Combined X-ray scattering and spectroscopy techniques

Gives element specific structural information

X-ray resonance scattering = X-ray scattering + X-ray Absorption Near-Edge Spectroscopy (XANES)

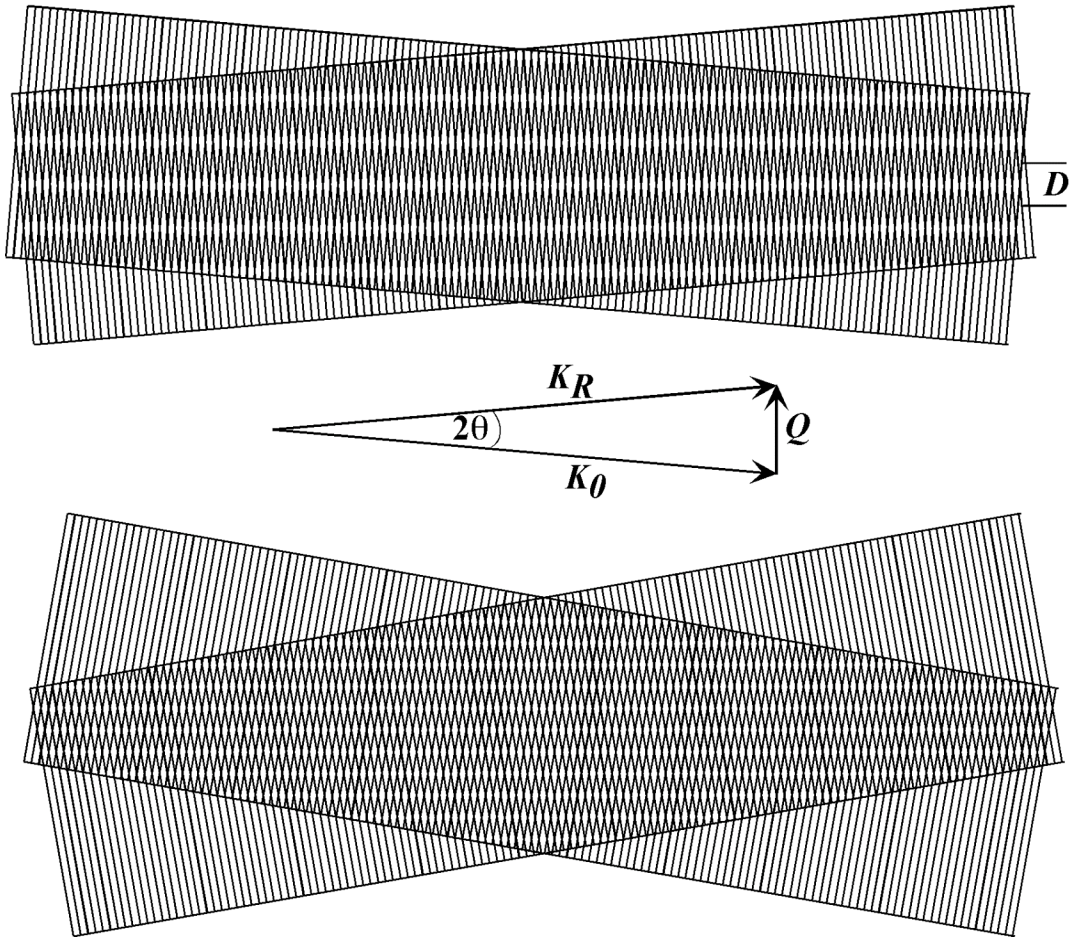
X-ray standing waves (XSW) = single xtal Bragg diffraction + XRF

Long-Period XSW = XRR + XRF

X-ray Standing Wave Fundamentals

Superposition of 2 Plane-Waves

$$\mathbf{E}_T = \mathbf{E}_0\, e^{i(\mathbf{k}_0 \bullet \mathbf{r} - \omega t)} + \mathbf{E}_R\, e^{i(\mathbf{k}_R \bullet \mathbf{r} - \omega t)}$$



SW Intensity:

$$I = \left|\mathbf{E}_T\right|^2$$
$$= I_0 + I_R + 2\sqrt{I_0 I_R}\,\cos(v - Qz)$$

SW Period:

$$D = \frac{2\pi}{Q} = \frac{\lambda}{2\sin\theta}$$

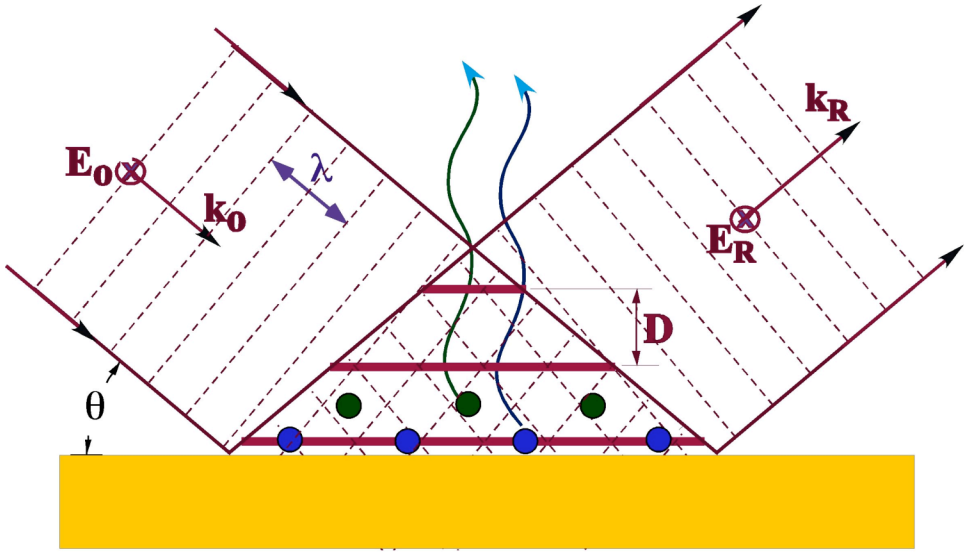
SW Vector:

$$\mathbf{Q} = \mathbf{k}_R - \mathbf{k}_0$$

X-ray Standing Wave Generated by Reflection

XSW Period: $D = \frac{\lambda}{2\sin\theta}$

Fringe Visibility: $V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}$



XSW Generated by Strong Reflection: R=1 → V = 1

1. Dynamical Bragg Diffraction: D = d-spacing
   a) Single crystal d = 1 to 10 Å surface structure
   b) Multilayer (LSM) d = 20 to 300 Å ultrathin organic film

