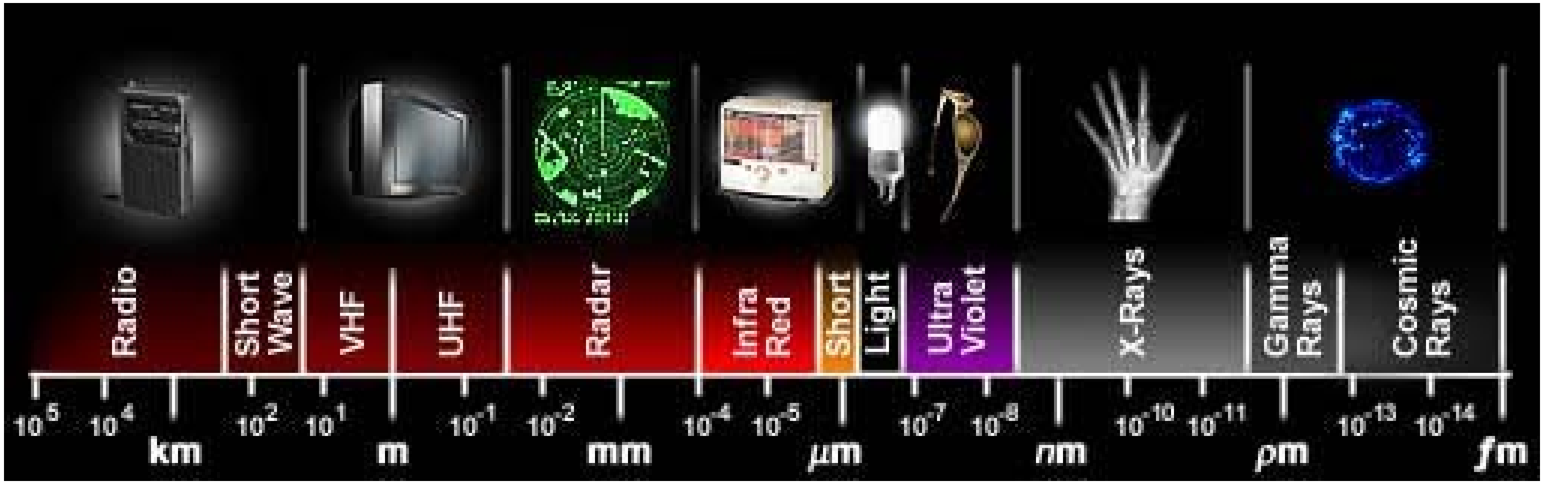
Making Functional Surfaces and Thin Films: Where are the Atoms?

K. Ludwig, A. DeMasi, J. Davis and G. Erdem
Department of Physics
Materials Science and Engineering Program

Why x-rays?



$\lambda \sim 10^{-10}$ m ~ distance between atoms

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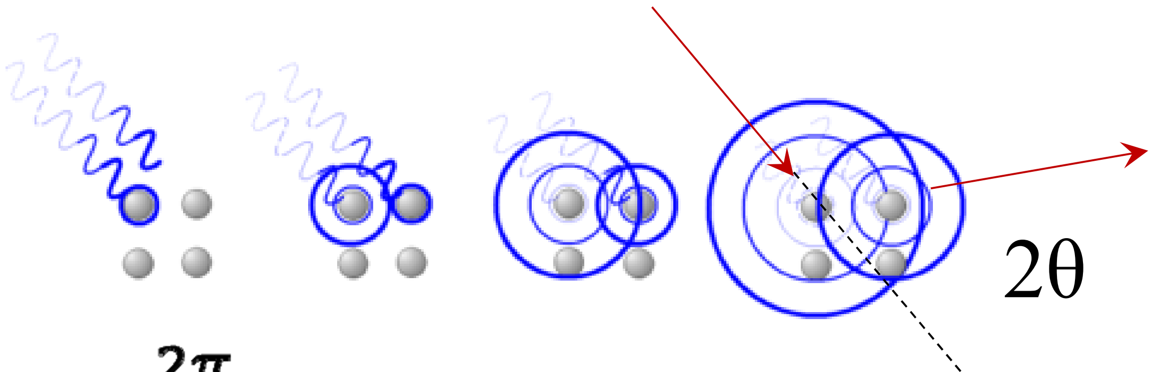
X-ray Scattering (Diffraction)



$$p = \hbar k = \hbar \frac{2\pi}{\lambda}$$

images-mediawiki-sites.thefullwiki.org

The momentum transfer to an elastically scattered photon is:

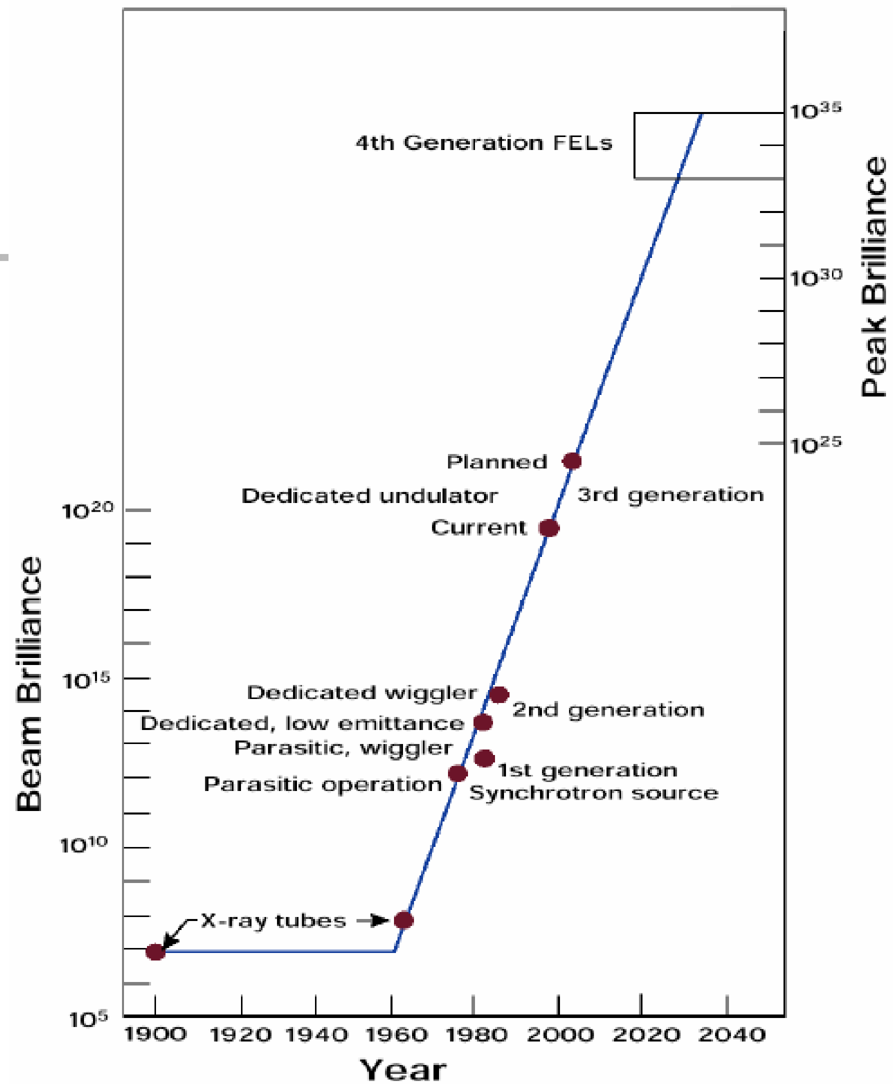
$$\Delta\vec{p} = \hbar\Delta\vec{k} = \hbar\vec{q} \qquad q = \frac{4\pi sin\theta}{\lambda}$$

X-ray Scattering (Diffraction)

In the Born Approximation, the intensity of x-ray scattering is equal to the structure factor *S(q)* of atom positions:

$$I(\vec{q}) = \left| \sum_i e^{i\vec{q}\cdot\vec{r_i}} \right|^2 \equiv S(\vec{q}) = \sum_{i,j} e^{i\vec{q}\cdot(\vec{r_i}-\vec{r_j})}$$

Thanks to synchrotron x-ray sources, available x-ray brightness has been growing fast – faster than computer speeds!



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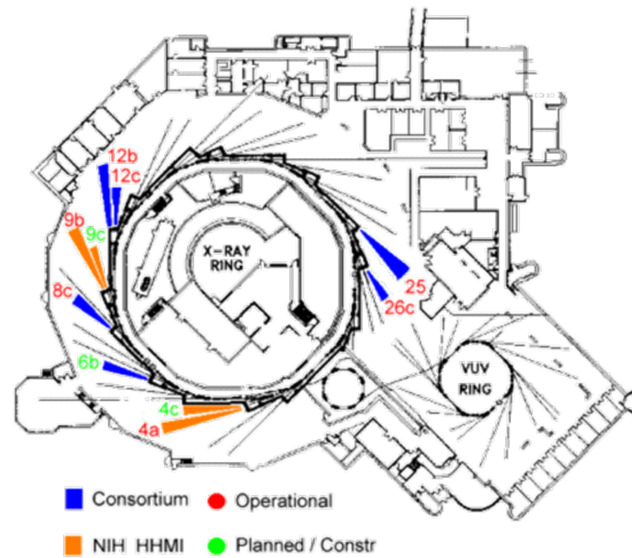
National Synchrotron Light Source (NSLS) and NSLS-II Brookhaven National Laboratory (Long Island)



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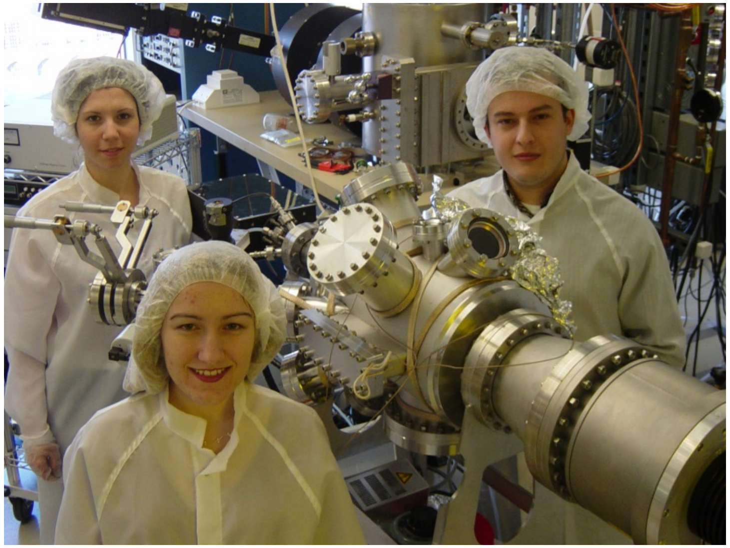
National Synchrotron Light Source (NSLS) and NSLS-II Brookhaven National Laboratory (Long Island)

