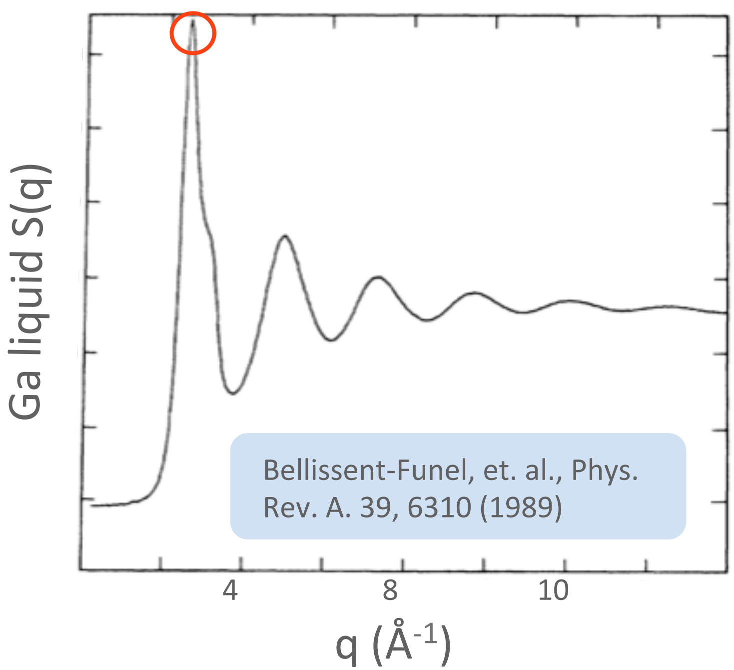
Relaxed film peak
Shifted to high-2θ

Scattering from liquids and glasses

Scattering from atomic liquids and glasses was collected at the LCLS with single and multi-pulse exposure at atomic resolution ($q \approx 3$ Å^{-1})



- XPP hutch at LCLS
- High angle diffracted speckle recorded by CCD
- Samples:
  - $Pd_{40}Ni_{40}P_{20}$ -> heavy glass
  - B_2O_3 -> light glass
  - Ga -> atomic liquid
- Si (111) monochromator
- Be lenses focus to 1.7 microns



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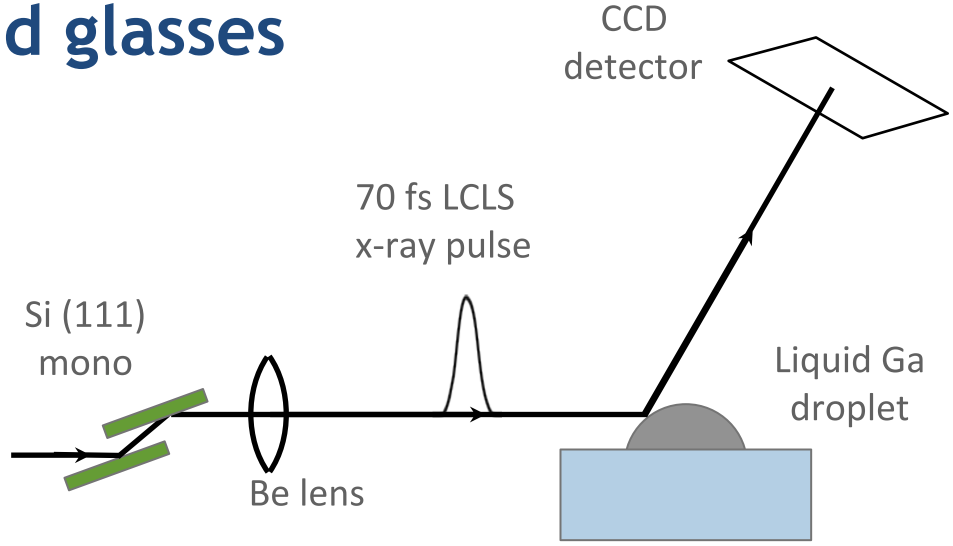

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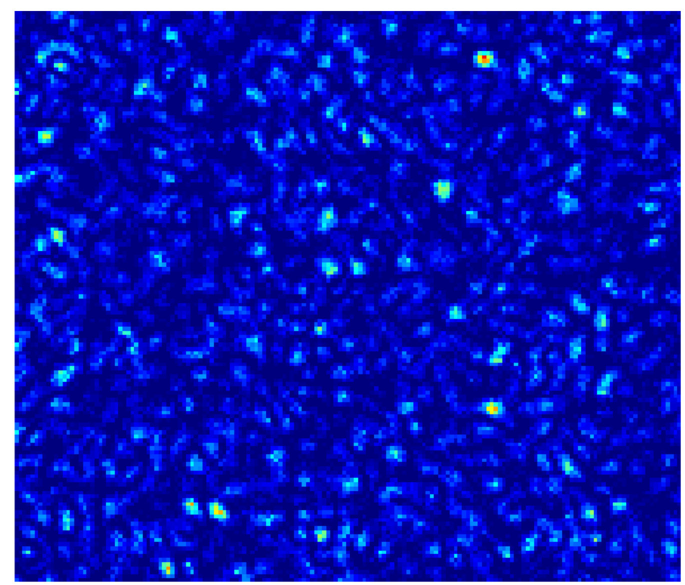
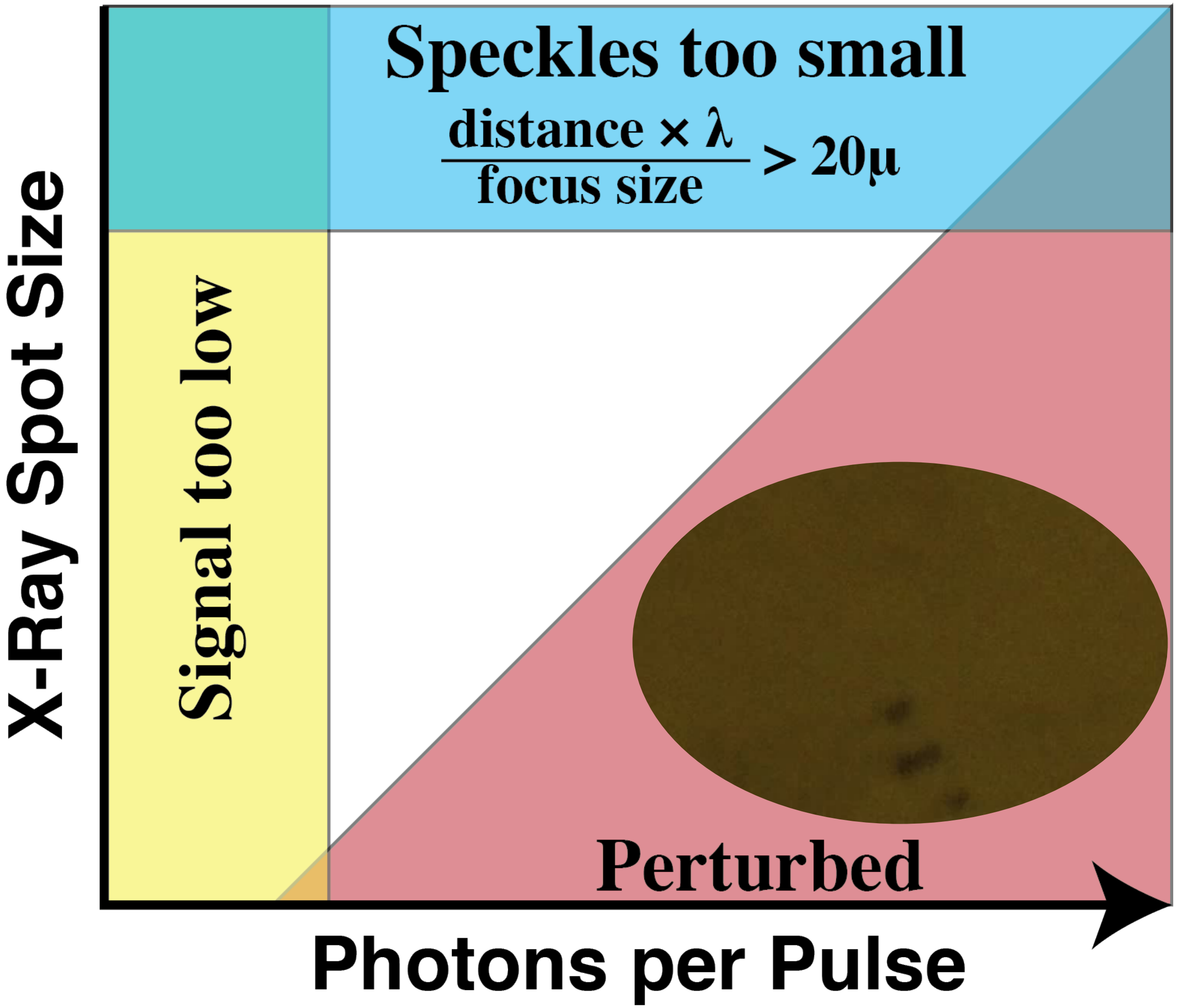
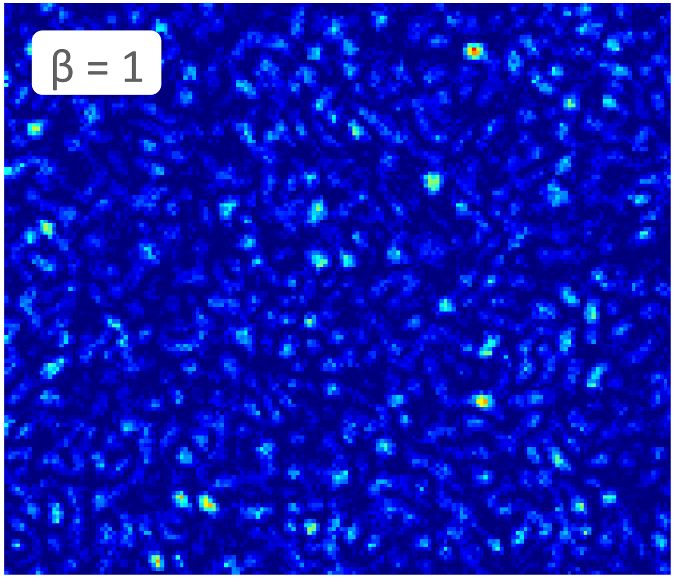


Is There a Useful Non-Perburbative Window?