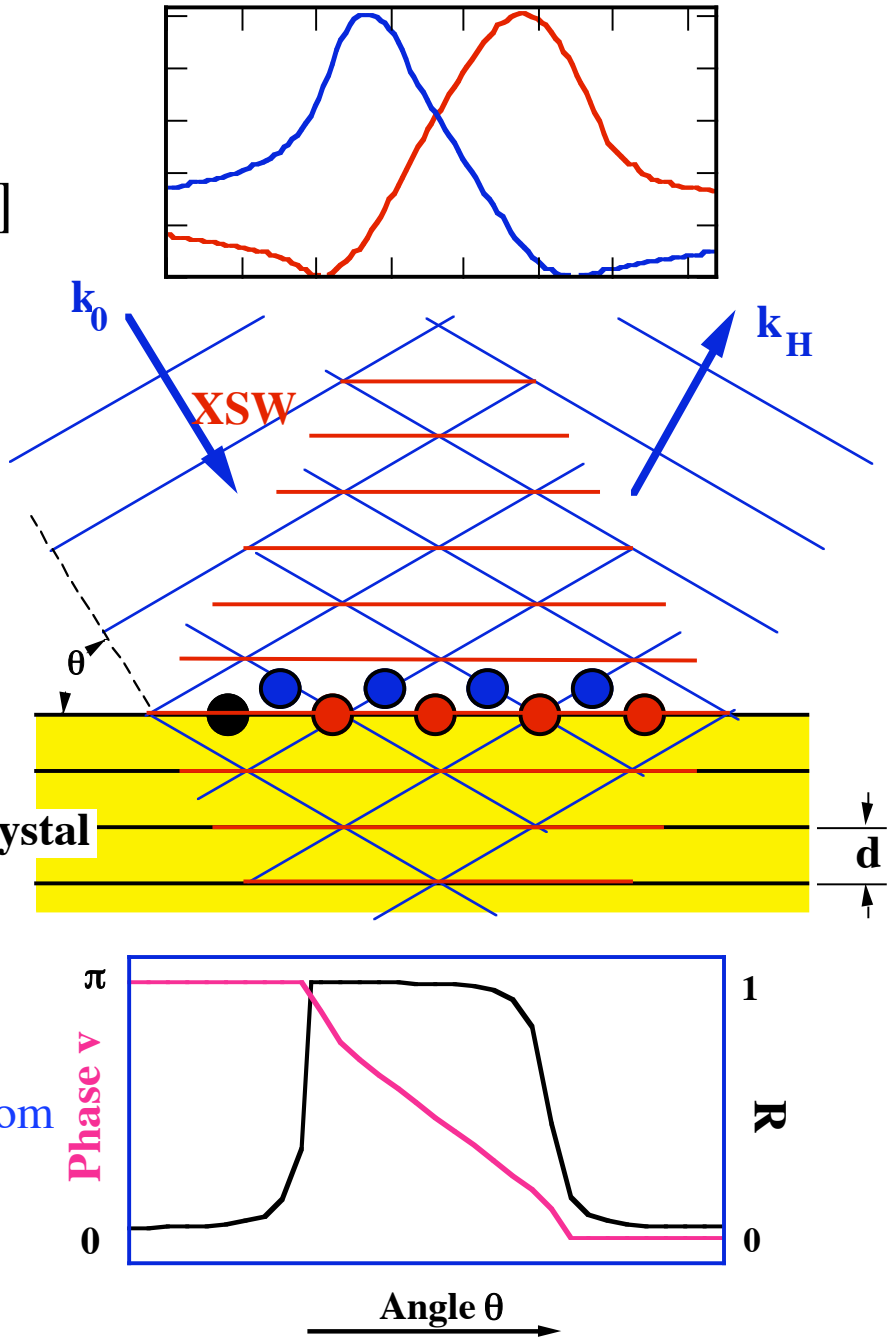
2. **Total External Reflection:** D = 70 Å to 1 μm diffuse double-layer biomolecular adsorption

XSW Generated by Dynamical Bragg Diffraction from Single Xtal

$$I(\theta) = I_0[1 + R + 2\sqrt{R}\cos(v - 2\pi\mathbf{H}\bullet\mathbf{r})]$$

$$2\pi\mathbf{H} = \mathbf{G} \qquad \mathbf{H}\bullet\mathbf{r} = \Delta d/d$$

XSW π phase shift → d/2 inward shift
Low-angle side → Nodes on diffraction planes
Hi-angle side → Antinodes on diffraction planes