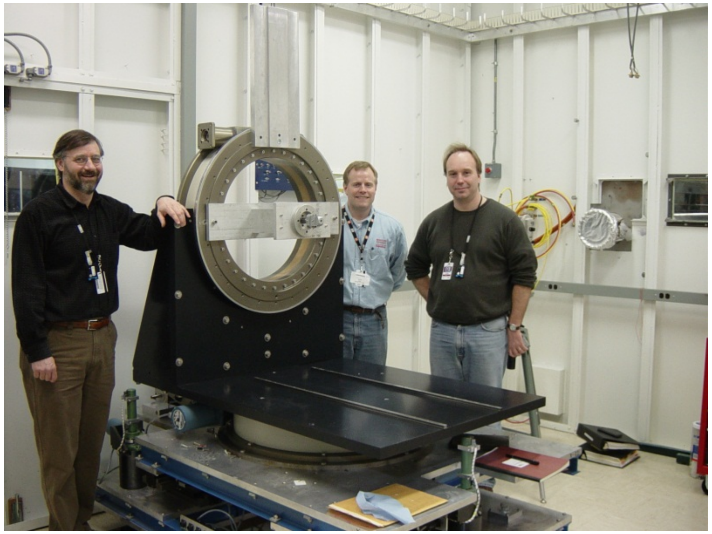
Facility for Real-Time Studies of Surface and Thin Film Growth Processes

NSLS insertion device beamline X21 back hutch

Experimental conditions can be optimized in ultra-high vacuum (UHV) chambers at the home laboratory …



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



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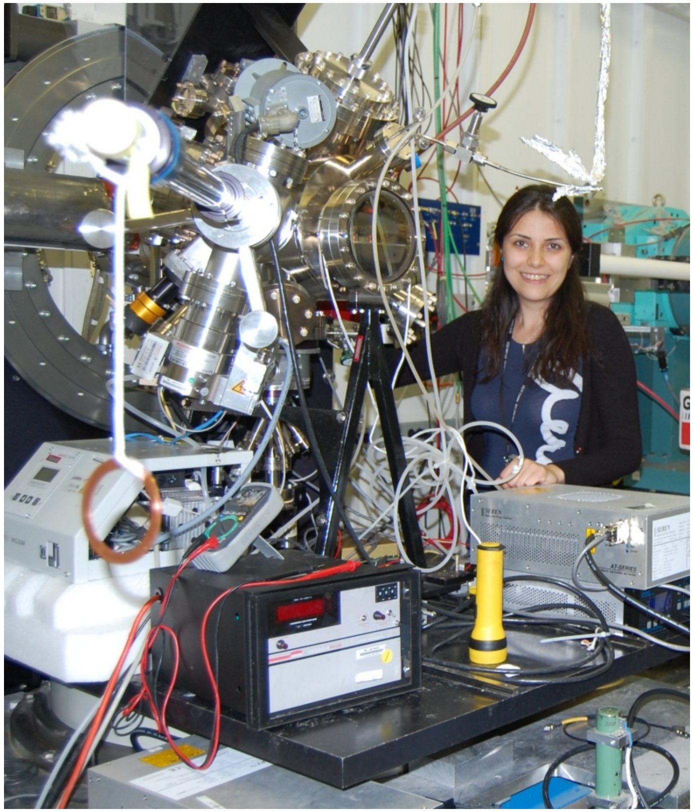
Surface Modification and Characterization Instrumentation

System installed on base diffractometer with UHV chamber, surface modification and characterization equipment



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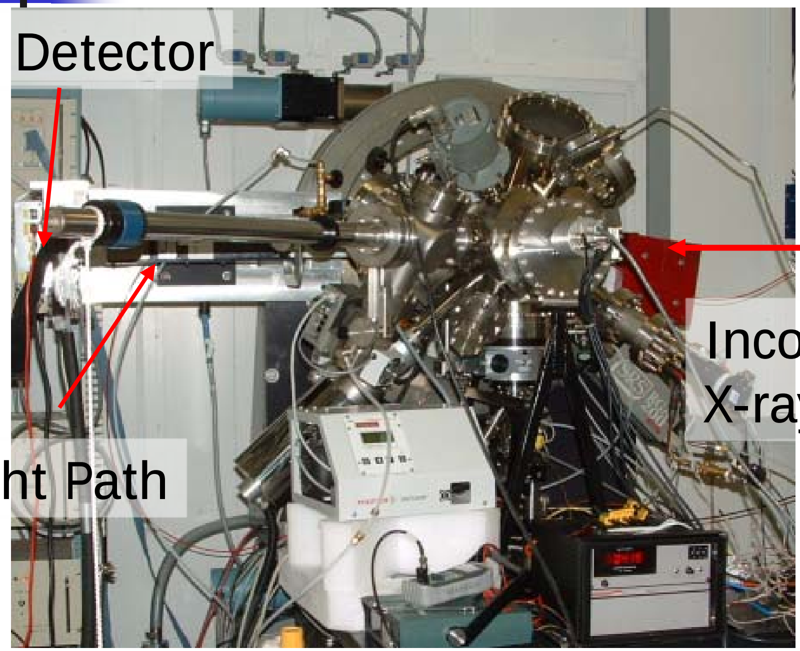
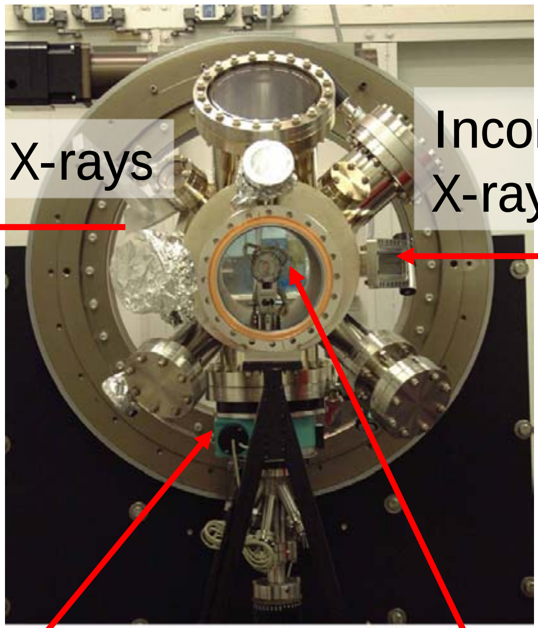
Facility for Real-Time X-ray Studies of Thin Film and Surface Processes

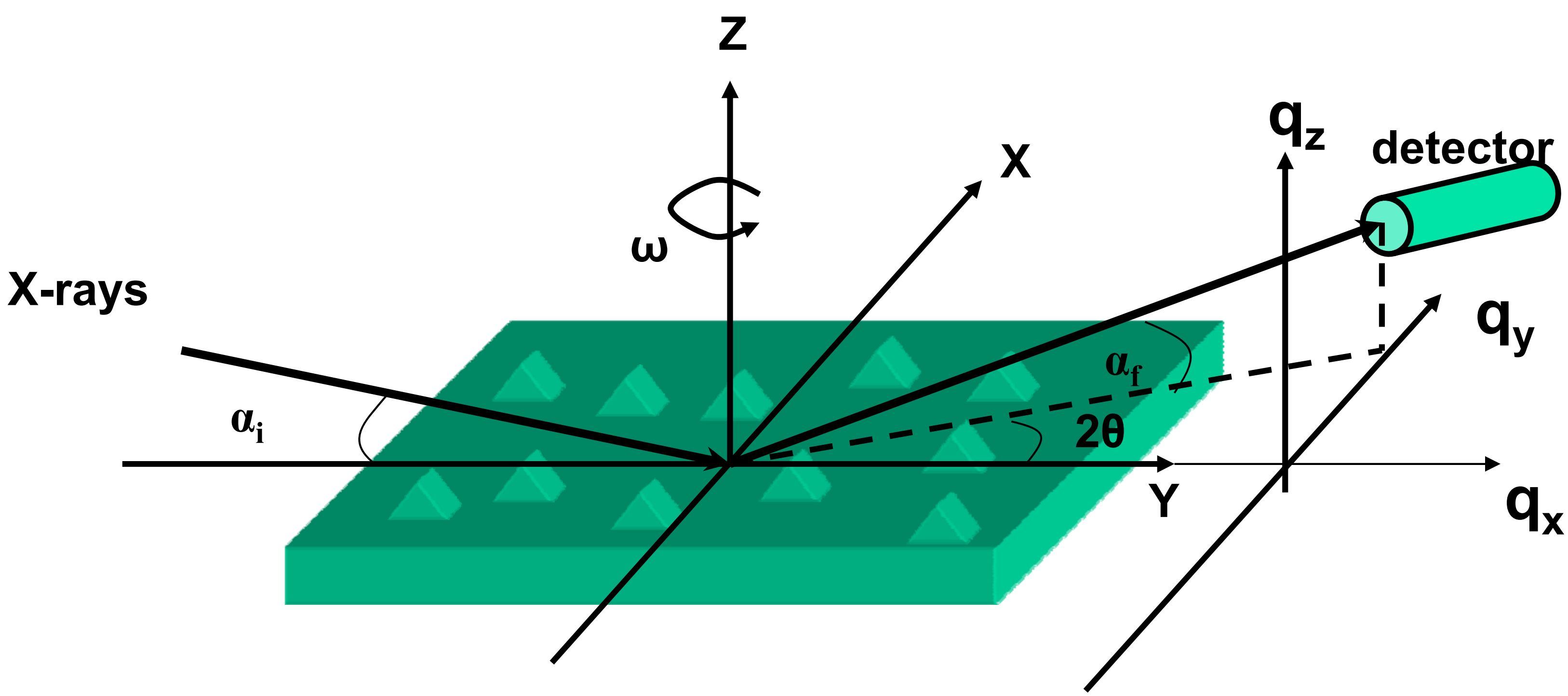
National Synchrotron Light Source (NSLS) – X21
Brookhaven National Laboratory





Physical Electronics PHI ion gun
~ 2 x 10^{12} ions/cm^{2}s

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



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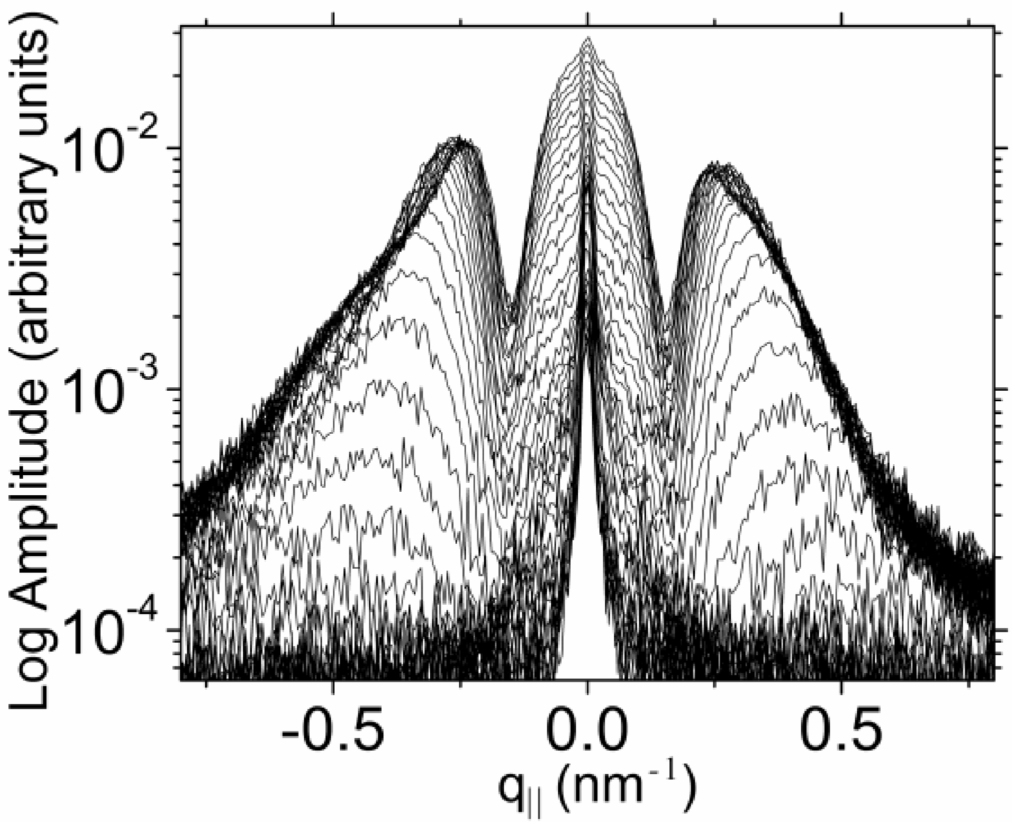
Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)