Noise and Speckle

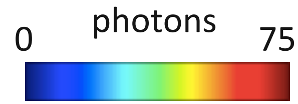
Coherent Speckle



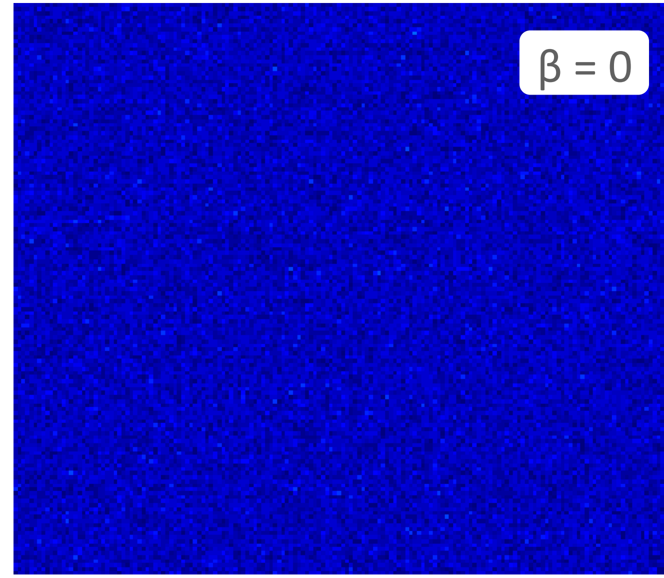
Contrast

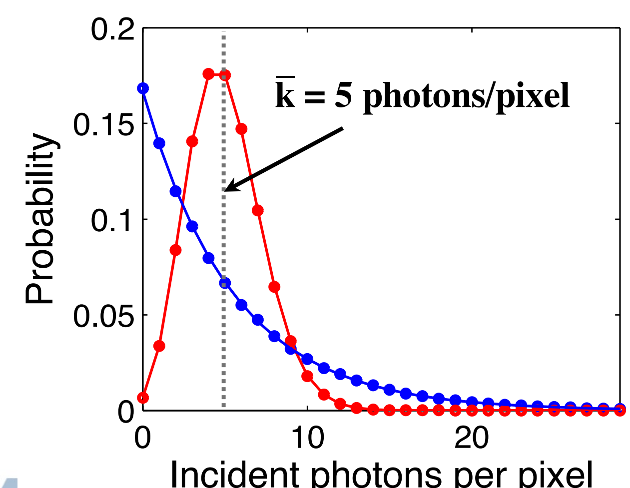
$$\beta \equiv \frac{1}{M}$$

Mean count rate:
5 photons / pixel



Poisson "Shot Noise"





Observed probabilities

- Poisson image
- Coherent speckle image

Probability distribution functions

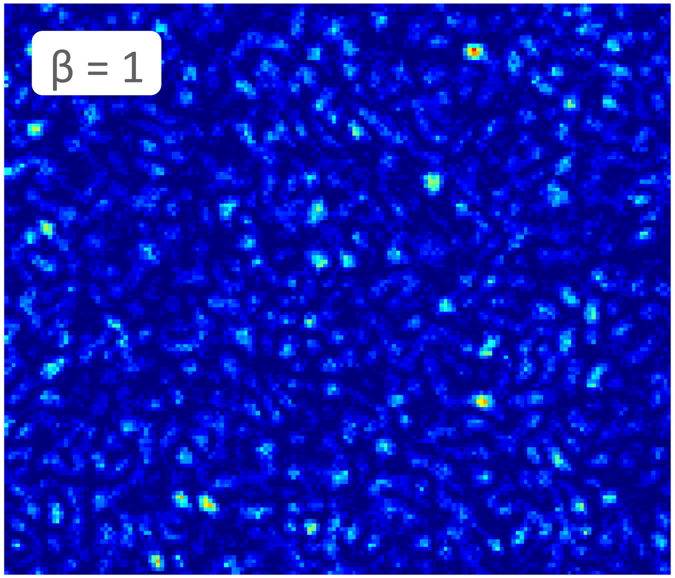
Poisson: $P_{pois}(k,\bar{k}) = \bar{k}^k e^{-k} / k!$

Negative Binomial (M=1):

$$P_{NB}(k,\bar{k},M) = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)}\left(1+\frac{M}{k}\right)^{-k}\left(1+\frac{\bar{k}}{M}\right)^{-M}$$

Noise and Speckle

Coherent Speckle



Contrast

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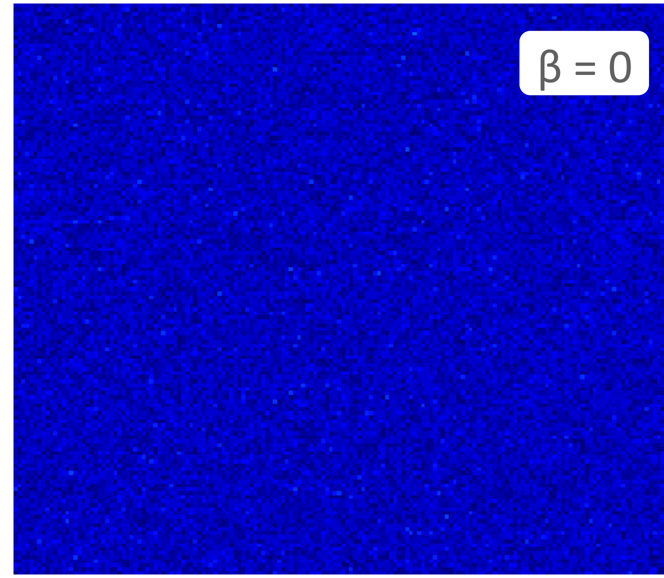
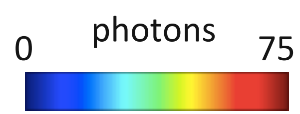
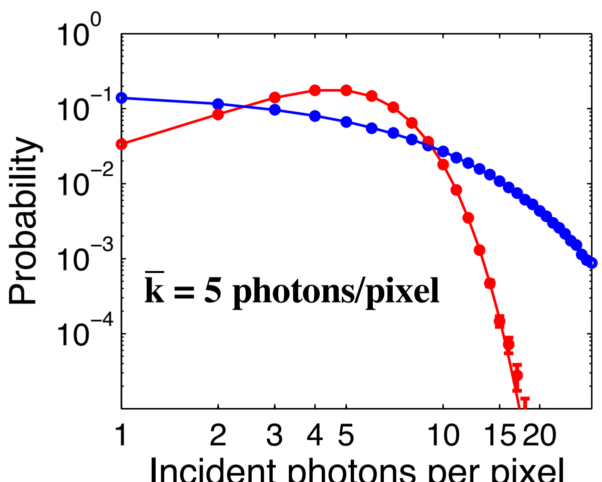
5 photons / pixel

Poisson "Shot Noise"







Observed probabilities

- ● Poisson image
- ● Coherent speckle image

Probability distribution functions

Poisson: $P_{pois}(k,\bar{k}) = \bar{k}^{k} e^{-k} / k!$

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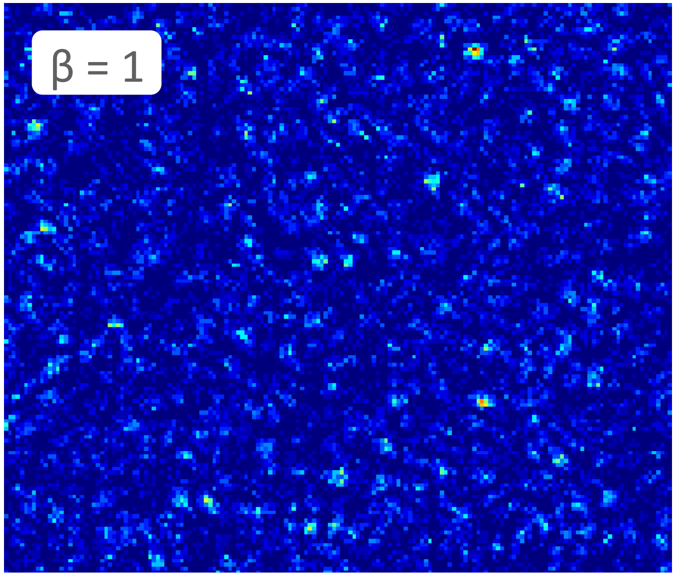
Noise and Speckle