XSW Fluorescence Yield

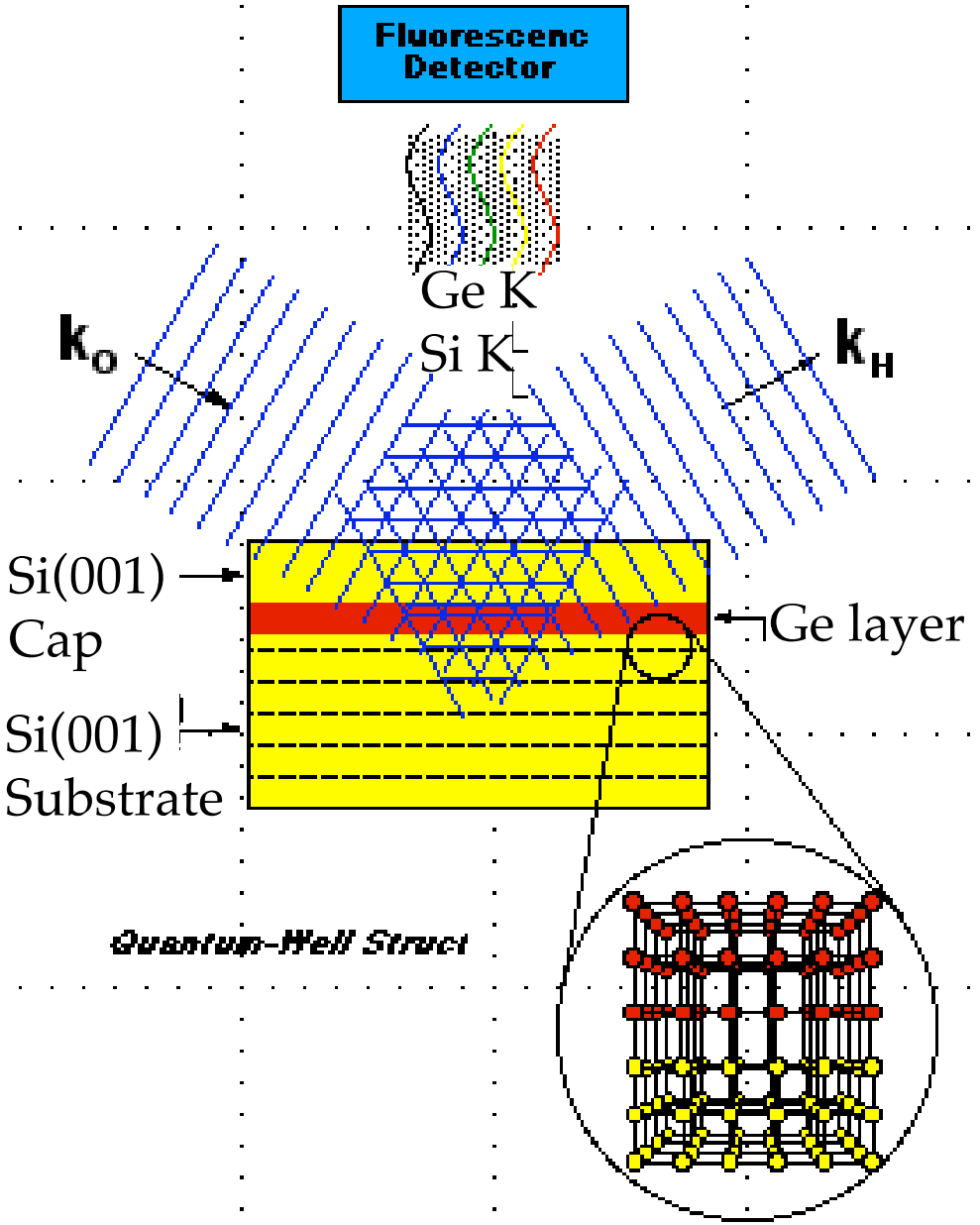
$$Y(\theta) = \int I(\theta,r)\rho(r)\,dr$$

$$Y(\theta) = \left[1 + R(\theta) + 2f_H\sqrt{R(\theta)}\cos\left(v(\theta) - 2\pi P_H\right)\right]$$

f_H : Coherent Fraction: Amplitude: 0 --> 1
P_H : Coherent Position: Phase : 0 --> 1

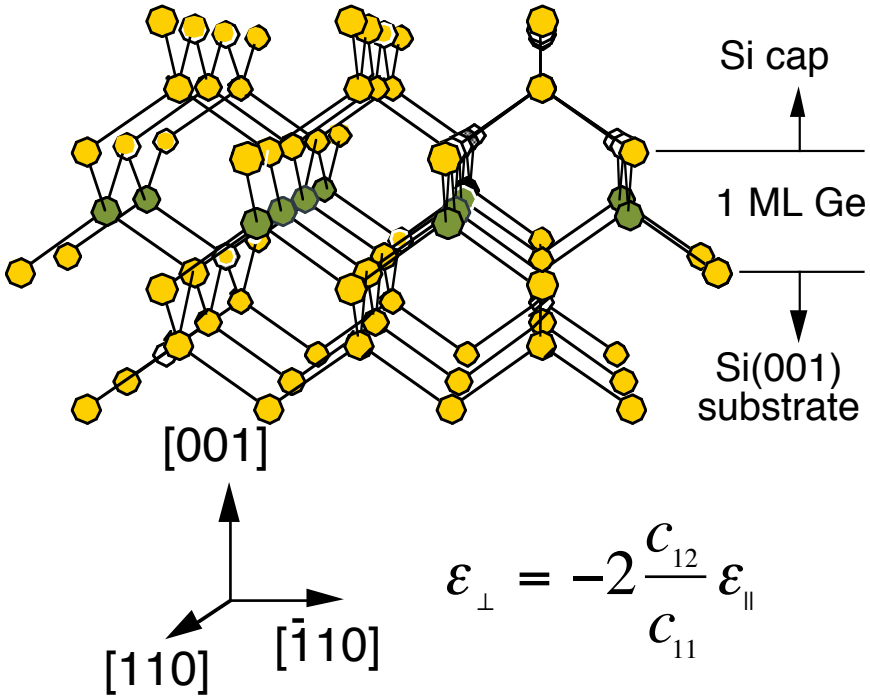
H^{th} Fourier Comp. of the fluorescence-selected atom distribution $\rho(r)$.

XSW analysis of strain in MBE grown buried heteroepitaxial film



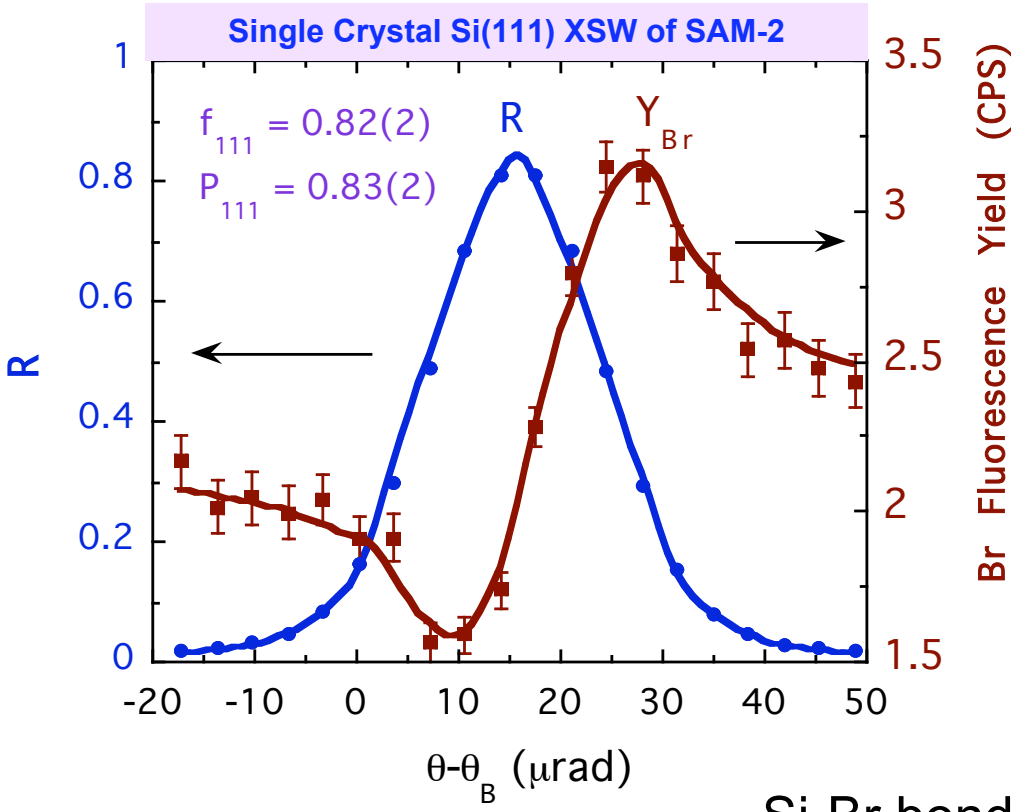
Can measure strain down to the level of 1 atomic layer.