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BU Research Program

- Spontaneous Nano-Patterning of Surfaces during Ion Bombardment
  – Aziz group (Harvard)

- III-V Nitride Semiconductor Growth (lasers, detectors, solar cells)
  – T. Moustakas (BU), O. Malis (Purdue)

- Solid Oxide Fuel Cell (SOFC) Cathodes
  – S. Basu, S. Gopalan, U. Pal (BU)

- Fundamental Processes in Thin Film Growth
  – Headrick group (UVM)

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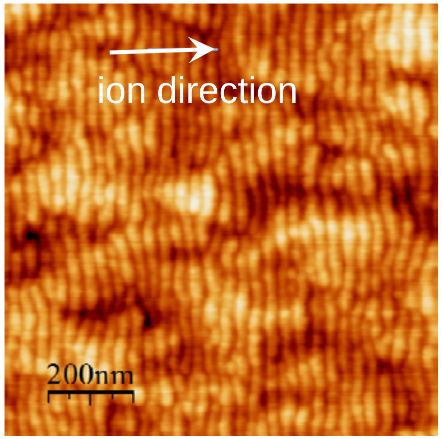
Spontaneous Nanopatterning of Semiconductor Surfaces by Ion Bombardment

Off-Axis Bombardment –

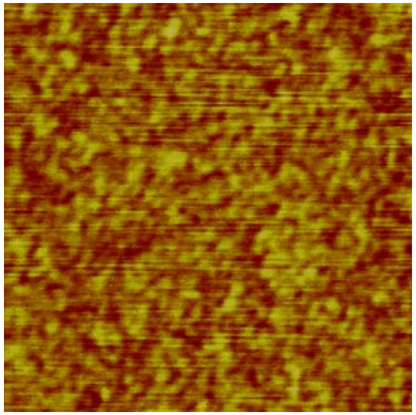
Ripples:



Si(100)

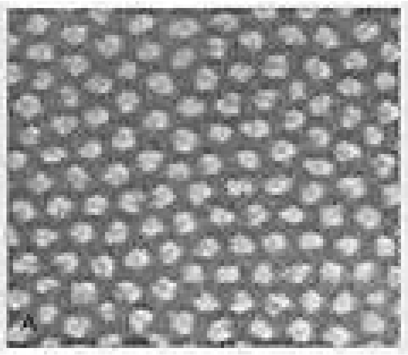
Normal Incidence Bombardment–

Smoothening:



Si(100)

Dots:

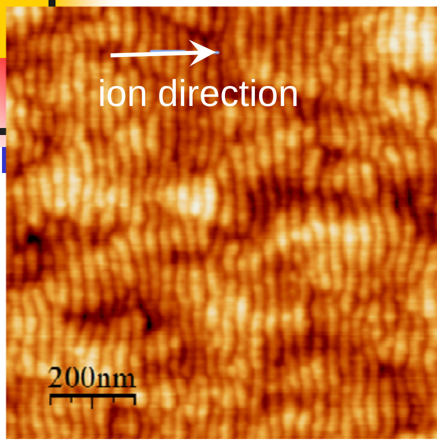


GaSb (100)

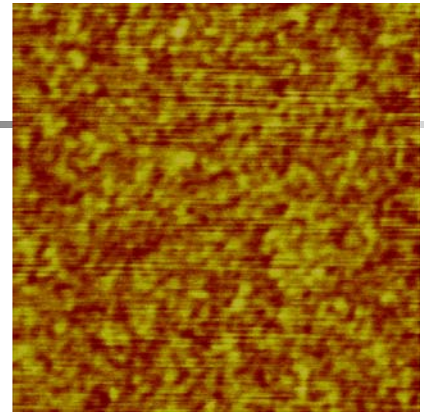
Facsko *et al*., Science **285**, 1551 (1999)

Off-Axis Bombardment – Normal Incidence Bombardment–

Ripples: Smoothening: Dots:



Si(100)



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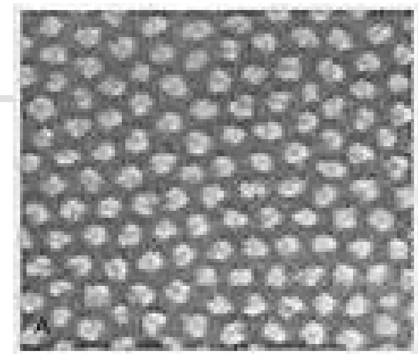


GaSb (100)

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

Importance of understanding patterning during bombardment:

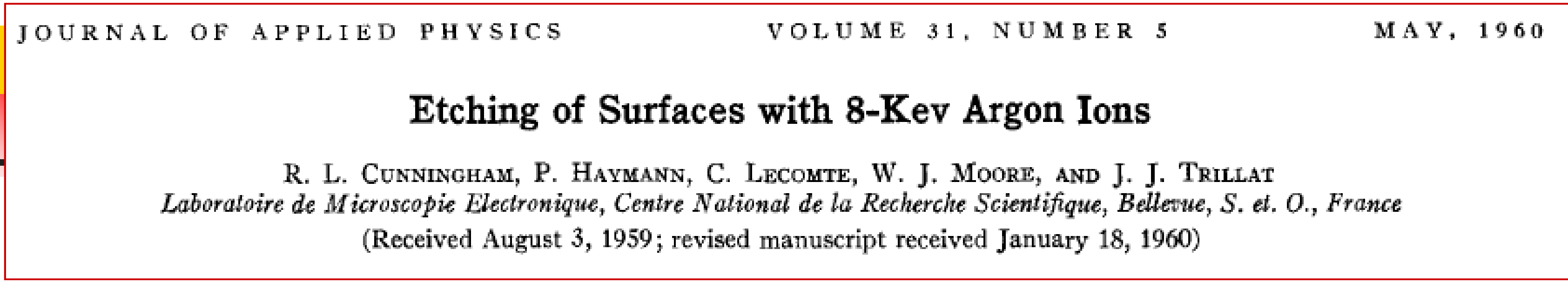
- Hyperthermal bombardment is a ubiquitous technological process (e.g. sputter deposition, ion-assisted deposition, PLD, sputter cleaning, plasma etching)

- Potential route for inexpensive nanopatterning of surfaces

Fundamental questions:

- What physical processes cause nanopattern formation?
- How can we control it?

Formation of ripple structures on surfaces during ion bombardment reported as early as 1960:


JOURNAL OF APPLIED PHYSICS VOLUME 31, NUMBER 5 MAY, 1960

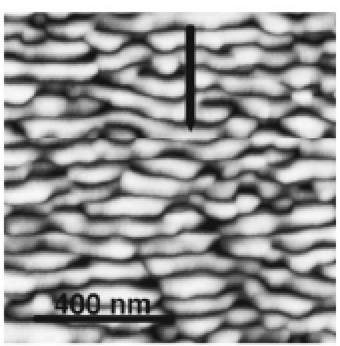
Etching of Surfaces with 8-Kev Argon Ions

R. L. CUNNINGHAM, P. HAYMANN, C. LECOMTE, W. J. MOORE, AND J. J. TRILLAT
Laboratoire de Microscopie Electronique, Centre National de la Recherche Scientifique, Bellevue, S. et. O., France
(Received August 3, 1959; revised manuscript received January 18, 1960)

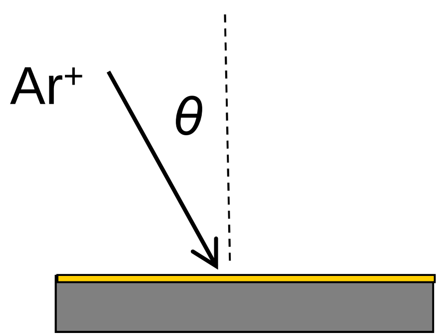
Key early observations:

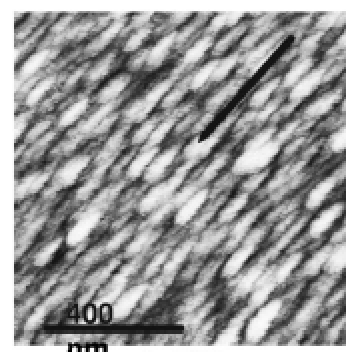
- Semiconductor surfaces are amorphized by ion bombardment at RT
- Wavelengths can be much longer than penetration depths of ions

- At low bombardment angles, ripple wavevector parallel to projected direction of ion beam
- At high bombardment angles, ripple wavevector perpendicular to projected direction of ion beam



θ=30°





θ=70°

5 keV Xe+ on graphite: Habenicht *et al*. PRB **60**, R2200 (1999).