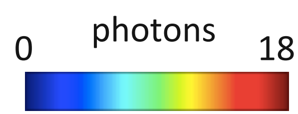
Coherent Speckle



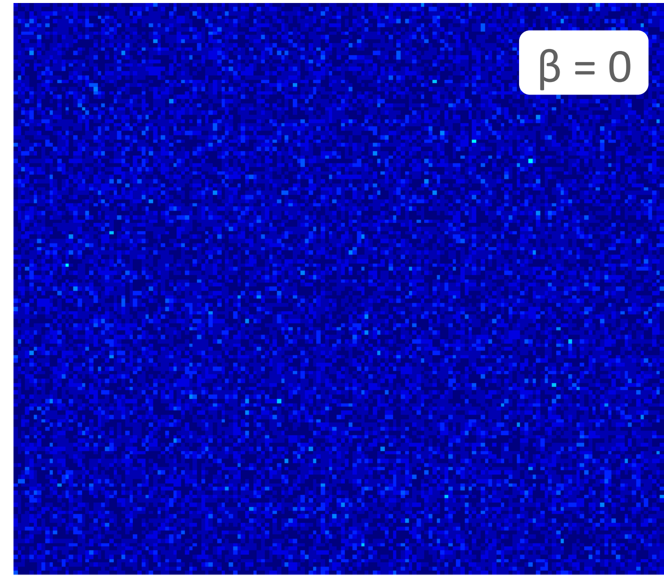
Contrast

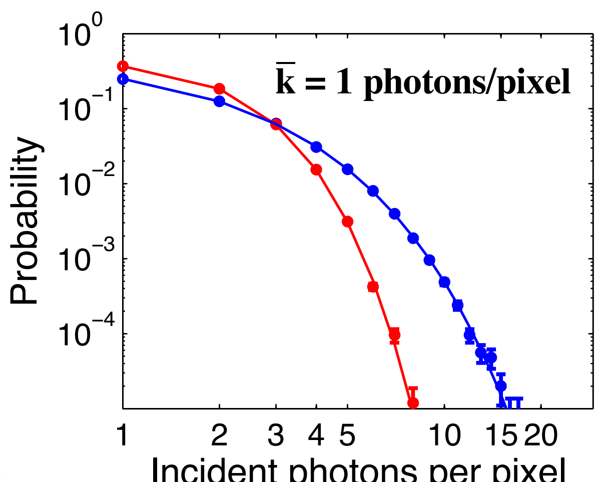
$$\beta \equiv \frac{1}{M}$$

Mean count rate:
1 photons / pixel



Poisson "Shot Noise"





Observed probabilities

- ● Poisson image (red)
- ● Coherent speckle image (blue)

Probability distribution functions

Poisson (red line):

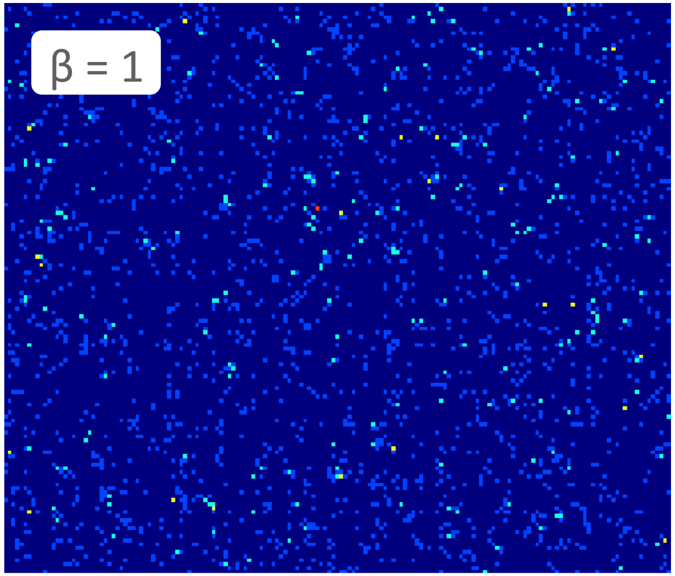
$$P_{pois}(k,\bar{k}) = \bar{k}^k e^{-k} / k!$$

Negative Binomial (M=1) (blue line):

$$P_{NB}(k,\bar{k},M) = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)}\left(1+\frac{M}{k}\right)^{-k}\left(1+\frac{\bar{k}}{M}\right)^{-M}$$

Noise and Speckle

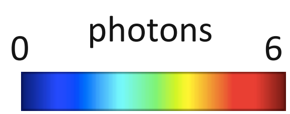
Coherent Speckle



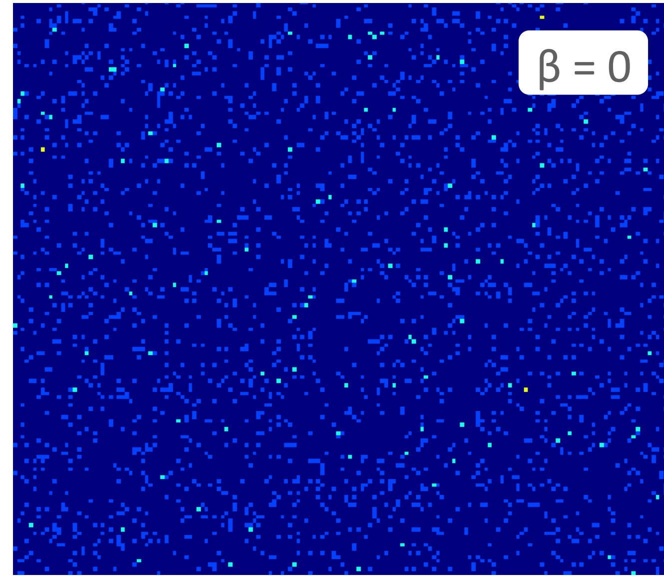
Contrast

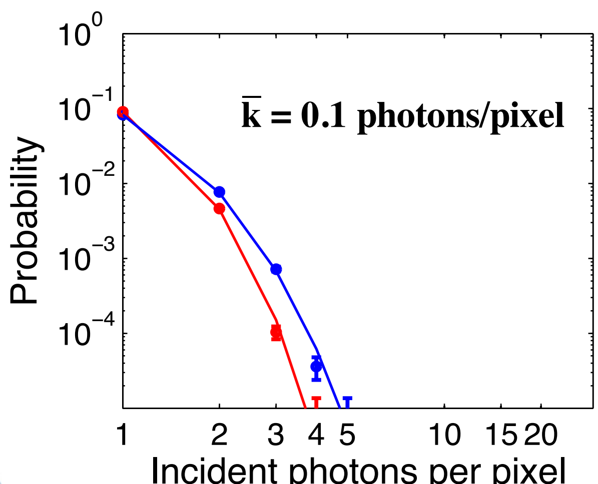
$$\beta \equiv \frac{1}{M}$$

Mean count rate:
0.1 photons / pixel



Poisson "Shot Noise"





Observed probabilities

- ● Poisson image
- ● Coherent speckle image

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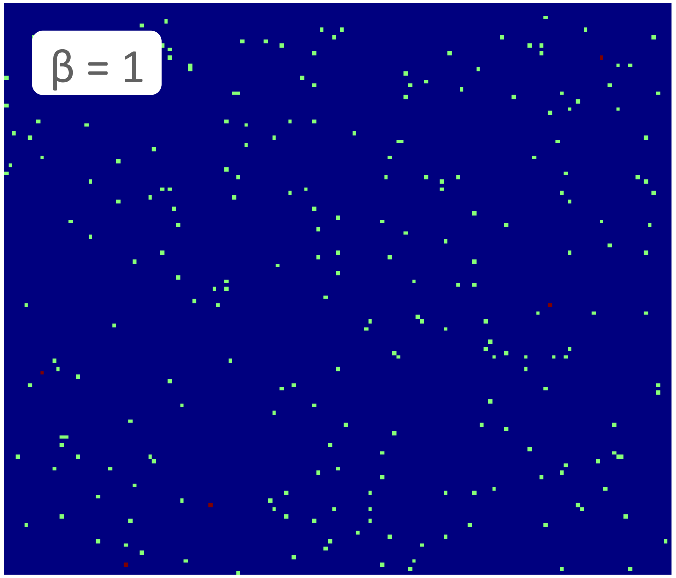
Noise and Speckle

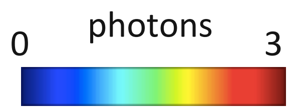
Coherent Speckle



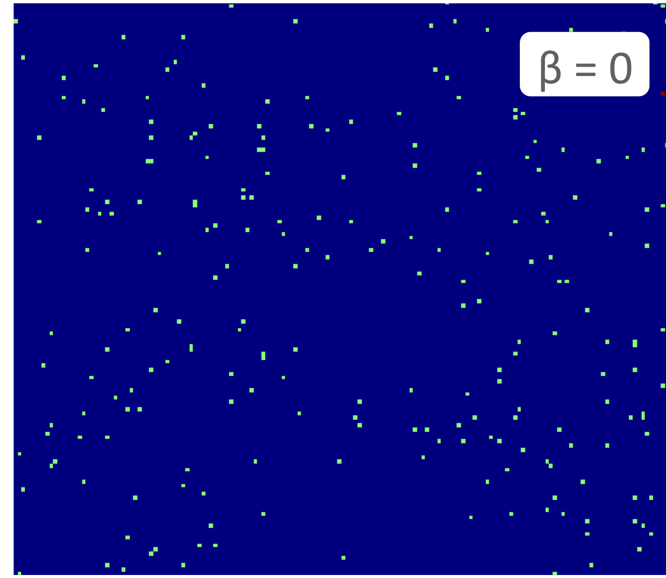
Contrast

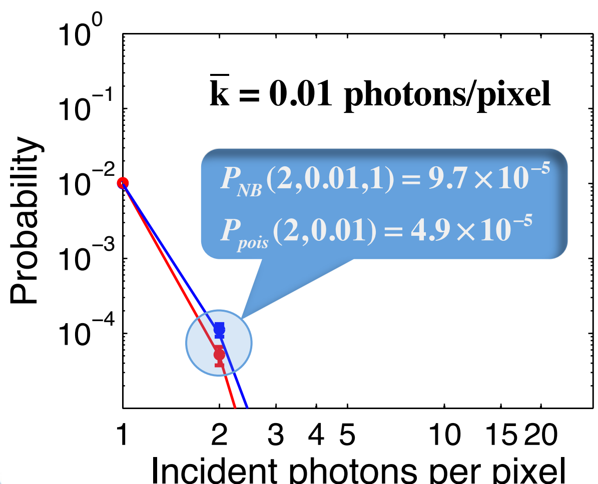
$$\beta \equiv \frac{1}{M}$$

Mean count rate:
0.01 photons / pixel



Poisson "Shot Noise"