HRXRD needs > 10 layers



$$\varepsilon_{\perp} = -2\frac{c_{12}}{c_{11}}\varepsilon_{\parallel}$$

Where is Br in SAM-2?



XRF → Total Θ_{Br} = 0.6 ML

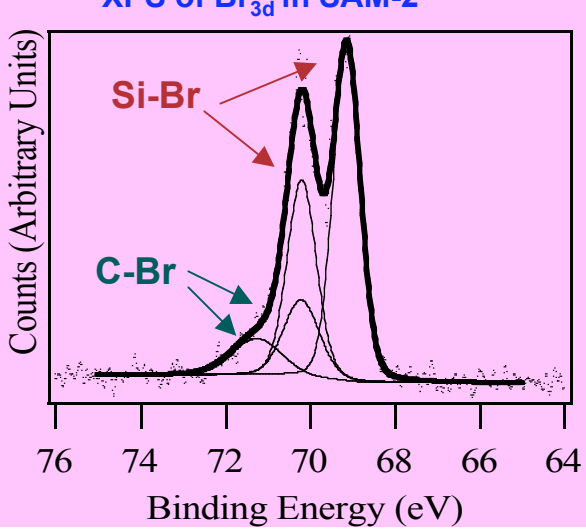
Si-Br bond

⇩

Br detachment to Si surface

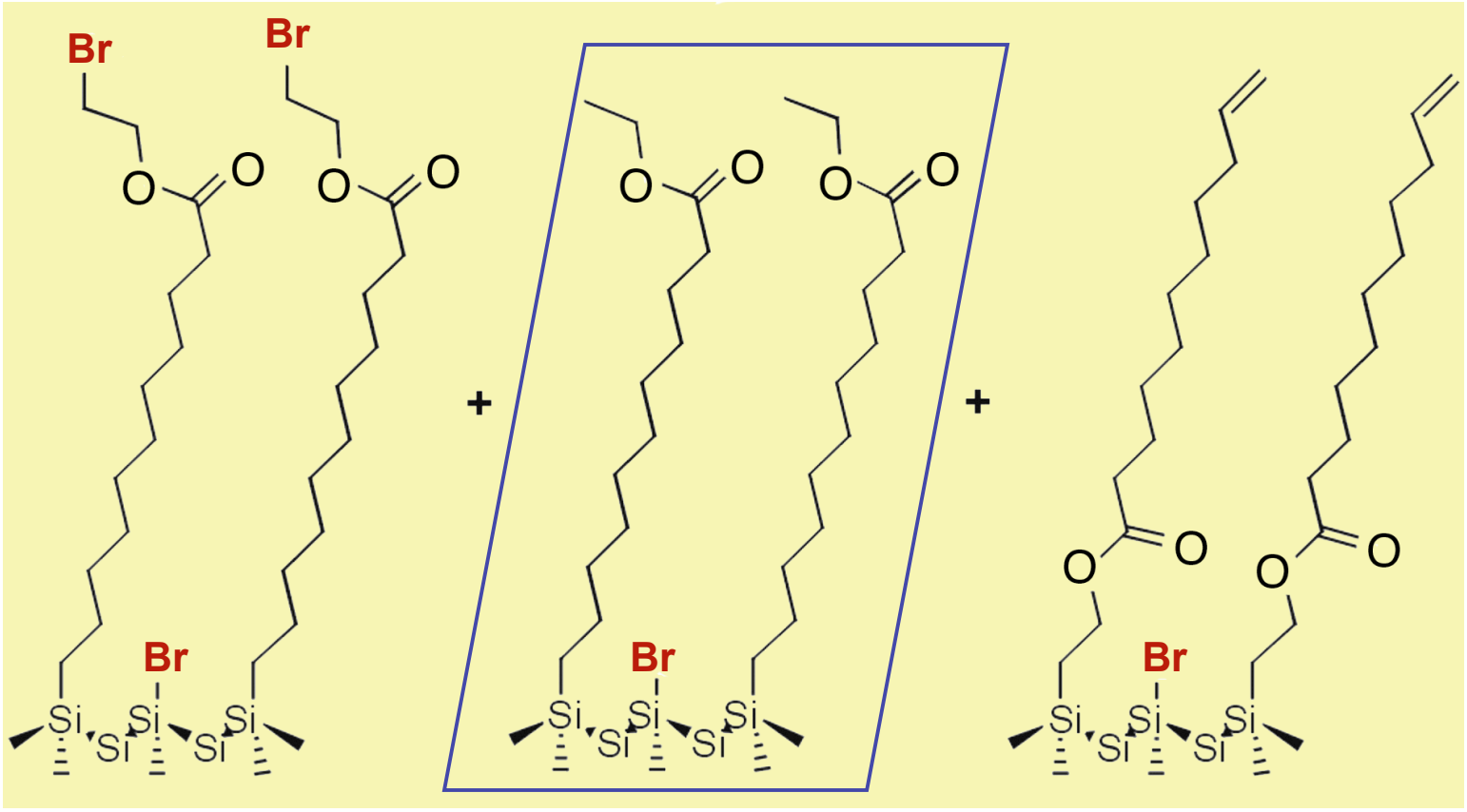
- Identical to monoatomic Br adsorbed on Si(111)
- 0.5 ML Br covalently bonded to surface Si atoms at T_1 site at h = 2.17 Å, i.e., Br detached from UDAME