Theoretical treatment of Sputter Erosion – 1973:

JOURNAL OF MATERIALS SCIENCE 8 (1973) 1545–1553

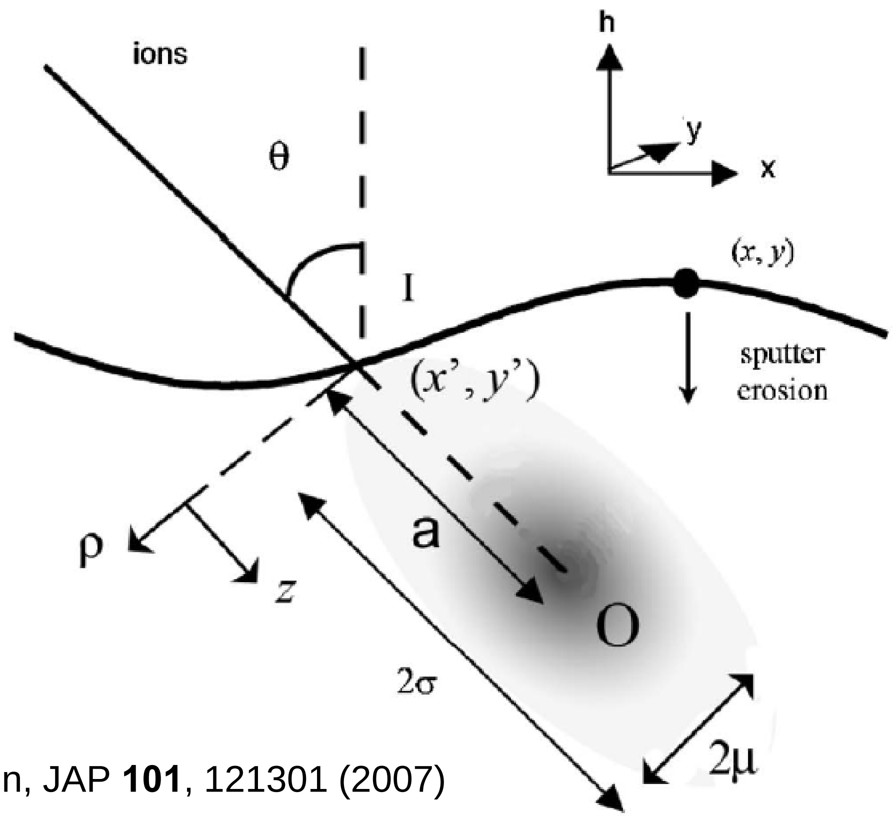
A mechanism of surface micro-roughening by ion bombardment

PETER SIGMUND
H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Model of sputter erosion process:

• Energy deposited by incident ion assumed to be a Gaussian ellipsoid

• Sputter rate from a given point on the surface assumed to be proportional to energy deposited there



Chan and Chason, JAP **101**, 121301 (2007)

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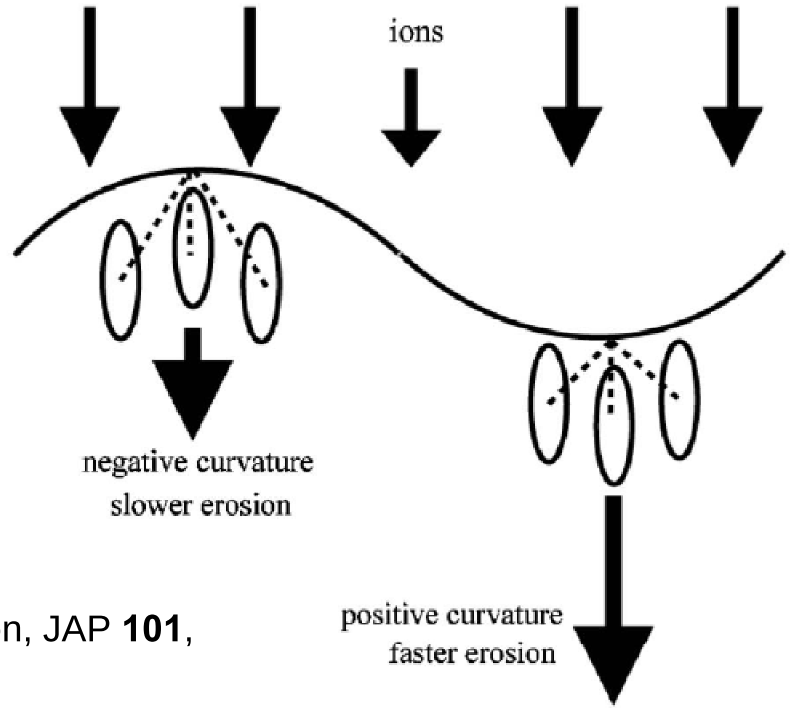
→ Surface Instability to Ion Bombardment due to curvature-dependent sputter erosion rate



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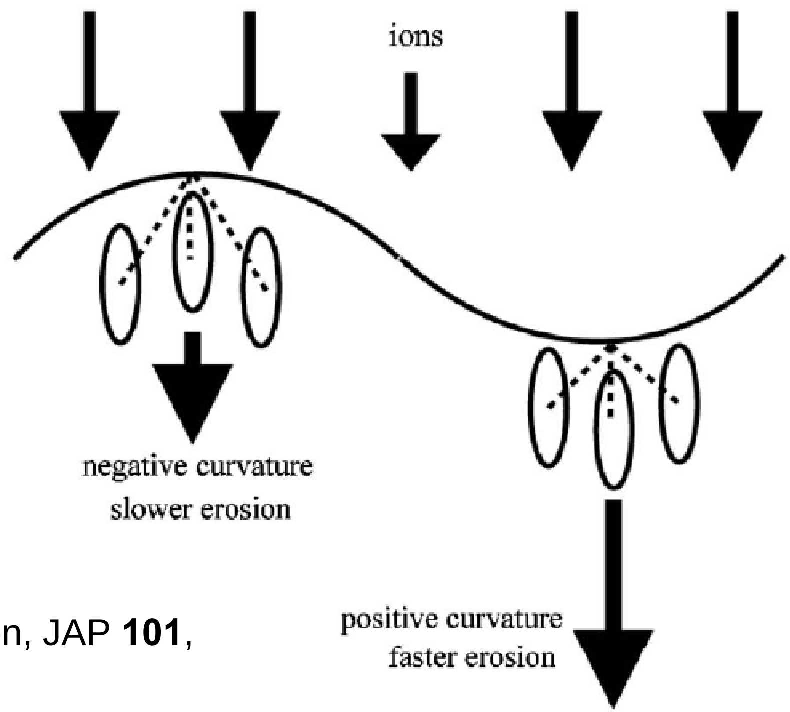

Chan and Chason, JAP **101**, 121301 (2007)

Key Questions Not Addressed by Sigmund Mechanism:

- What determines ripple wavelength?
- Why determines ripple orientation?

These are potentially answered by the

Bradley-Harper Model – primary paradigm for last 20 years:

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

2390 J. Vac. Sci. Technol. A 6 (4), Jul/Aug 1988

Calculate local surface height evolution from Sigmund model to first order in (*ion penetration depth/surface radius of curvature*):

$$\frac{\partial h(\vec{r},t)}{\partial t} = -v_0 + \Gamma \frac{\partial h}{\partial x} + \frac{1}{2} S_x \frac{\partial^2 h}{\partial x^2} + \frac{1}{2} S_y \frac{\partial^2 h}{\partial y^2}$$

Average sputter erosion rate

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Average sputter erosion rate

Slope-dependent erosion rate causes motion of ripples across surface

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$$\frac{\partial h(\vec{r},t)}{\partial t} = \underbrace{-v_0}_{\text{Average sputter erosion rate}} + \underbrace{\Gamma \frac{\partial h}{\partial x}}_{\text{Slope-dependent erosion rate causes motion of ripples across surface}} + \underbrace{\frac{1}{2} S_x \frac{\partial^2 h}{\partial x^2} + \frac{1}{2} S_y \frac{\partial^2 h}{\partial y^2}}_{\text{Curvature-dependent erosion rate}}$$

Average sputter erosion rate

Slope-dependent erosion rate causes motion of ripples across surface

Curvature-dependent erosion rate

$$\frac{\partial h(\vec{r},t)}{\partial t} = \frac{1}{2} S_x \frac{\partial^2 h}{\partial x^2} + \frac{1}{2} S_y \frac{\partial^2 h}{\partial y^2} - \frac{1}{2} B \nabla^4 h$$

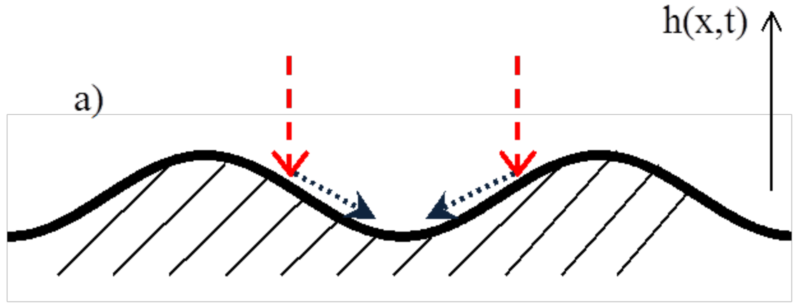
Bradley-Harper: Add relaxation at short length-scales due to diffusion or viscous flow

Stability or instability of surface for a ripple of a given wavelength is determined by tradeoff between curvature-dependent erosion rate and surface smoothening by diffusion/viscous flow

PHYSICAL REVIEW B VOLUME 54, NUMBER 24 15 DECEMBER 1996-II

Roughening and ripple instabilities on ion-bombarded Si

G. Carter and V. Vishnyakov
Department of Electronic and Electrical Engineering, University of Salford, M5 4WT United Kingdom
(Received 29 July 1996)



- Lateral mass redistribution (CV) effect smoothens at low incidence angles
- Magnitude proportional to cos(2θ)

$$\frac{\partial h}{\partial t} = -\nabla \cdot \vec{j} \qquad \vec{j} \propto \nabla h$$

$$\Rightarrow \quad \frac{\partial h}{\partial t} = \alpha \nabla^2 h \rightarrow q^2$$

$$h(x,t) = A(t)\cos(\mathrm{qx}) \qquad q = \frac{2\pi}{\lambda}$$

More General Linear Theory Formalism

Linear theory growth or decay of local surface height fluctuations:

Curvature coefficients S_x and S_y can include both curvature-dependent Bradley-Harper erosion instability and stabilization due to lateral mass redistribution

$$\frac{\partial h}{\partial t} = \frac{1}{2} S_x \partial_x^2 h + \frac{1}{2} S_y \partial_y^2 h - \frac{1}{2} B \nabla^4 h + \eta(x, y, t)$$

Uncorrelated Noise: $\langle \eta(x,y,t) \rangle = 0 \qquad \langle \eta(x,y,t)\eta(x',y',t') \rangle = n\delta(x-x')\delta(y-y')\delta(t-t')$

Ensemble-averaged height-height structure factor evolution:

$$I(q,t) = \langle h(q,t) h^*(q,t) \rangle = e^{R(q)t} I_0(q) + \frac{n}{-R(q)}\left[1 - e^{R(q)t}\right]$$

Amplification Factor: $R(q) = -\left(S_x q_x^2 + S_y q_y^2 + Bq^4\right)$

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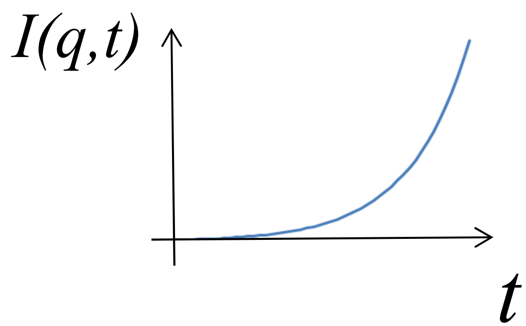
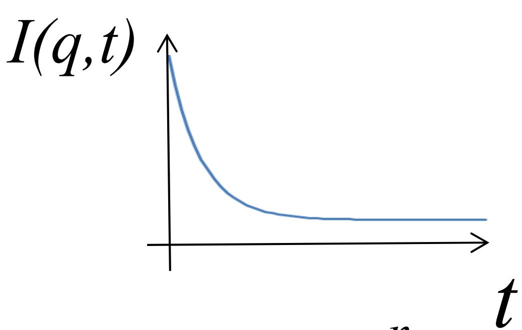
Linear Theory of Surface Stability/Instability: Amplification Factor