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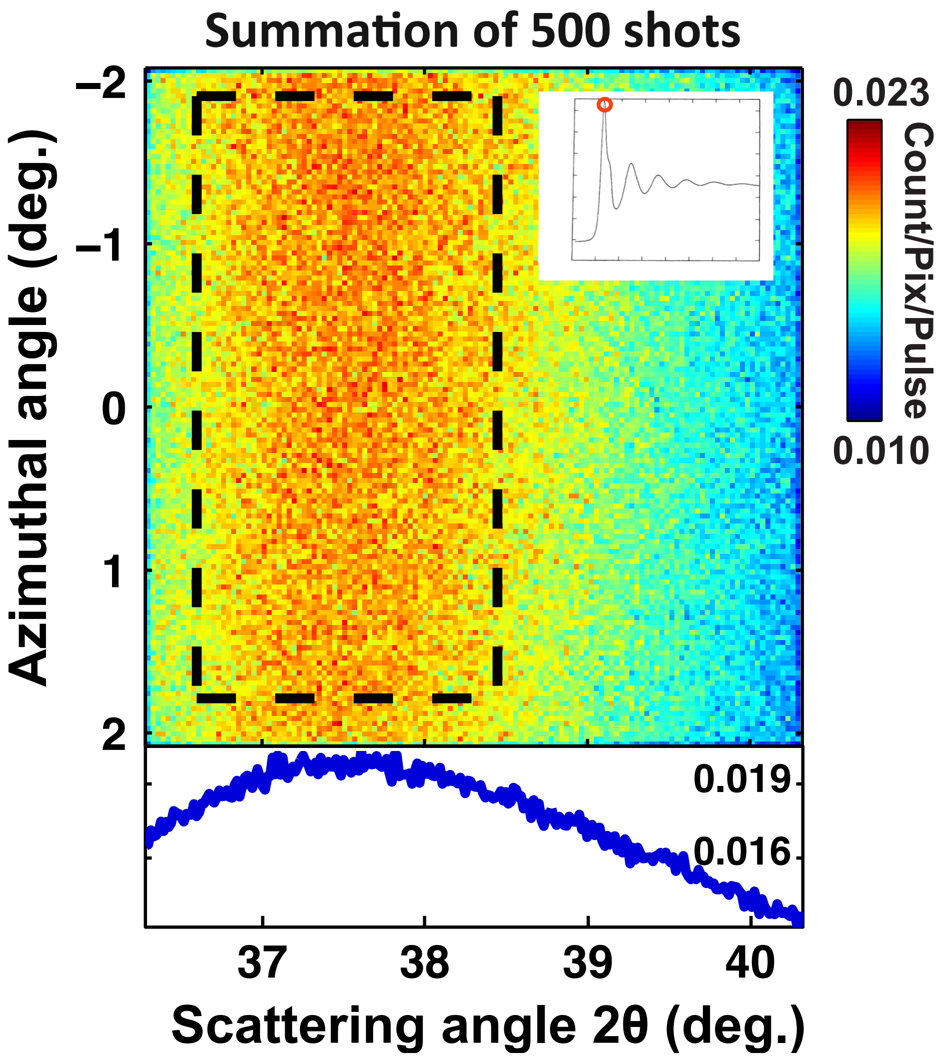
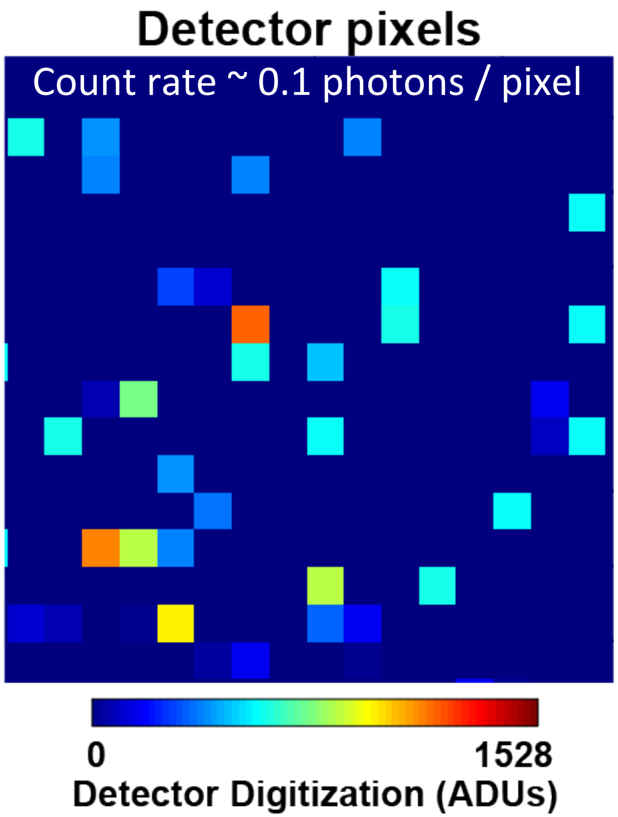
High angle liquid scattering

Single pulse scattering patterns are very weak and need to be carefully analyzed in order to determine contrast.

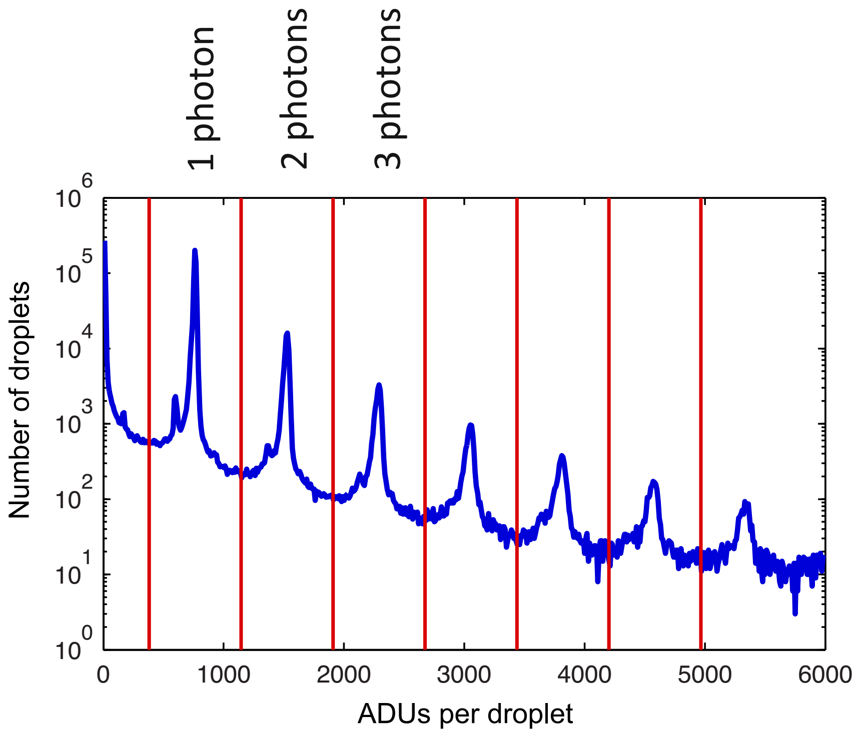




The droplet algorithm

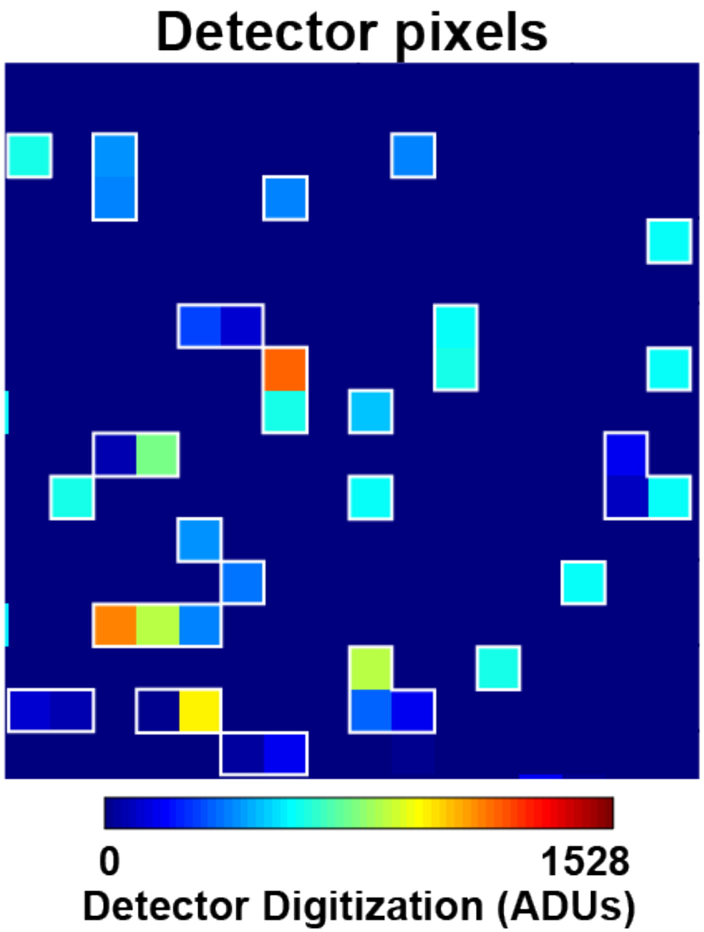
Step 1: Identify regions of connectivity, i.e. droplets

- **Histogram of droplets by their total counts clearly separates photon events**



F. Livet et al., Nucl. Instrum. Meth. A 451, 596 (2000).

Droplets accurately identify regions of correlated intensity.