Br-Si bonding confirmed by XPS



Conclusion

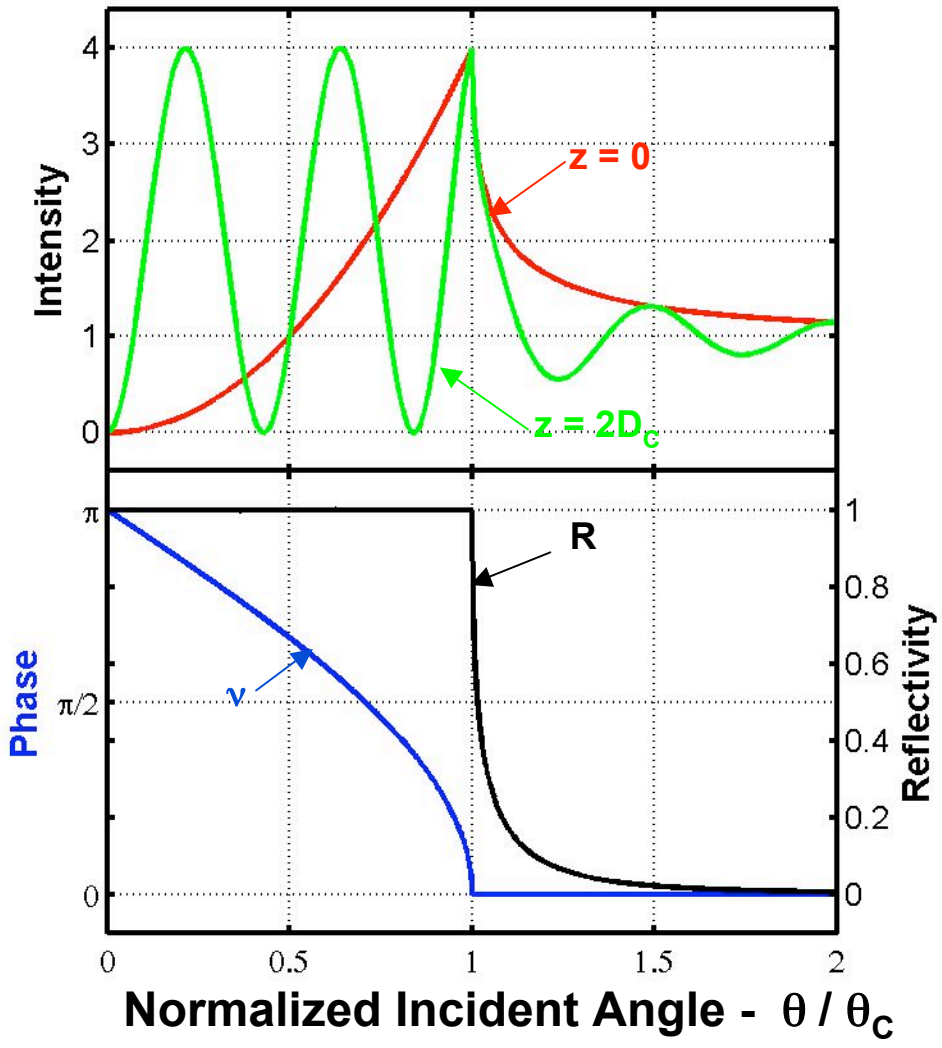
The 1/2 ML of Br-UDAME (SAM-2) can be partitioned as:

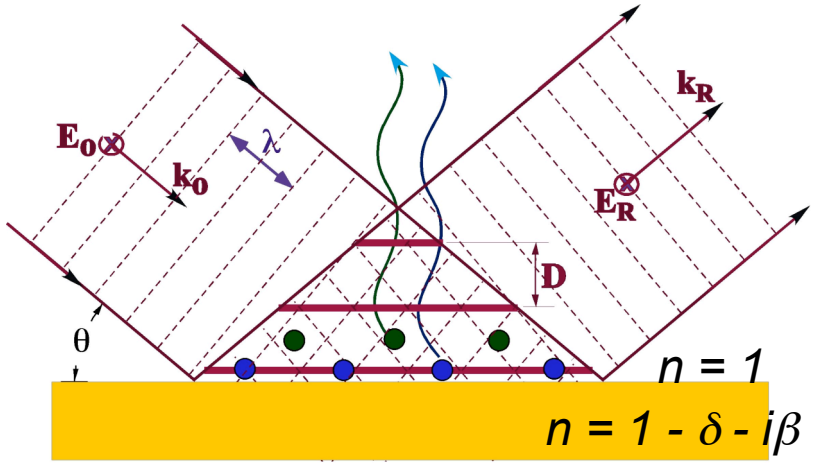


≤ 0.1 ML ≥ 0.25 ML ≤ 0.15 ML

Br at the interface -> more stable and provides marker layer

Total External Reflection X-ray Standing Waves





Fresnel Theory :

$$\frac{E_R}{E_0} = \left|\frac{E_R}{E_0}\right| e^{iv} = \frac{\theta - \left(\theta^2 - 2\delta - 2i\beta\right)^{1/2}}{\theta + \left(\theta^2 - 2\delta - 2i\beta\right)^{1/2}}$$

E – Field Intensity :