Amplification Factor: $R(q) = -\left(S_x q_x^2 + S_y q_y^2 + B q^4\right)$

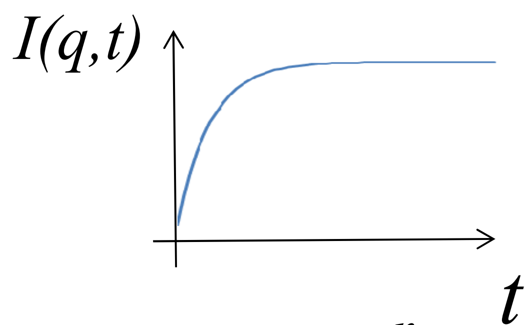
If $R(q) > 0$, surface is *unstable*:



If $R(q) < 0$, surface is *stable*:



$$S_0(q) > \frac{n}{R(q)}$$

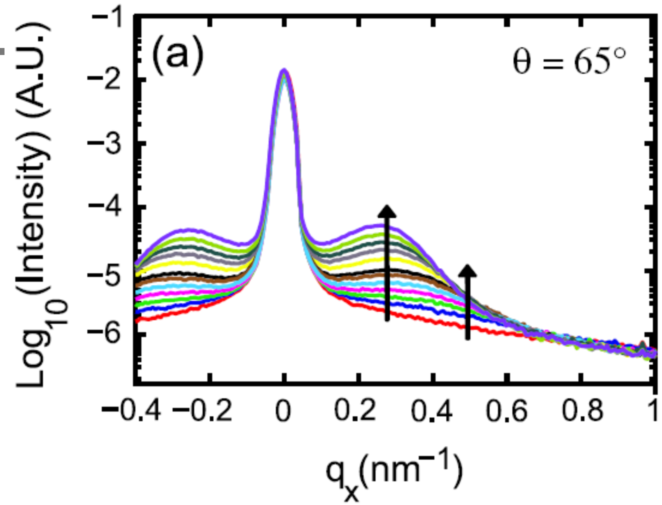


$$S_0(q) < \frac{n}{R(q)}$$

1 keV Ar^+ on Si: For each ion bombardment angle θ use real-time GISAXS to measure $I(q_{x,y}, t)$

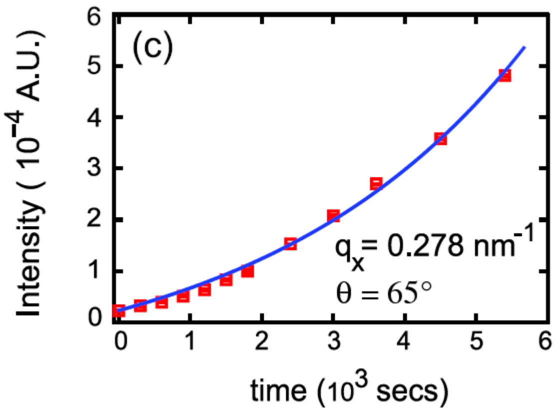
Madi, Anzenberg, Ludwig and Aziz, PRL **106**, 066101 (2011)

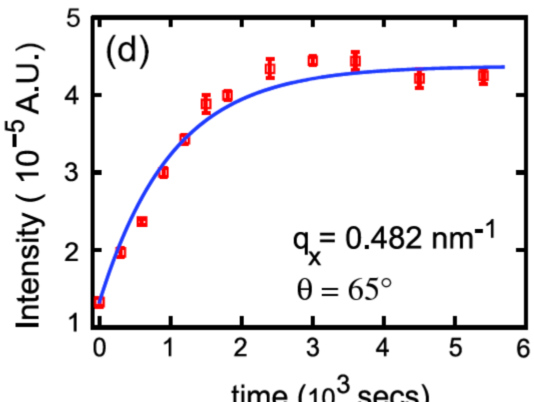
Anzenberg, Madi, Aziz and Ludwig, PRB **84**, 214108 (2011)

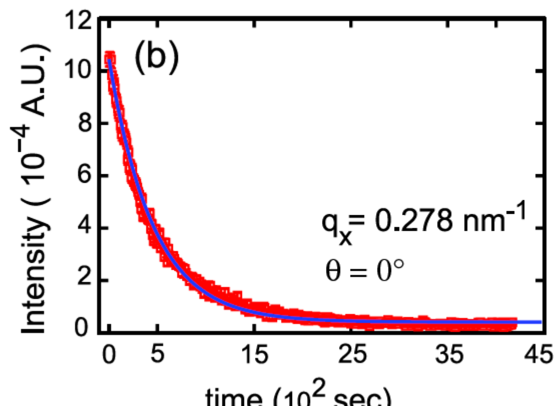


GISAXS evolution during 2 hours of 1 keV Ar^+ bombardment of Si (100)

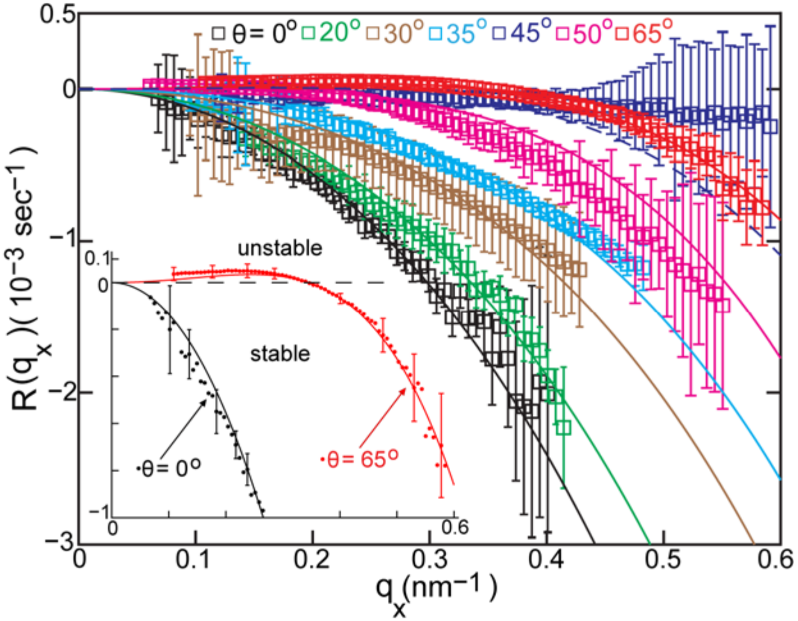
At each wavenumber, fit $I(q_{x,y}, t)$ to determine Amplification Factor $R(q_{x,y})$

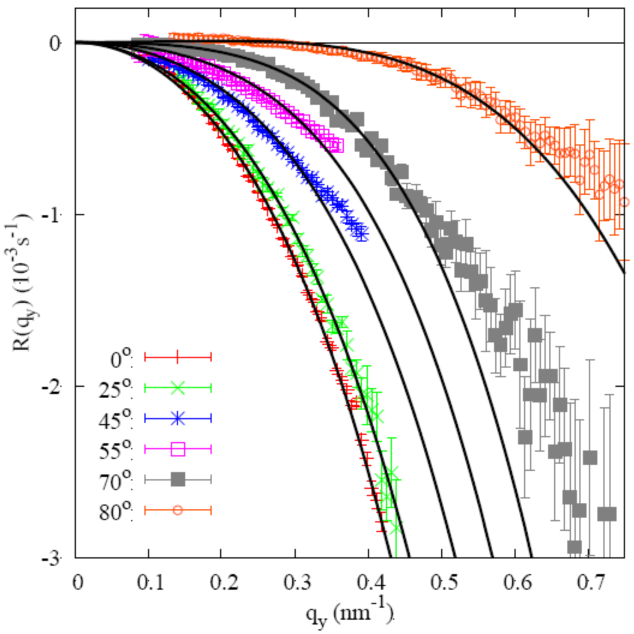






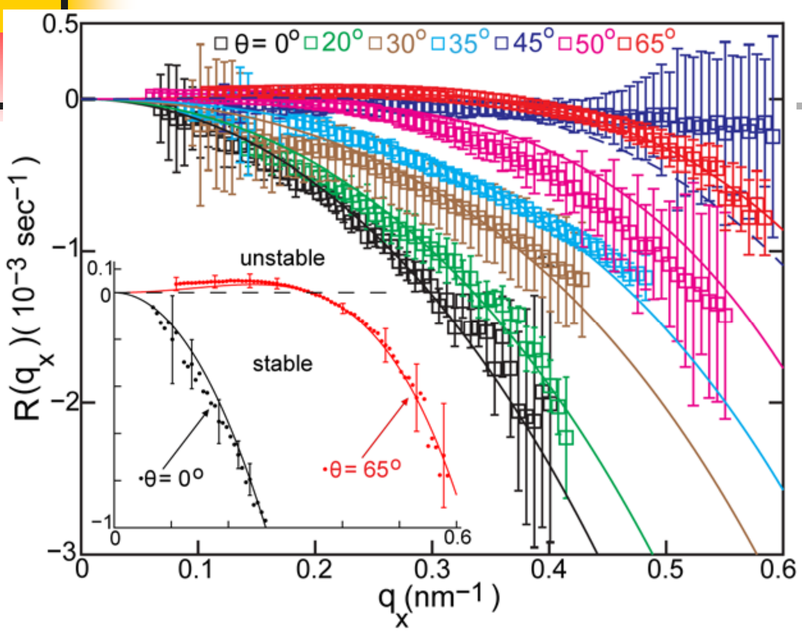
Measured Amplification Factor $R(q_{x,y})$ as a function of incident angle in *x*- and *y*-directions

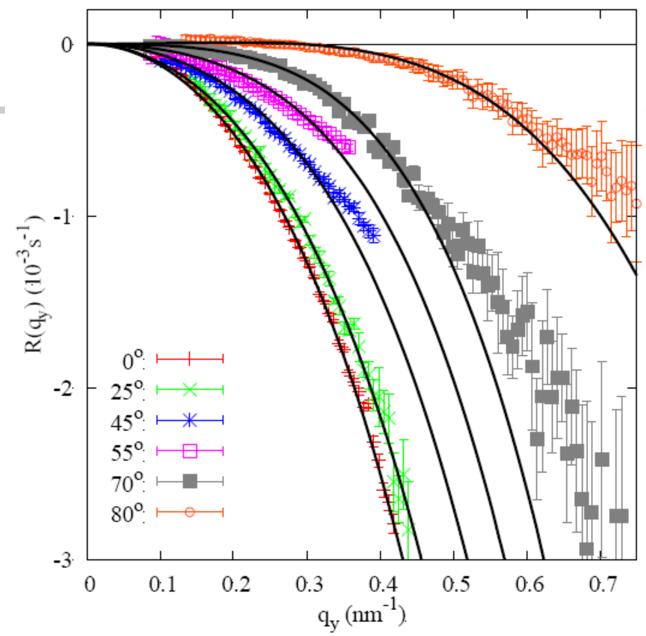




Transition from smoothening to ripple formation at ion bombardment angle *θ ~ 45°*.