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Step 1: Identify regions of connectivity, i.e. droplets

- Histogram of droplets by their total counts clearly separates photon events

Step 2: Fit each droplet by least squares to identify positions of photons

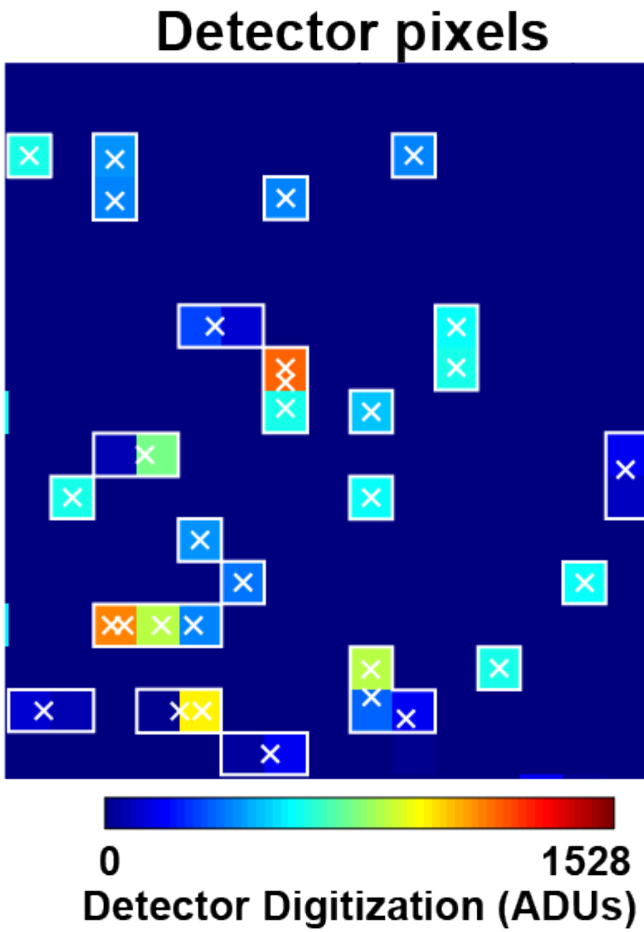
Step 3: After photons were extracted, they were re-gridded onto the detector pixels.

- **Accurate determination of P(1) and P(2)**

$$P(1) \approx \bar{k} - (1+\beta)\bar{k}^2$$

$$P(2) \approx \frac{(1+\beta)\bar{k}^2}{2} - \frac{(1+\beta)(1+2\beta)\bar{k}^3}{2}$$

Technique identifies the x,y coordinate of every photon.



Measuring contrast from liquid Ga

Experimental considerations define maximum attainable contrast:

$$\beta_{calc}(p, L, Q, t, \theta, \Delta E / E, s_x, s_y)$$

The experimental value

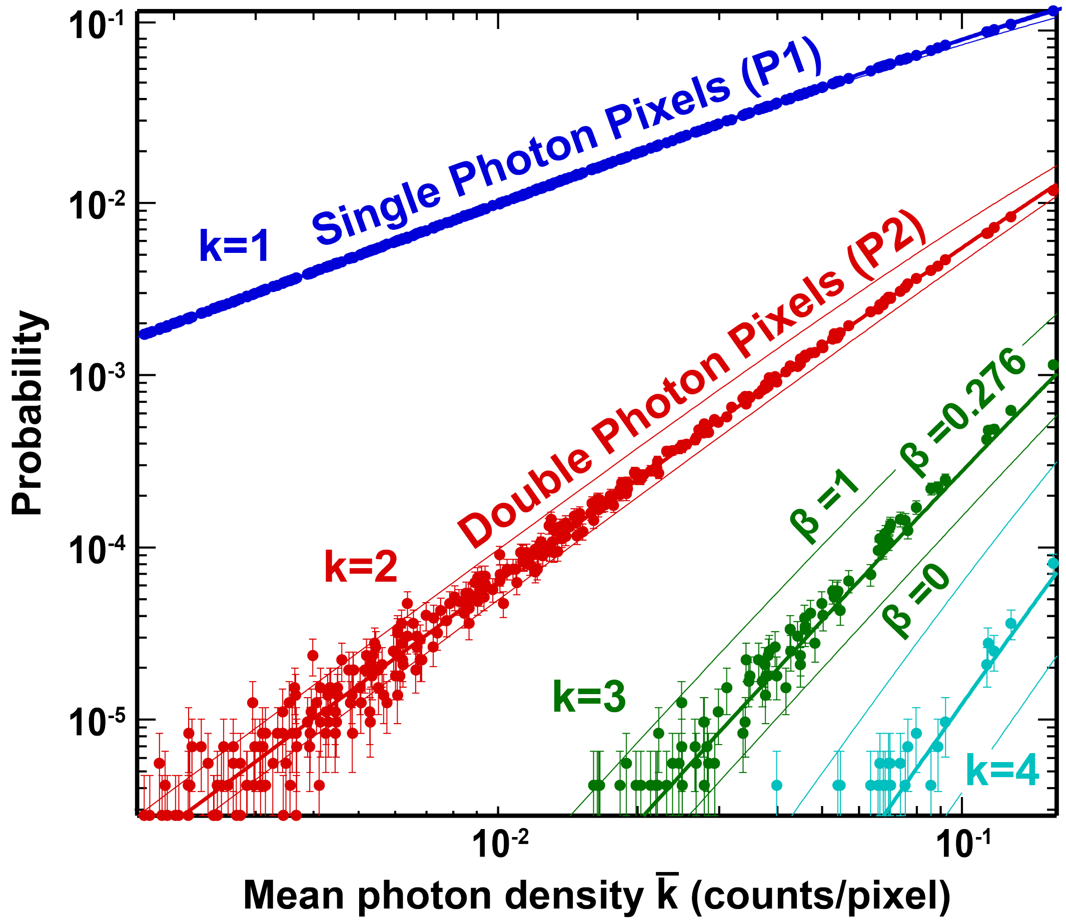
$\beta_{Ga} = 0.276 \pm 0.004$

was determined from droplet fitting analysis, and matches the maximum attainable

$\beta_{calc} = 0.307$

for this geometry

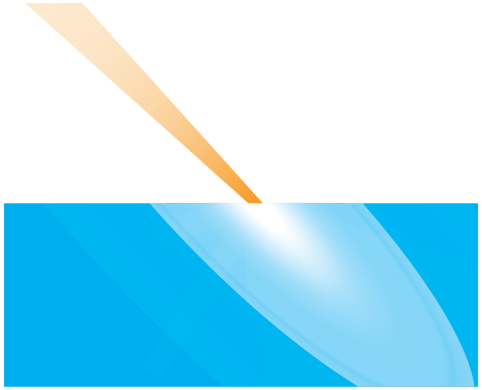
$$P_{NB}(k, \bar{k}, M) = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)} \left(1 + \frac{M}{k}\right)^{-k} \left(1 + \frac{\bar{k}}{M}\right)^{-M}$$

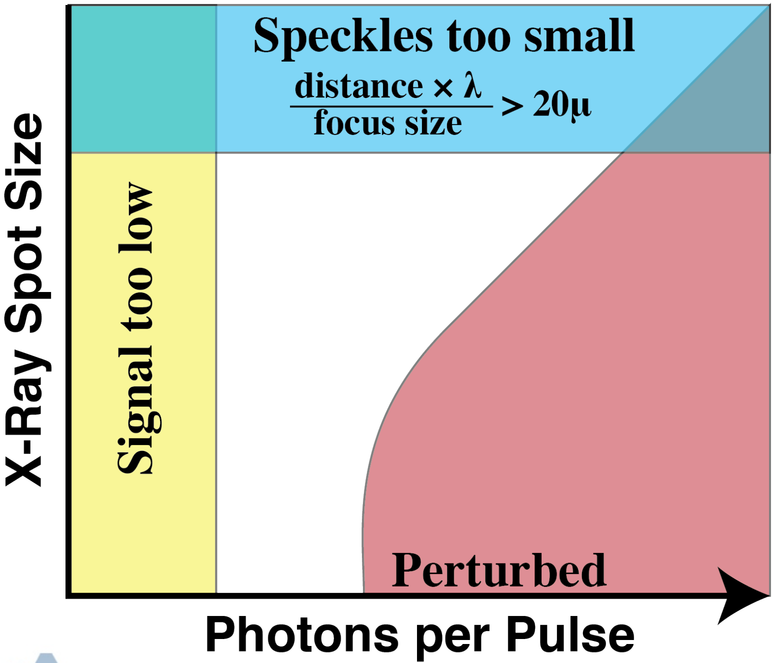


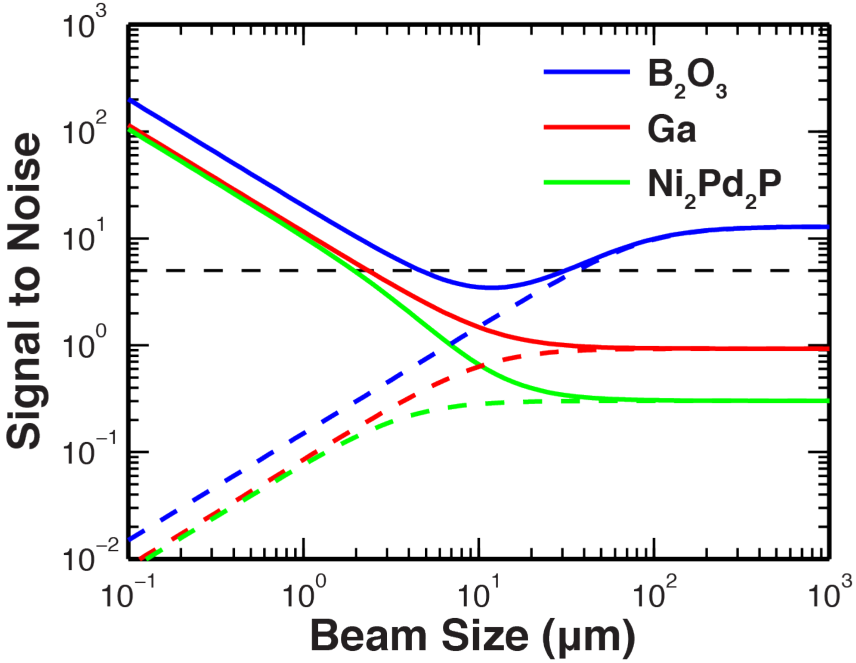
(Note the large range of incident pulse energies)