$$I(\theta, z) = 1 + R + 2\sqrt{R}\cos(v - Qz)$$

$$Q = 4\pi \sin\theta/\lambda$$

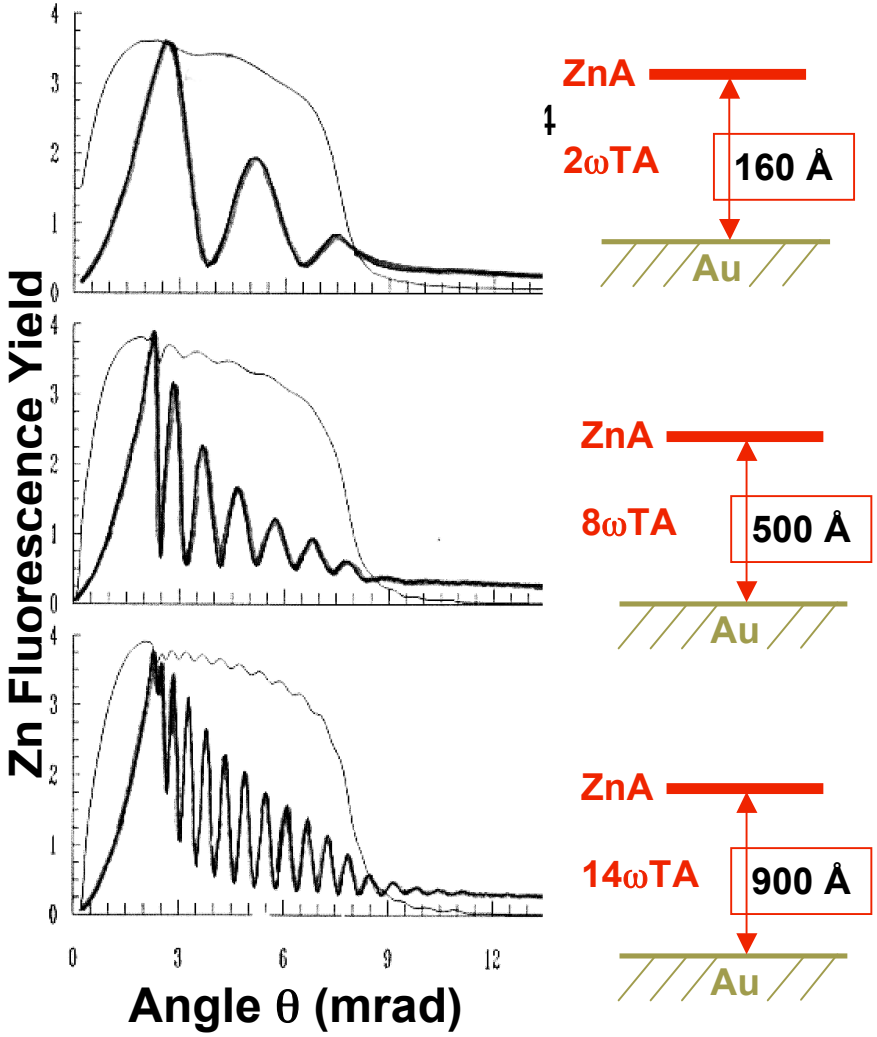
Critical Period :

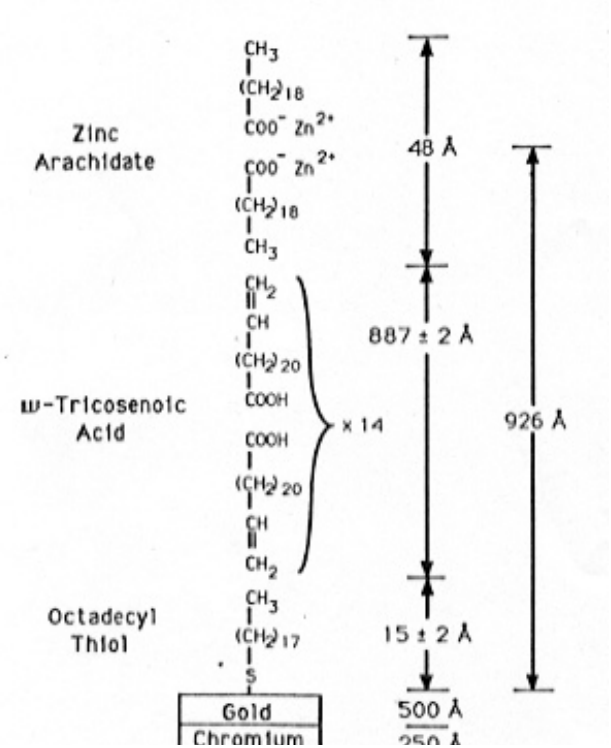
$$D_C = \frac{\lambda}{2\theta_C} = \frac{\sqrt{\pi}}{2\sqrt{r_e N_e}} = \begin{cases} 80\ \text{Å for Au} \\ 200\ \text{Å for Si} \end{cases}$$

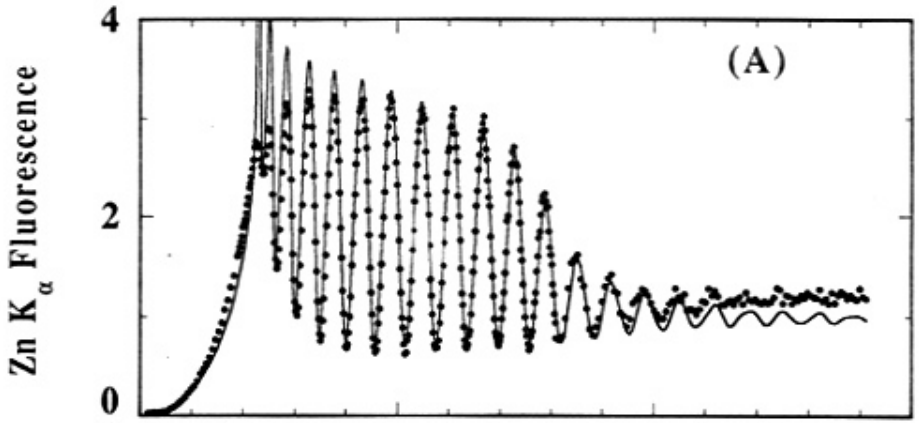
LB Multilayer Film / Au Mirror

Wang, Bedzyk, Penner, Caffrey *Nature* (1991).