Measured Amplification Factor *R(q)* as a function of incident angle in *x*- and *y*-directions





Simultaneously fit all $R(q_{x,y})$ to form:

$$R(q_x) = -(S_x(\theta)q_x^2 + Bq_x^4)$$
$$R(q_y) = -(S_y(\theta)q_y^2 + Bq_y^4)$$

to determine curvature coefficients $S_{x,y}(\theta)$

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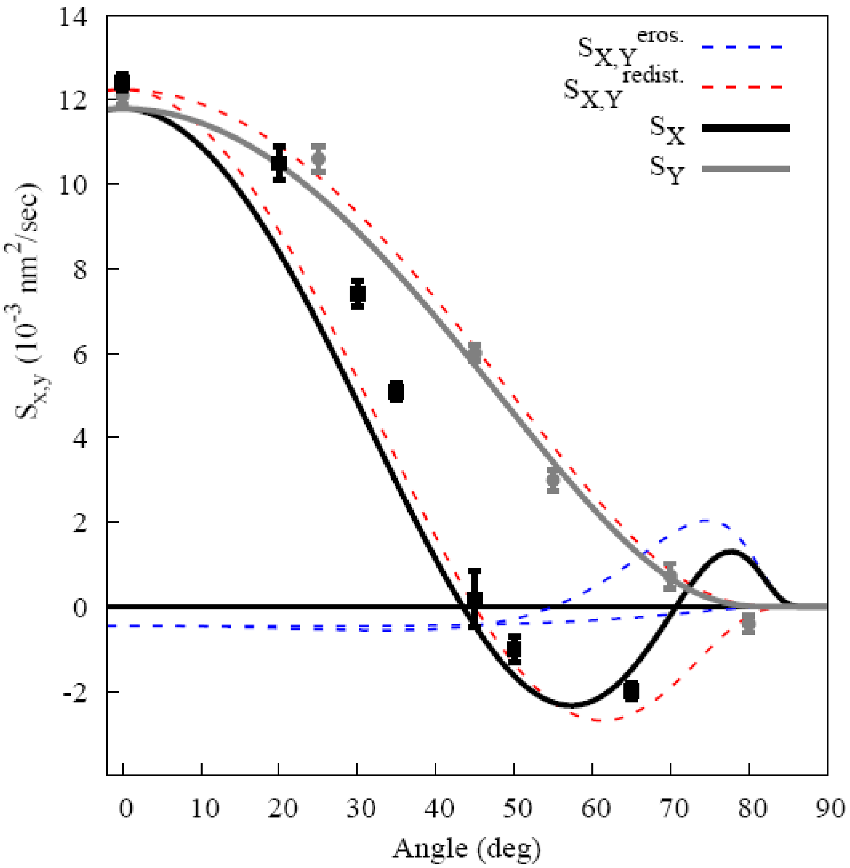
Angular Dependence of Curvature Coefficients $S_{x,y}(\theta)$



Fits show dominance of mass redistribution – both for smoothing at low angles and for creating ripples. Consistent also with simulations.

(Kalyanasundaram *et al*., APL 92, 131909 (2008); Norris *et al*., Nature Comm. 10.1038/ncomms1280 (2011))

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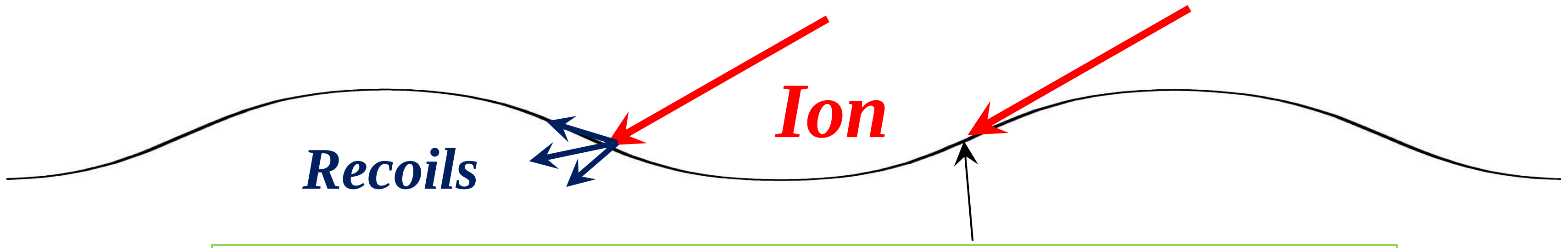
Data show dominance of Lateral Mass Redistribution through most of angular range

Above 45° ion incidence angle, roughening caused by ion momentum knocking surface atoms uphill !



Ions also knock atoms downhill when hitting downhill slope, but effective ion flux density is lower because of the slope…

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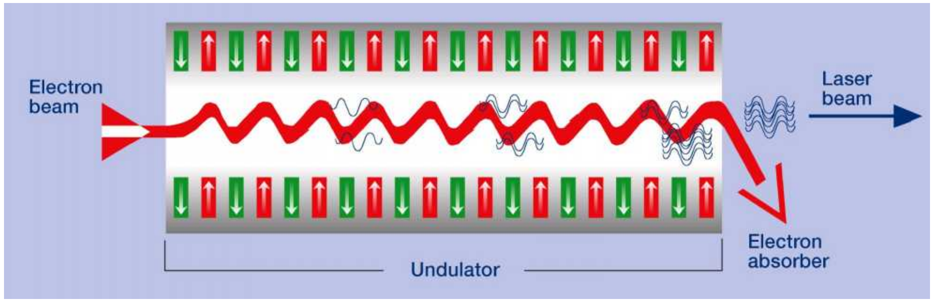
In these studies, structure evolution has been on seconds time scale. Can we use x-rays to look at much faster time scales (e.g. motion of atoms in liquids)?



X-ray Free-Electron Laser (XFEL)

Self Amplified Spontaneous Emission (SASE)

Femtosecond (10^{-15} s) x-ray laser pulses!

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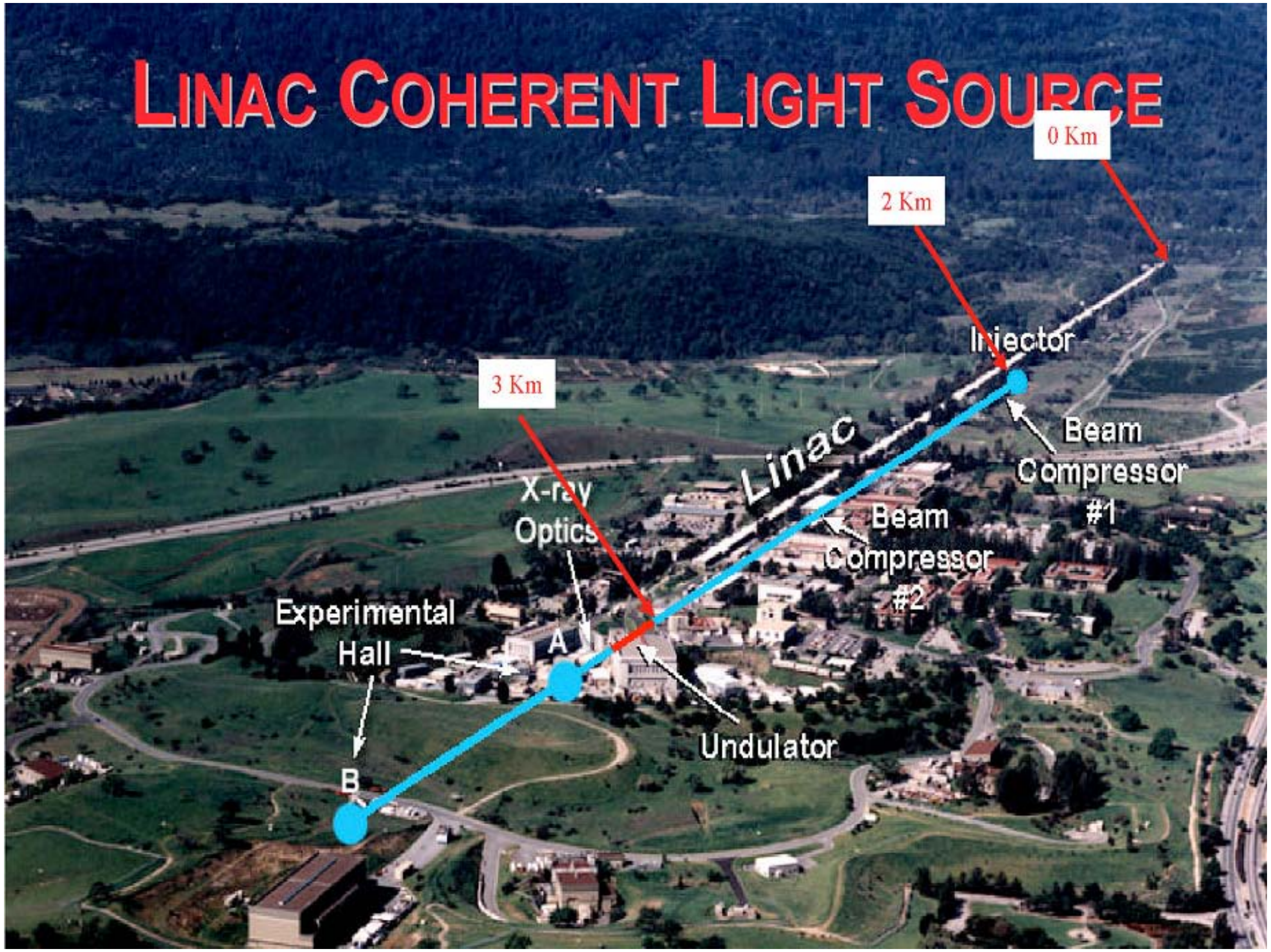
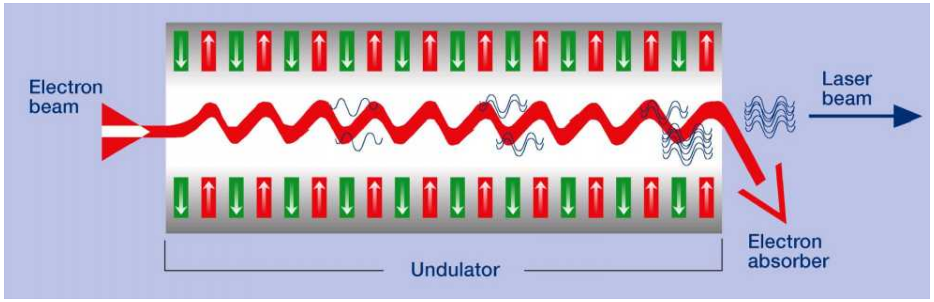
LCLS Linac Coherent Light Source

Stanford Linear Accelerator Center

Stanford Synchrotron Radiation Laboratory



X-ray Free-Electron Laser (XFEL)