X-Ray Energy Deposition is Larger Than Focus

- Most of the x-ray energy is carried away by high energy electrons and fluorescent photons that have a range of many microns.
- Energy is deposited well outside a sub-micron focus.
- **Sample perturbation doesn't scale like the inverse of the focal spot size.**

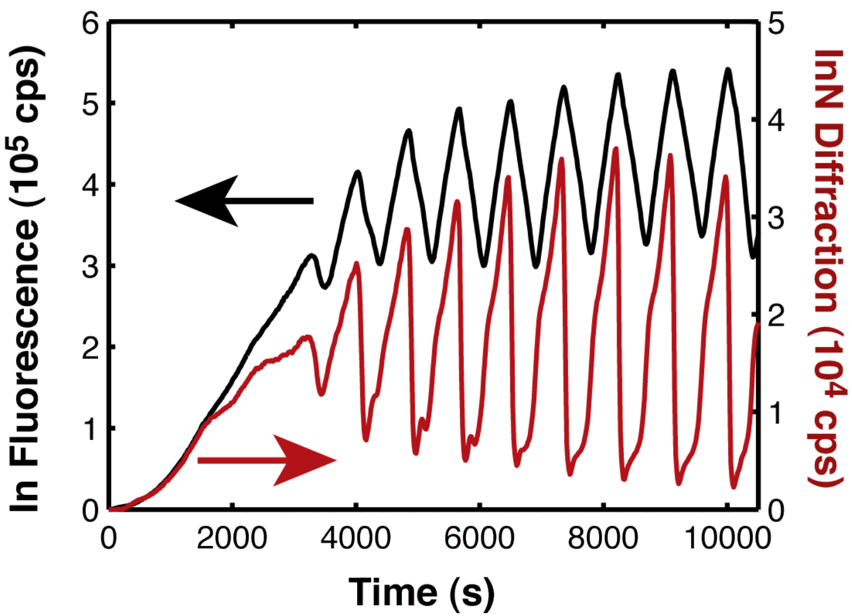


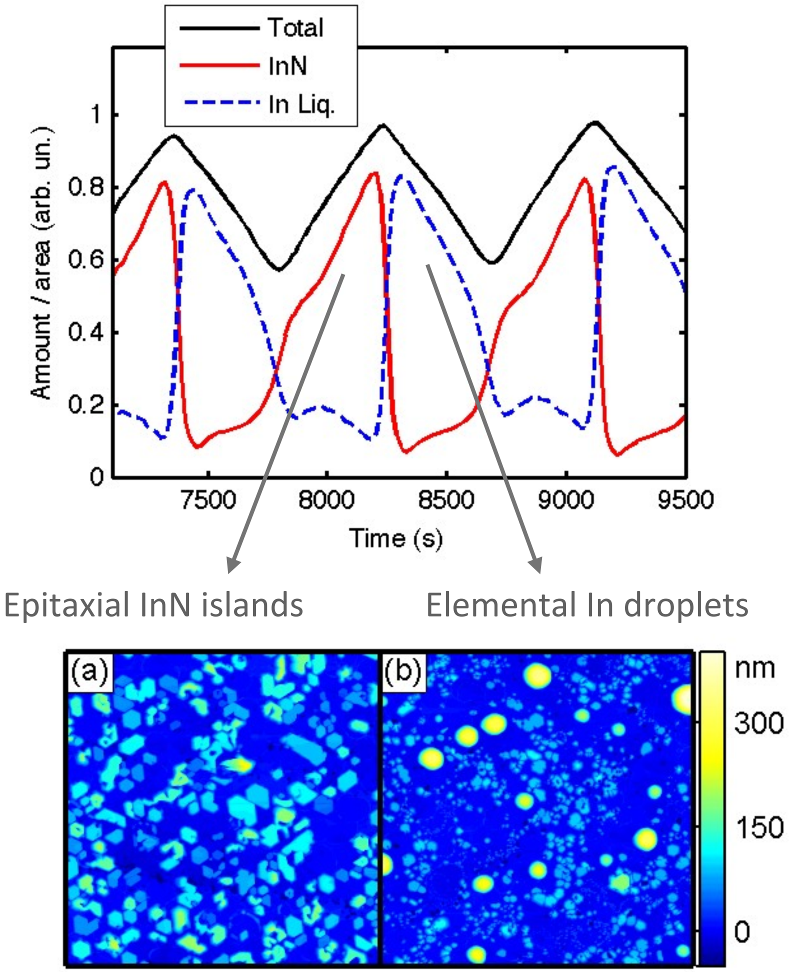




Oscillatory Growth and Decomposition

- Near phase boundaries system can spontaneously oscillate
  - Inter-conversion between InN and liquid In
- AFM of quenched samples shows microstructure of distinct surface species





F. Jiang, et al. PRL 101, 086102 (2008)

Real-time Observations of Chemical Waves during Oscillatory Growth and Decomposition of InN

Oscillatory Pattern Formation during MOCVD of InN on GaN

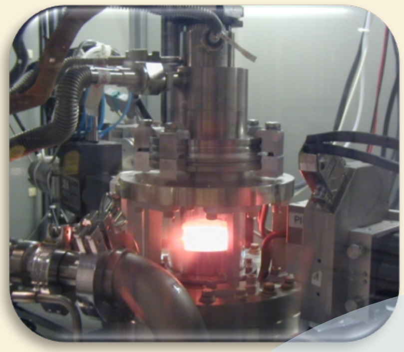
1. Expanding circular pattern

Actual elapsed time:	1 hour 25 min
Temperature:	664ºC
TMI flow rate:	0.145 μmol/min
NH_3 partial pressure:	27 Torr
Total pressure:	200 Torr
Sample size:	15x15 mm^2

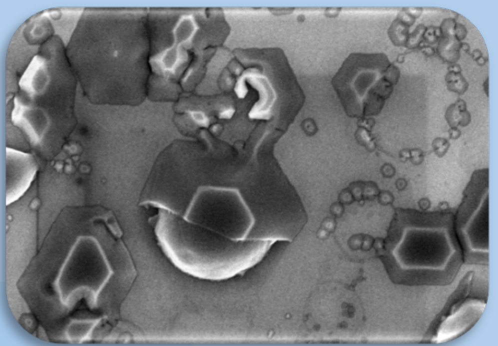
Attacking the Problem on Multiple Fronts

Understanding complicated problems such as WBG synthesis and fabrication requires a variety of *in-situ* probes and computational techniques

In-situ X-ray Analysis



X-Ray Imaging of Defects



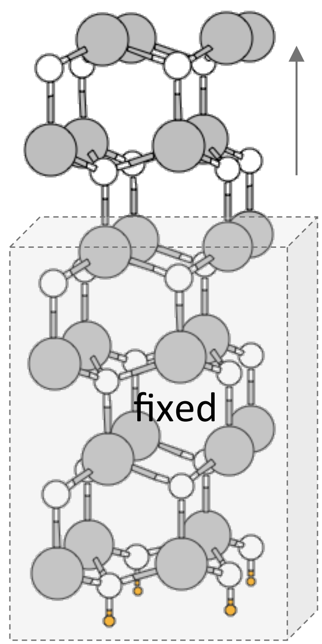
Theory & Modeling

First-principles Calculations

- Calculate the lowest energy configurations of NH_3, NH_2, NH, N, and H on a GaN and InN surface
- Create a phase diagram predicting the equilibrium coverage species for given conditions

(2x2) surface unit cell
- 4 H3 "hollow" sites
- 4 T1 "on top" Ga sites
- 4 T4 "on top" N sites
- 12 br "bridge" site

~10^3 structures possible



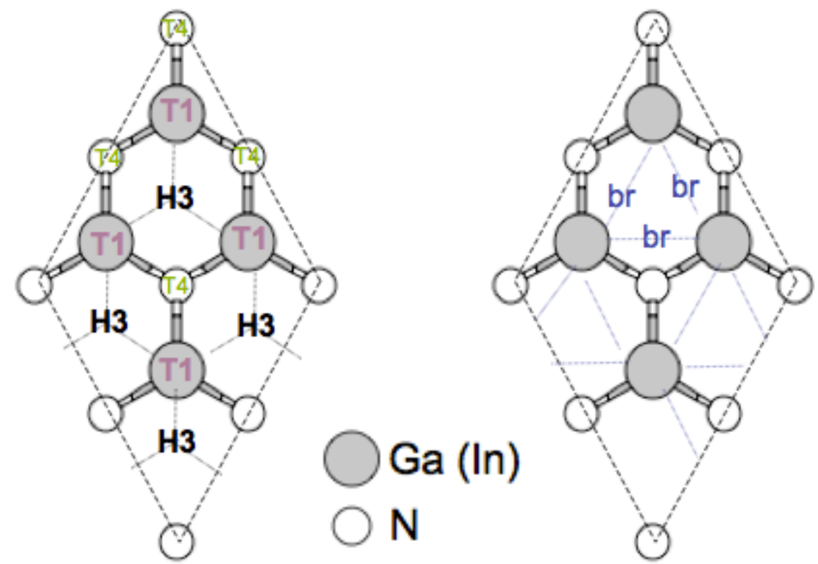
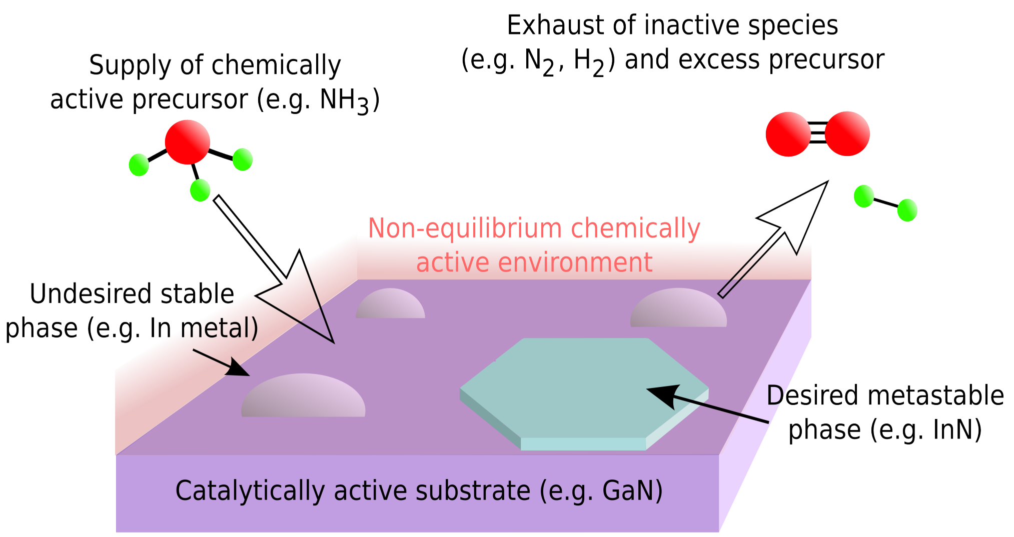