Raw TER-XSW Data





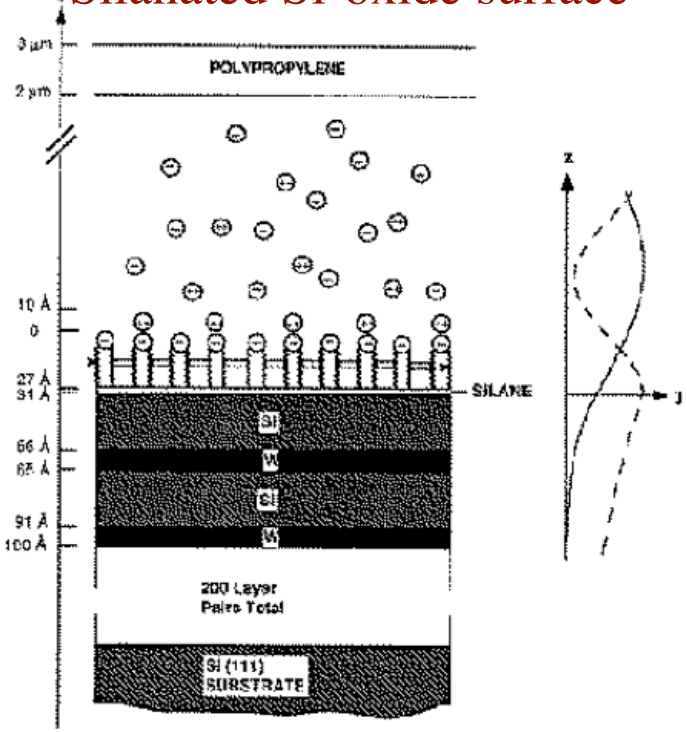


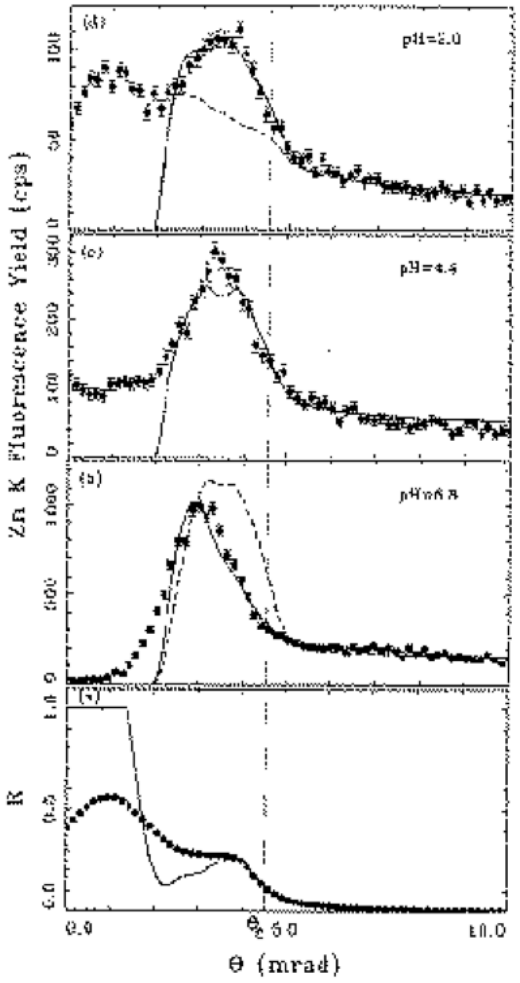
$$Y(\theta) = \int \rho(z)\, I(\theta,z)\, dz$$

Diffuse-Double Layer at Membrane-Aqueous Interface Measured by X-ray Standing Waves

Bedzyk, Bommarito, Caffrey, Penner, Science (1990)

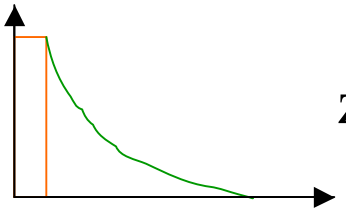
100 μM $ZnCl_2$
Phospho-Lipid
Membrane
Silanated Si-oxide surface



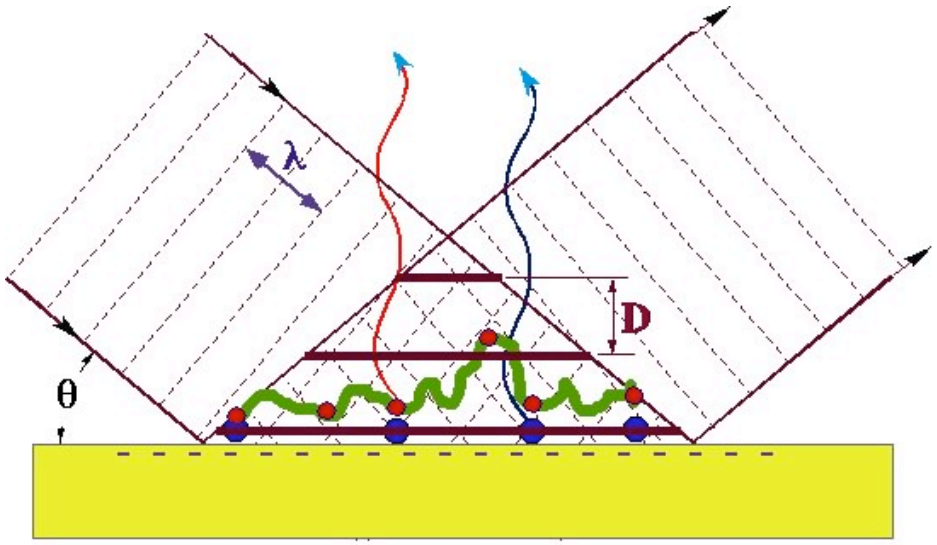


pH	ρ_C (M)	L_D (Å)
2.0	0.2	3
4.4	0.3	8
6.8	0.3	58

Zn distribution profile:
$\rho(z) = \rho_C \exp(-z/L_D)$



In situ X-ray Standing Wave Profiling of RNA Adsorption at a Charge Interface



Negatively-charged poly-ion
adsorbed to
negatively-charged surface
via divalent cation

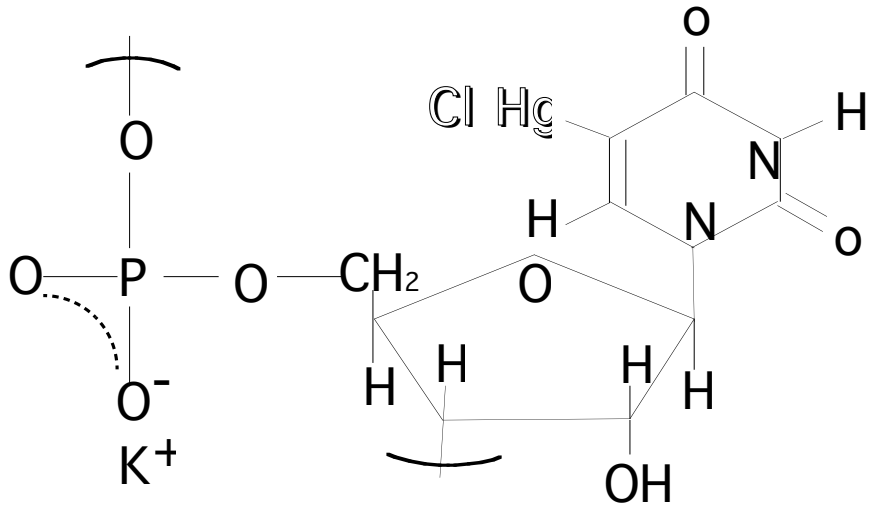
J.A. Libera, H. Cheng, M.J. Bedzyk, M. Olvera de la Cruz, M.J. Bedzyk, *J. Phys. Chem. B* **109**, 23001 (2005).