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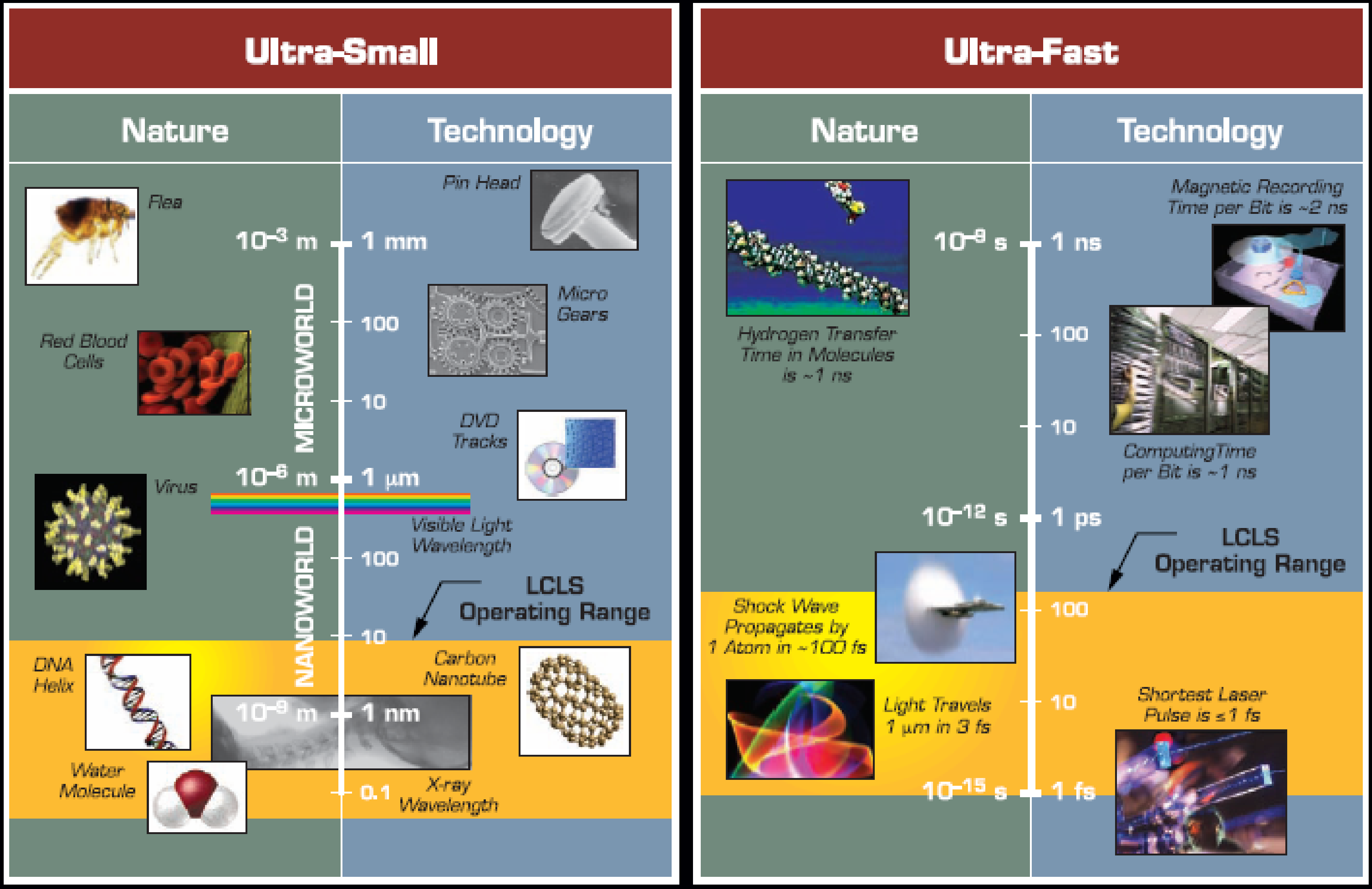
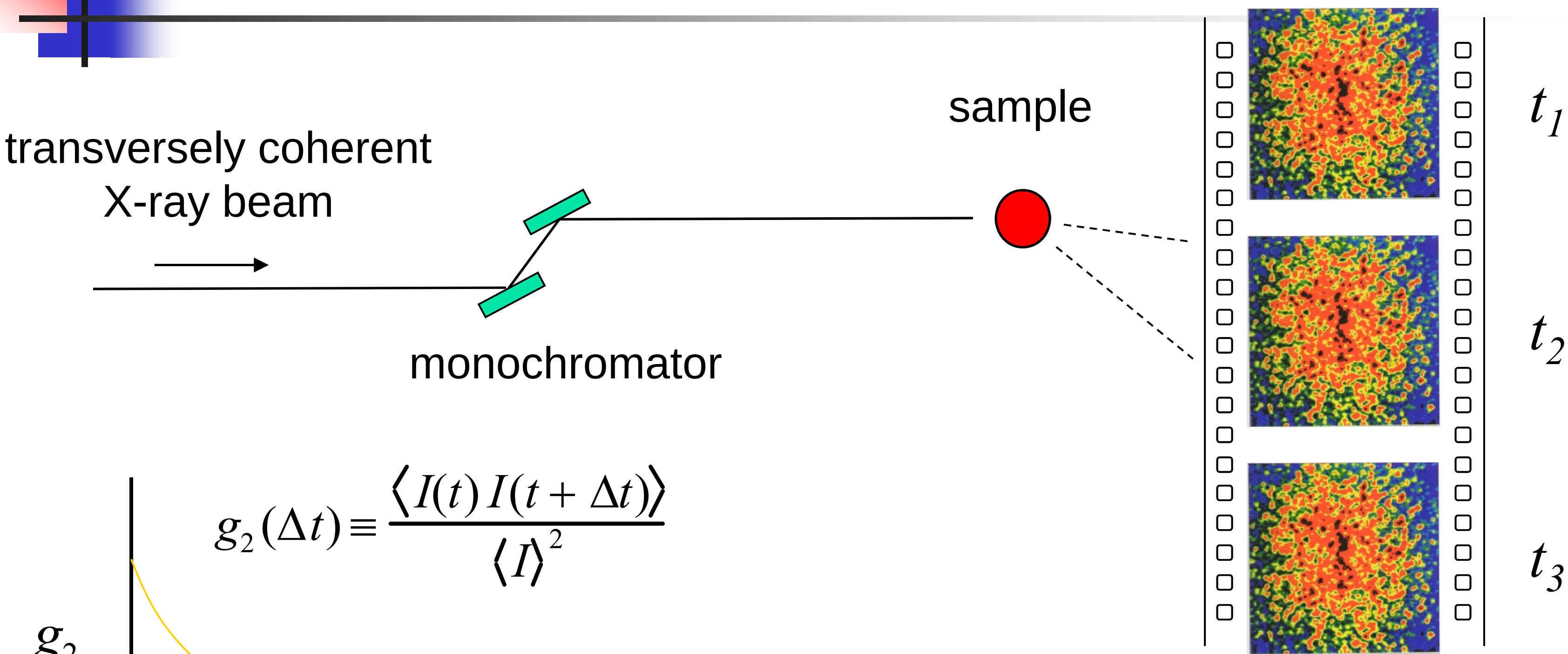

Ultra-Small
Nature
Technology
Flea
Pin Head
10^{-3} m
1 mm
MICROWORLD
100
Micro Gears
Red Blood Cells
10
DVD Tracks
10^{-6} m
1 µm
Virus
Visible Light Wavelength
NANOWORLD
100
LCLS Operating Range
10
DNA Helix
Carbon Nanotube
10^{-9} m
1 nm
Water Molecule
0.1
X-ray Wavelength
Ultra-Fast
Nature
Technology
Magnetic Recording Time per Bit is ~2 ns
10^{-9} s
1 ns
100
Hydrogen Transfer Time in Molecules is ~1 ns
10
ComputingTime per Bit is ~1 ns
10^{-12} s
1 ps
LCLS Operating Range
Shock Wave Propagates by 1 Atom in ~100 fs
100
10
Light Travels 1 µm in 3 fs
Shortest Laser Pulse is ≤1 fs
10^{-15} s
1 fs

X-ray Photon Correlation Spectroscopy (XPCS)

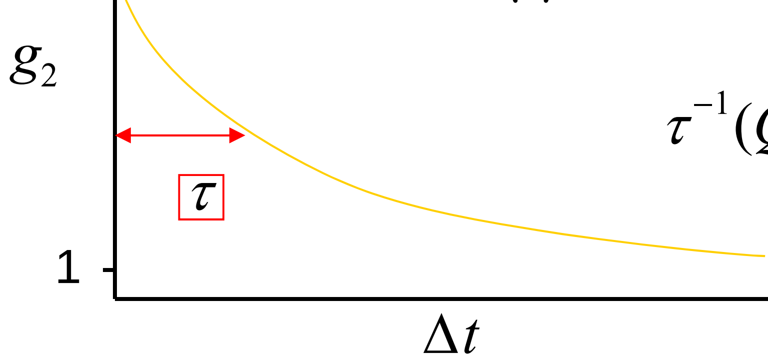
Study evolution of x-ray scattering “speckle” pattern to learn about motion of atoms, molecules



“movie” of speckle recorded by CCD

$$I(Q,t)$$

$$g_2(\Delta t) \equiv \frac{\langle I(t)\, I(t+\Delta t)\rangle}{\langle I\rangle^2}$$



$$\tau^{-1}(Q) = Rate(Q)$$

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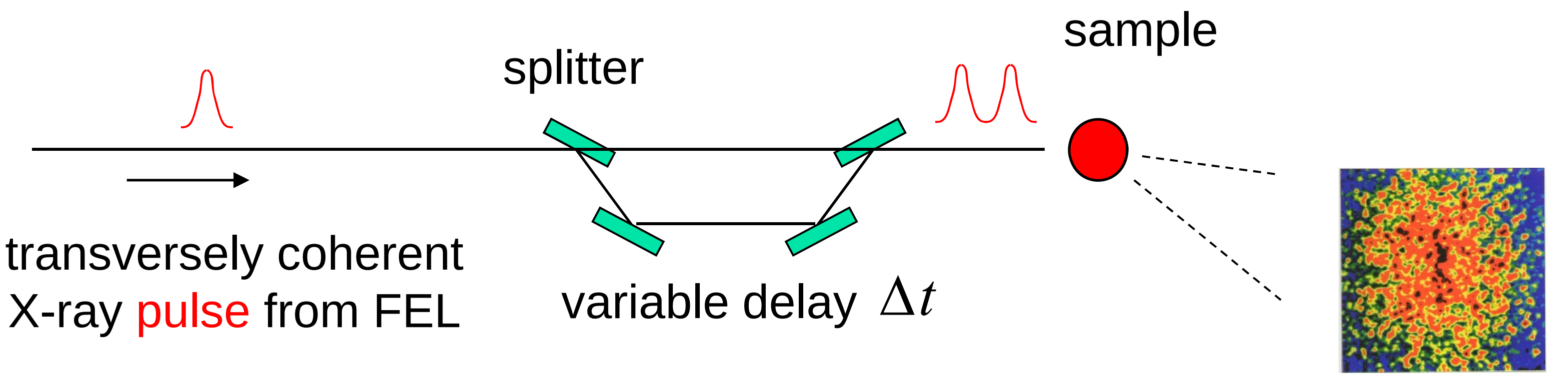
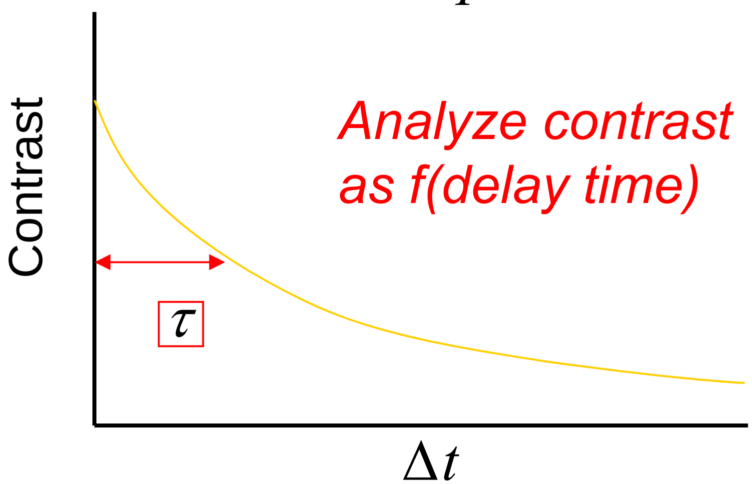
XPCS at LCLS using “Split Pulse” Mode