Fig.1 Fig.2

"We" = Peter Zapol, Weronika Walkosz, and Xin Tan

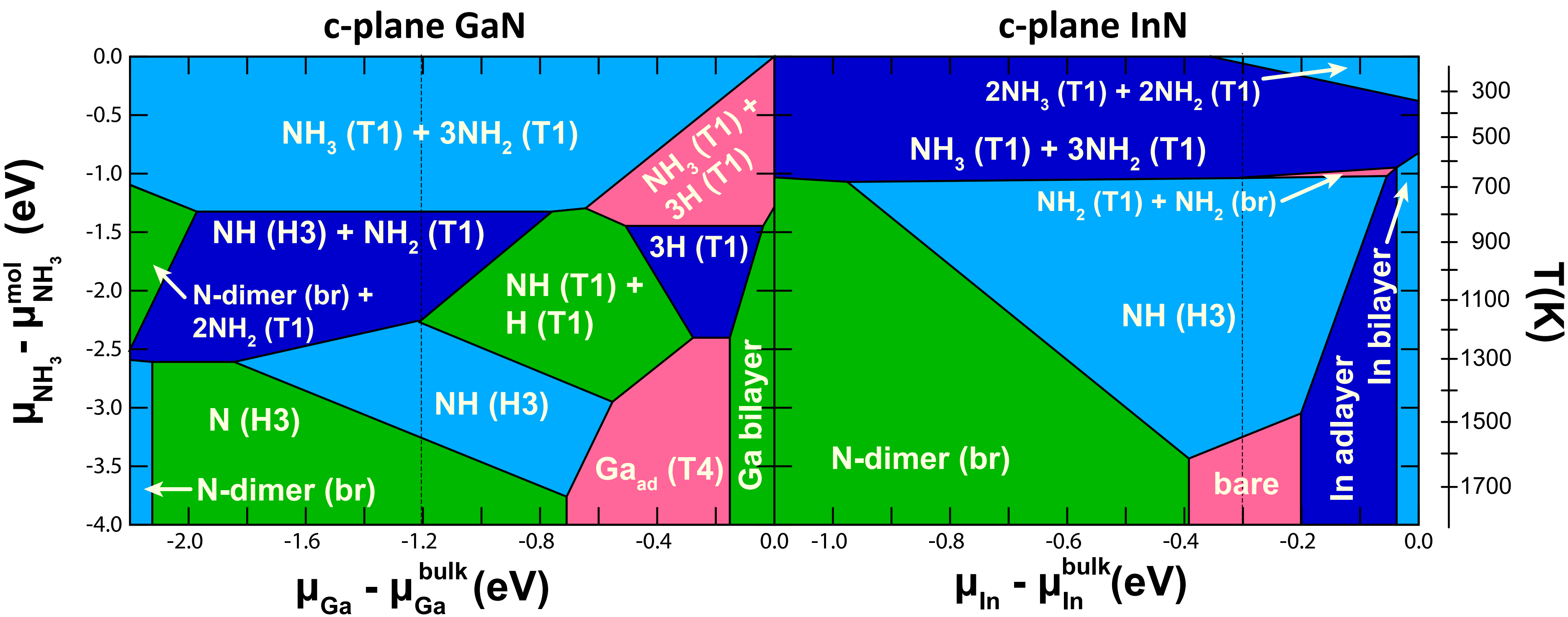
Intermediate Chemical Species

- The local intermediate chemical species dictate growth behavior
- Different surfaces catalytically crack NH_3 differently and possibly change residence time of intermediate species
- If we can understand which intermediate species enable InN growth, then we can better stabilize and encourage its formation
- **What are the intermediate nitrogen species?**
  - **First principle calculations**
  - **Additional *in-situ* probes**



Phase Diagrams at Finite Temperatures

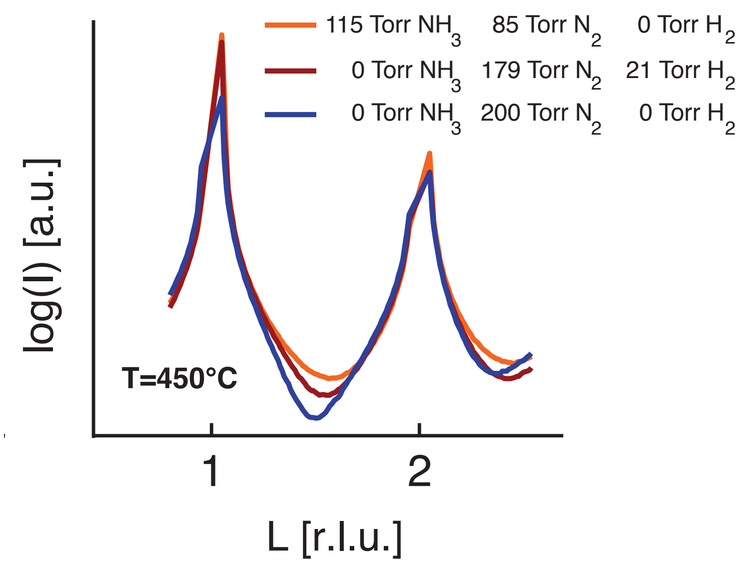
- Many possible structures depending on the chemical potential (μ)
- Surprisingly, some structures do not obey electron-counting rule
- Can we identify these structures experimentally?

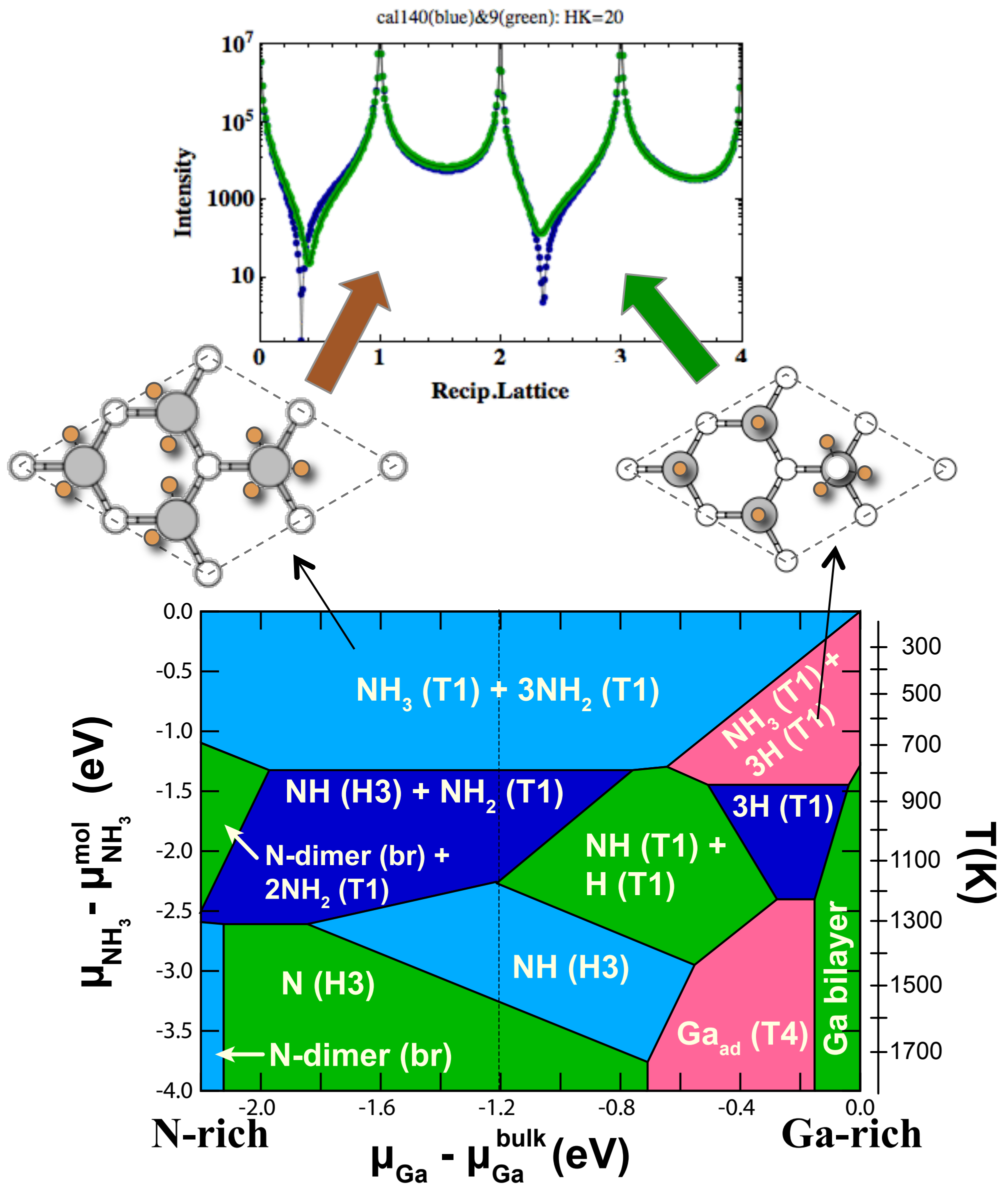


W.Walkosz, P. Zapol and G. B. Stephenson, *Phys. Rev. B* 85, 033308 (2012)

