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?

$\lambda \sim 10^{-10} \text{ m} \sim$ distance between atoms
X-ray Scattering (Diffraction)

The momentum transfer to an elastically scattered photon is:

\[ p = \hbar k = \hbar \frac{2\pi}{\lambda} \]

\[ \Delta \vec{p} = \hbar \Delta \vec{k} = \hbar \vec{q} \]

\[ q = \frac{4\pi \sin \theta}{\lambda} \]
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!
National Synchrotron Light Source (NSLS) and NSLS-II
Brookhaven National Laboratory
(Long Island)
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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
Surface Modification and Characterization
Instrumentation

System installed on base diffractometer with UHV chamber, surface modification and characterization equipment
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
~ $2 \times 10^{12}$ ions/cm$^2$s
Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)
Grazing-Incidence Small-Angle X-ray Scattering (GISAXS)
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

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

Normal Incidence Bombardment – Smoothening:

Dots:

Si(100)  Si(100)  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:

**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

5 keV Xe+ on graphite: Habenicht et al. PRB 60, R2200 (1999).
Theoretical treatment of Sputter Erosion – 1973:

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)
Theoretical treatment of Sputter Erosion – 1973:

**A mechanism of surface micro-roughening by ion bombardment**

**PETER SIGMUND**

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

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

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

Key Questions Not Addressed by Sigmund Mechanism:
- What determines ripple wavelength?
- Why determines ripple orientation?

Chan and Chason, JAP 101, 121301 (2007)
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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\]

- **Average sputter erosion rate**
- **Slope-dependent erosion rate causes motion of ripples across surface**
- **Curvature-dependent erosion rate**
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.
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 $\cos(2\theta)$

\[
\frac{\partial h}{\partial t} = -\nabla \cdot \vec{j} \quad \Rightarrow \quad \frac{\partial h}{\partial t} = \alpha \nabla^2 h \rightarrow q^2
\]

\[
\vec{j} \propto \nabla h
\]

\[
h(x, t) = A(t)\cos(qx) \quad q = \frac{2\pi}{\lambda}
\]
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

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

Uncorrelated Noise:

\[
\langle \eta(x, y, t) \rangle = 0 \quad \langle \eta(x, y, t) \eta(x', y', t') \rangle = n \delta(x - x') \delta(y - y') \delta(t - t')
\]

Ensemble-averaged height-height structure factor evolution:

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

Amplification Factor:

\[
R(q) = -\left(S_x q_x^2 + S_y q_y^2 + B q^4 \right)
\]
Linear Theory of Surface Stability/Instability: Amplification Factor

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

If \( R(q) > 0 \), surface is unstable: \( I(q,t) \uparrow \)

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

\( S_0(q) > \frac{n}{R(q)} \)
At each wavenumber, fit $I(q_{x,y},t)$ to determine Amplification Factor $R(q_{x,y})$.

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

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

Anzenberg, Madi, Aziz and Ludwig, PRB 84, 214108 (2011)
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 $\theta \sim 45^\circ$. 
**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 $S_{x,y}(\theta)$
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))
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…
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} \text{s}) x-ray laser pulses!
X-ray Free-Electron Laser (XFEL)
## Ultra-Small

<table>
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<tr>
<th>Nature</th>
<th>Technology</th>
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</thead>
<tbody>
<tr>
<td>Flea</td>
<td>Pin Head</td>
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<tr>
<td>Red Blood Cells</td>
<td>Micro Gears</td>
</tr>
<tr>
<td>Virus</td>
<td>DVD Tracks</td>
</tr>
</tbody>
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**Dimensions:**
- $10^{-3}$ m to 1 mm
- $10^{-8}$ m to 1 μm
- $10^{-9}$ s to 1 ns
- $10^{-12}$ s to 1 ps

### Nanoworld
- DNA Helix
- Water Molecule
- Carbon Nanotube
- X-ray Wavelength

### Microworld
- LCLS Operating Range
- Hydrogen Transfer Time in Molecules is ~1 ns
- Computing Time per Bit is ~2 ns

### Operating Range
- Shock Wave Propagates by 1 Atom in ~100 fs
- Light Travels 1 μm in 3 fs
- Shortest Laser Pulse is ≤1 fs

## Ultra-Fast
X-ray Photon Correlation Spectroscopy (XPCS)

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

transversely coherent X-ray beam

monochromator

sample

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

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

“movie” of speckle recorded by CCD

$I(Q,t)$
XPCS at LCLS using “Split Pulse” Mode

Femtoseconds to nanoseconds time resolution
Uses high peak brilliance

transversely coherent X-ray pulse from FEL

variable delay $\Delta t$

splitter

sample

$10 \text{ ps} \Leftrightarrow 3 \text{ mm}$

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

$I(Q, \Delta t)$

Contrast as $f$ (delay time)

$\tau$
XPCS of Non-Equilibrium Dynamics using ‘Pumped’ Mode

- Femtoseconds to seconds time resolution
- Uses high peak brilliance

transversely coherent X-ray beam

monochromator

Correlate a speckle pattern from before pump to one at some $\Delta t$ after pump

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

before

$\Delta t$ after pump
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