Femtoseconds to nanoseconds time resolution
Uses high *peak* brilliance



$$10\,ps \Leftrightarrow 3\,mm$$

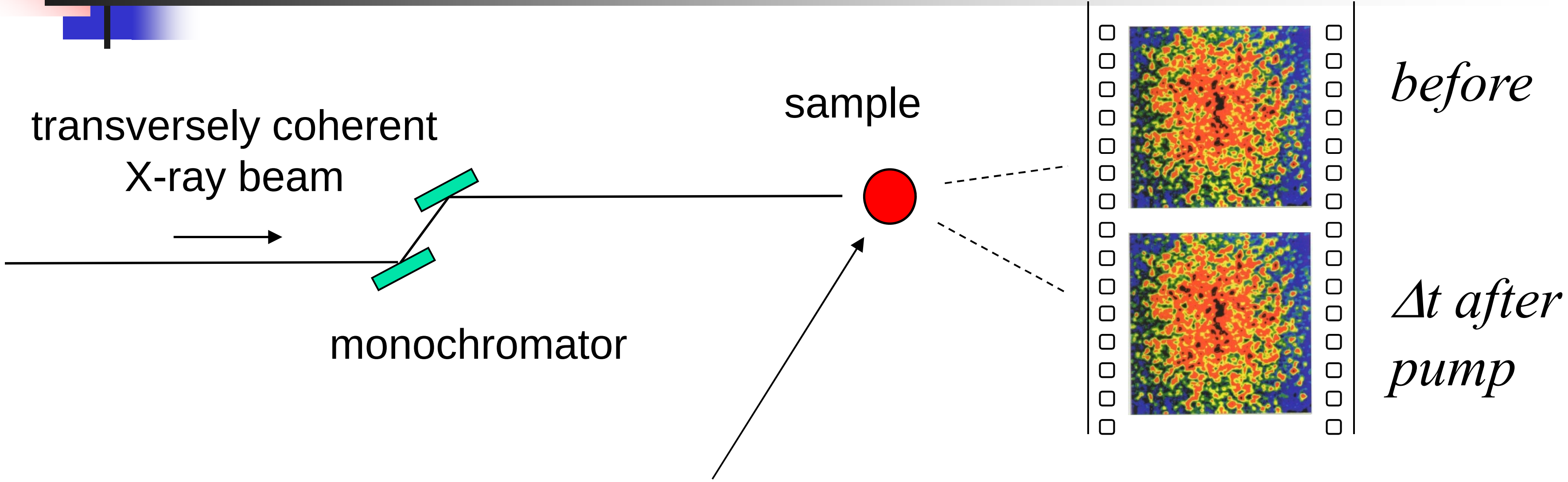


sum of speckle patterns
from prompt and delayed pulses
recorded on CCD

$$I(Q,\Delta t)$$

XPCS of Non-Equilibrium Dynamics using 'Pumped' Mode

- Femtoseconds to seconds time resolution
- Uses high *peak* brilliance



Pump sample e.g. with
laser, electric,
magnetic pulse

Correlate a speckle
pattern from before
pump to one at some
Δt after pump

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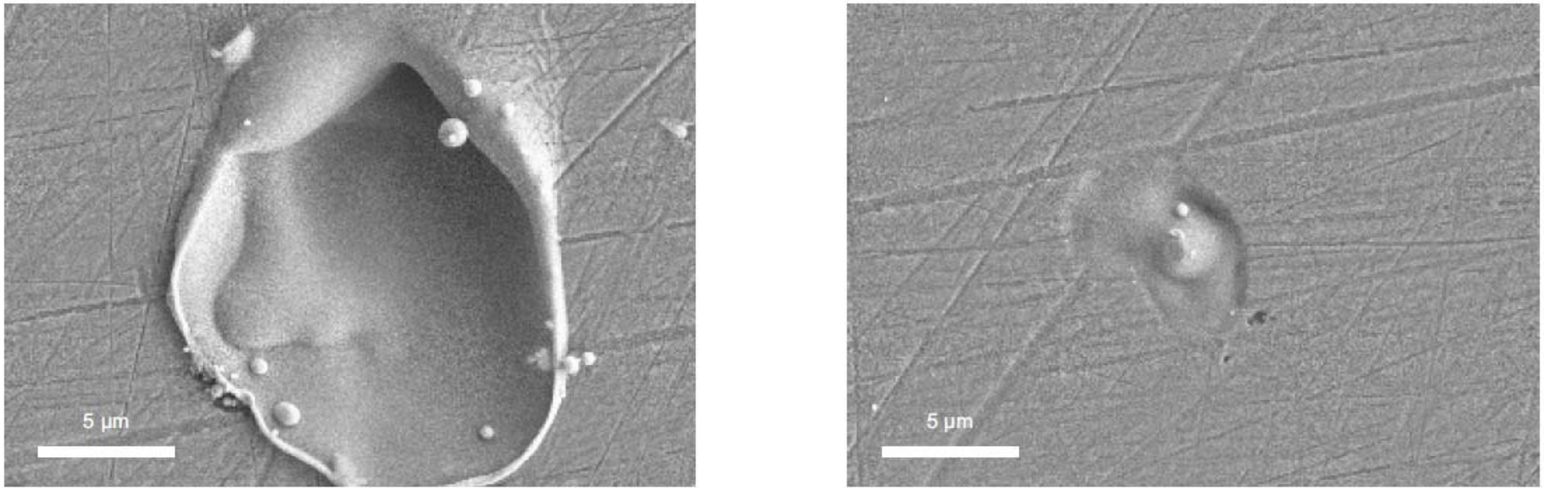
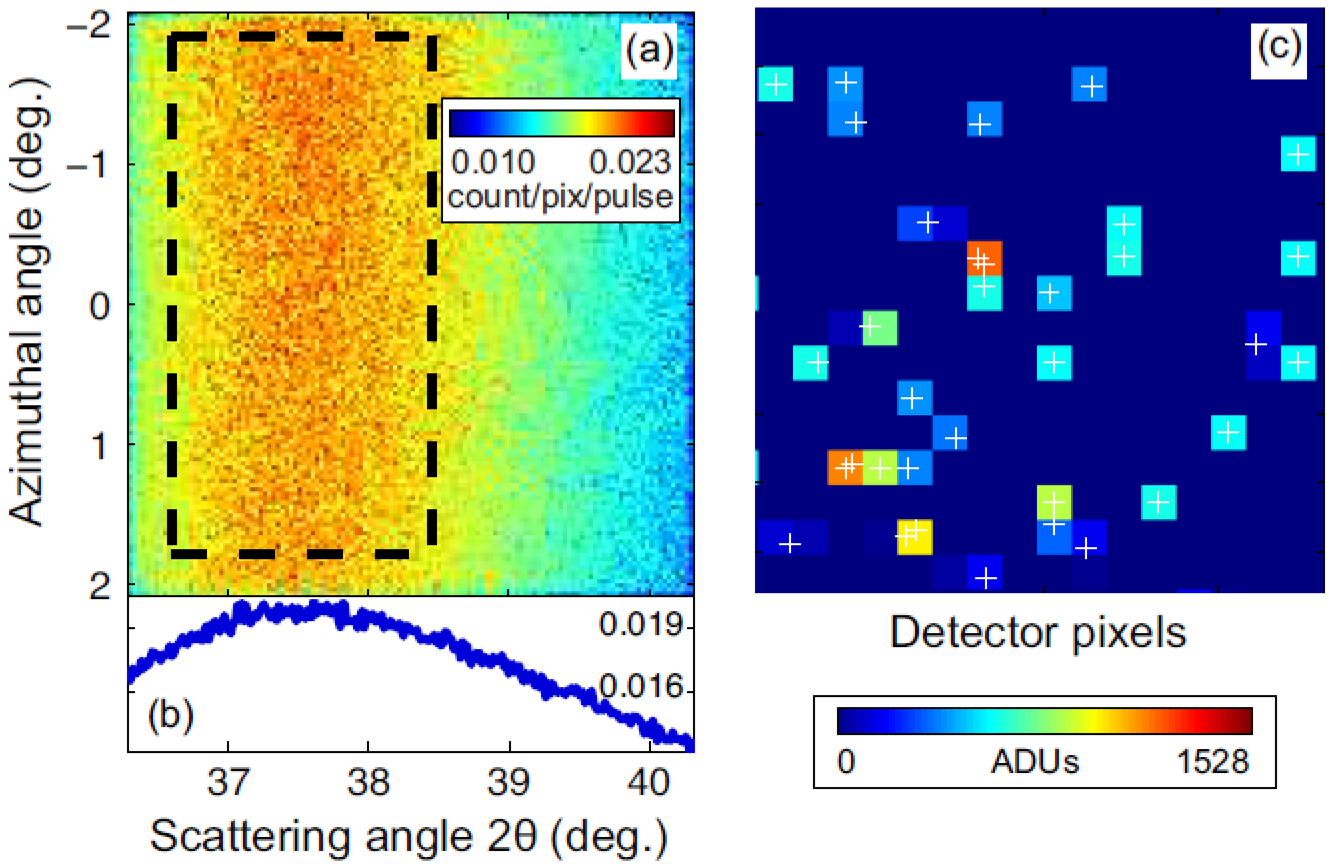
Key Problem:

High peak x-ray beam intensity can damage sample (e.g. vaporize it!)



Damage to Ni-Pd-P samples by single pulse of LCLS x-ray beam

First Experiments Show Success is Possible



X-ray scattering from liquid Gallium

Conclusions

- Goal of condensed matter physics research is to understand how materials behave and how new materials or material structures can be developed to meet societal needs
- The behavior of materials depends on the atomic structure and evolution
- X-ray scattering is a uniquely powerful tool for determining atomic structure (both static and evolving)
- Available x-ray intensities have been increasing dramatically due to development of new sources (synchrotrons, FEL's)
- X-ray scattering can give crucial information enabling us to understand and control materials behavior

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