CTR Analysis of Structures

- First Principle can be used to predict CTRs for each phase
- Can we see these changes with *in-situ* x-rays ?
- Have not found unique solutions





W. Walkosz, et al. PRB ***85****, 033308 (2012)*

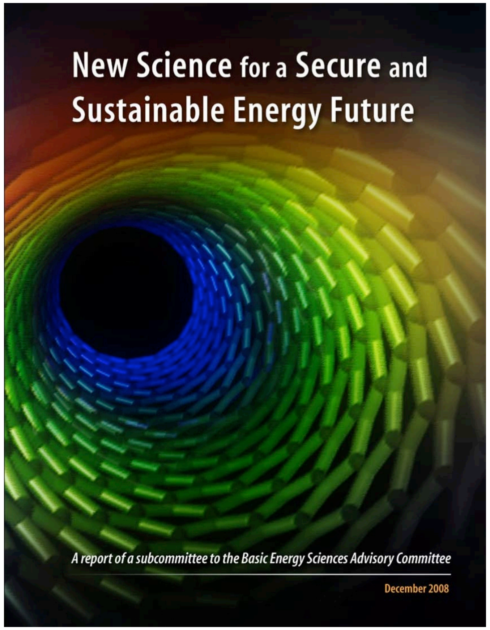
Fundamental Questions in Materials Science

What materials are present?

Where are the materials located?

When do crucial transformations and processes occur?

Why does a material have its structure and properties?



Advanced x-ray techniques provide unique information by looking into and through complex materials and devices.

Coupled with theory and advanced computing capabilities, this information enables a detailed understanding of material processing technologies and device physics.

Non-Perturbative Measurements
using
Minimum Photon Approaches

- **Perturbation Limits**
  - General physics of x-ray interactions (e.g. cross-sections)
  - Perturbation limits of soft and hard matter
  - Imaging resolution versus dose
- **Extracting maximum information from each photon**
  - Better algorithms
  - Improved optics
  - Advanced detectors
- **Integrated approaches to solving scientific problems**
  - X-ray measurements
  - Theory and large scale simulation
  - Other probes (e.g. TEM, optical spectroscopy)

Atomic Resolution, Ultrafast X-Ray Speckle from Liquids

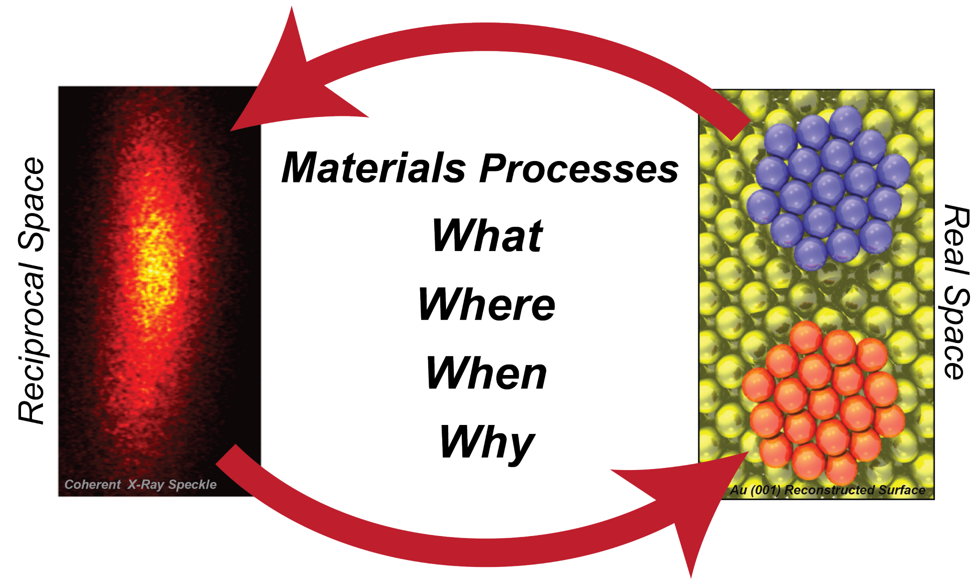
Paul Fuoss, **Stephan Hruszkewycz, Stephan Rosenkranz, Bernard Adams and Brian Stephenson**, *Argonne National Laboratory*

Mark Sutton, *McGill University*

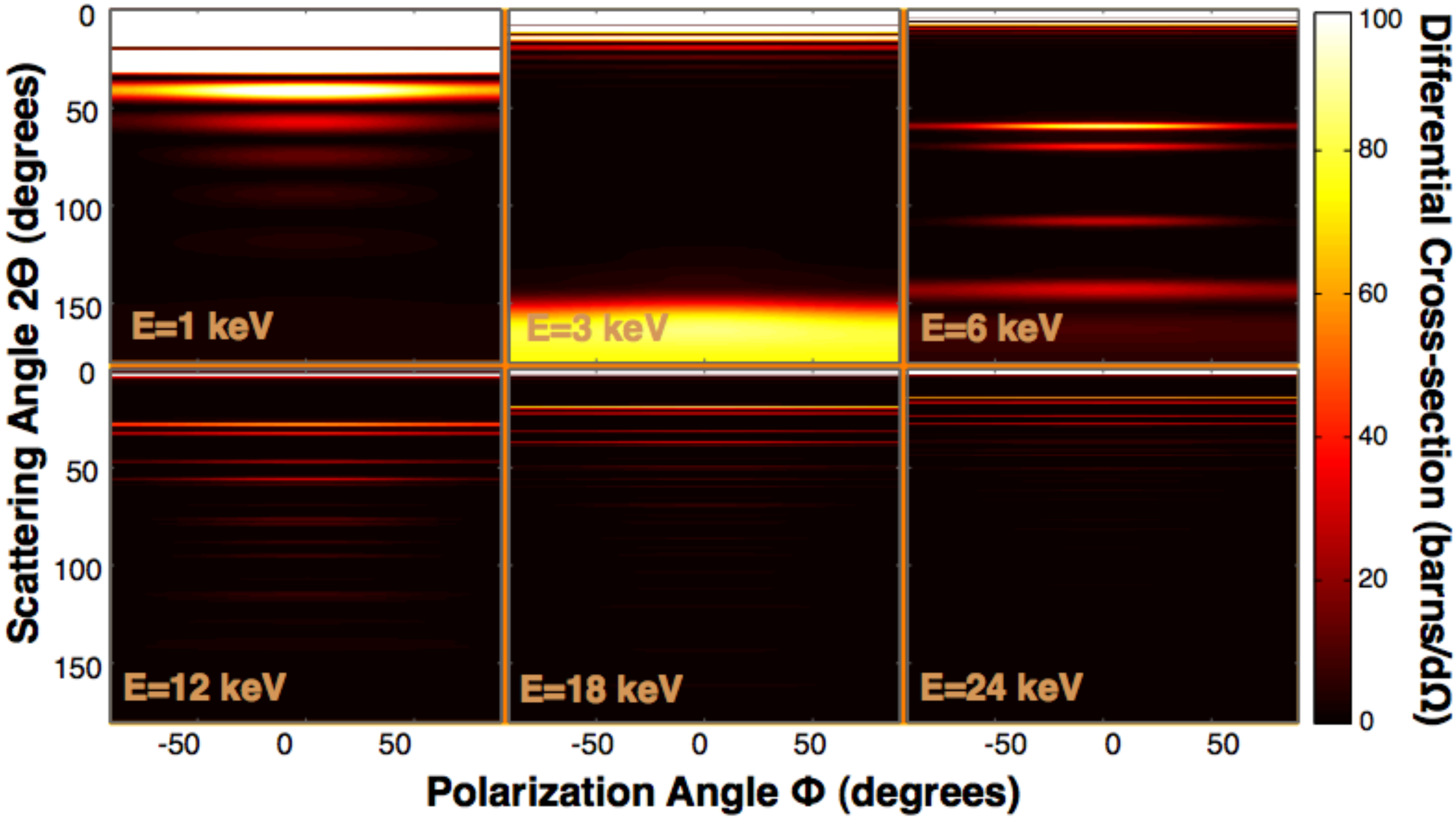
Karl Ludwig, *Boston University*

Aymeric Robert, Dave Fritz, Marcin Sikorski, Sooheyong Lee, Diling Zhu, Marco Cammarata and Henrik Lemke, *SLAC National Accelerator Laboratory*

Christian Gutt, Wojciech Roseker and Gerhard Grubel, *Deutsches Elektronen-Synchrotron*



Scattering Calculations: Cross-Section of a Copper



Scattering Considerations: Basic Equation

Now we'll develop the x-ray scattering in more detail because that strongly impacts experimental design. The basic scattering equation is:

$$d\sigma(\vec{Q}) = \left(\frac{e^4}{m^2c^4}\right)\sum_{i=1}^{N_{atoms}}\sum_{j=1}^{N_{atoms}} f_i(\vec{Q})f_j(\vec{Q})e^{-\vec{Q}\bullet\vec{R}_{ij}}d\Omega$$

where

$\vec{Q}$ = the difference between the exit and incident wavevectors

$\vec{R}_{ij}$ = the vector connecting atoms i and j

f_i = the atomic scattering factor of atom i