H. Cheng, K. Zhang, J. A. Libera, M. Olvera de la Cruz and M. J. Bedzyk , *Biophys. J.* **90**, 1164 (2006).

Mercurated Poly(U)

The RNA molecule → mercurated Poly-uridylic Acid Potassium salt

- Molecular weight: 1,400,000 - 1,700,000
- link number: 2382 - 2905



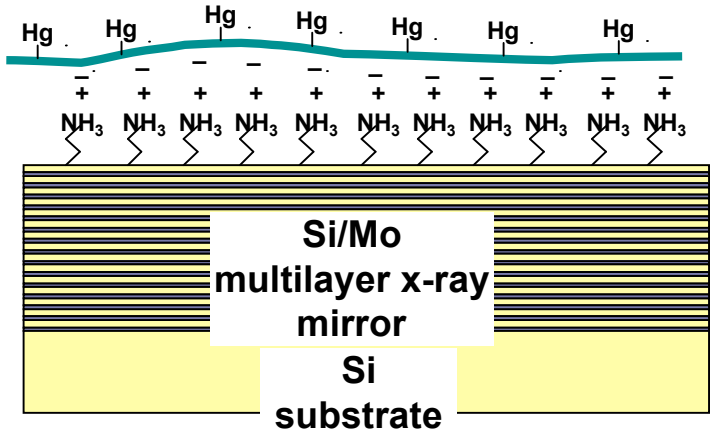
$C_9N_2O_8H_9KPHgCl$
(Hg replaced H)

Unit weight: 579.28

Concentration: 47 μg/mL

one Hg atom per units

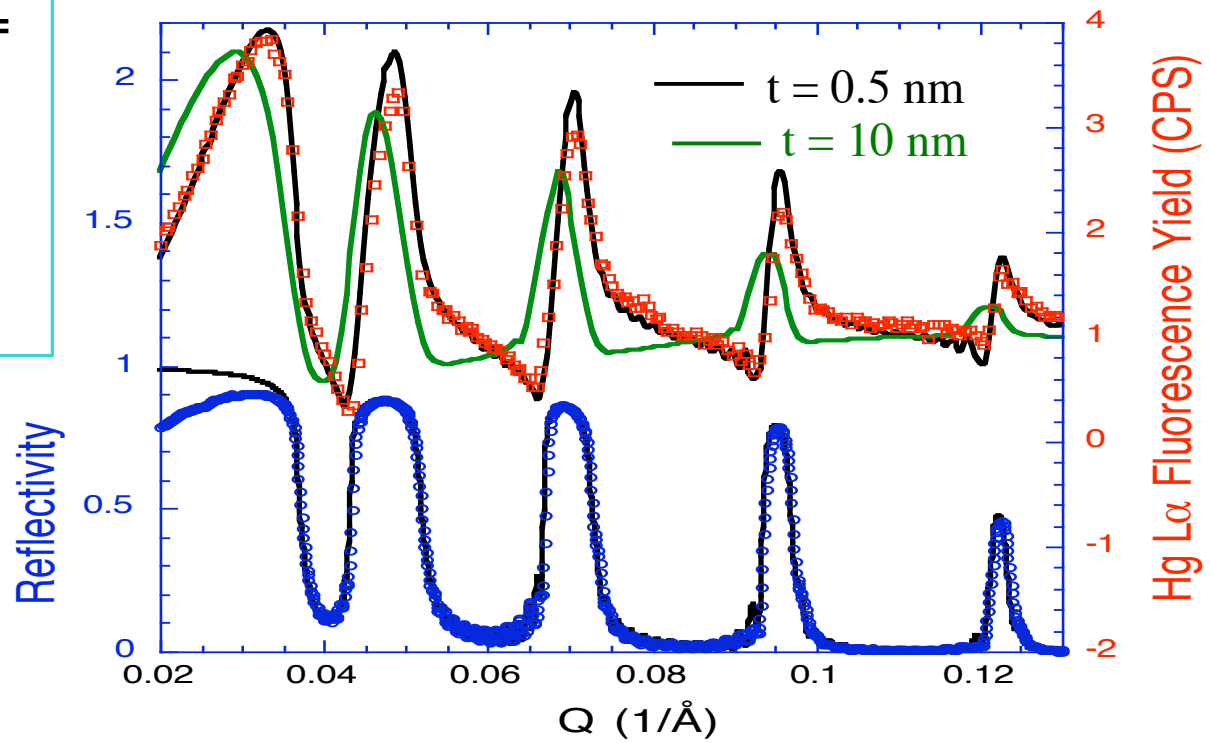
Multilayer X-ray Mirror -> Nanometer Variable Period XSW



- Si / Mo Layered -Synthetic Microstructure made by DC magnetron sputtering
- Large d-spacing (d = 22 nm) provides XSW periods of D = 5 - 20 nm
- Top Si surface w/ native oxide SiO_x supports primer layer for self-assembly

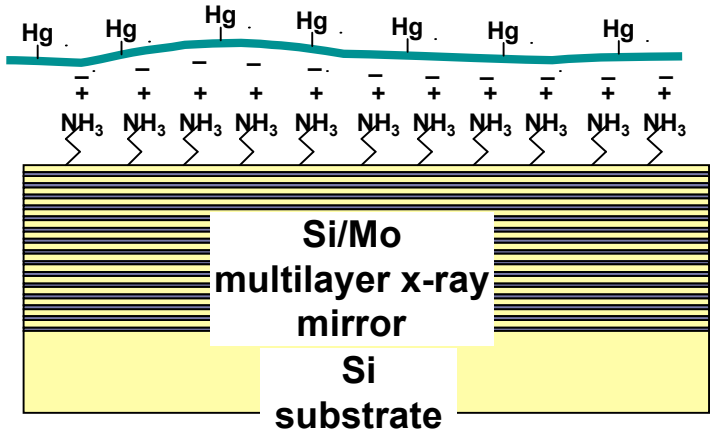
Case 1:
Hg-Poly(U) adsorbed to NH_3^+ terminated surface

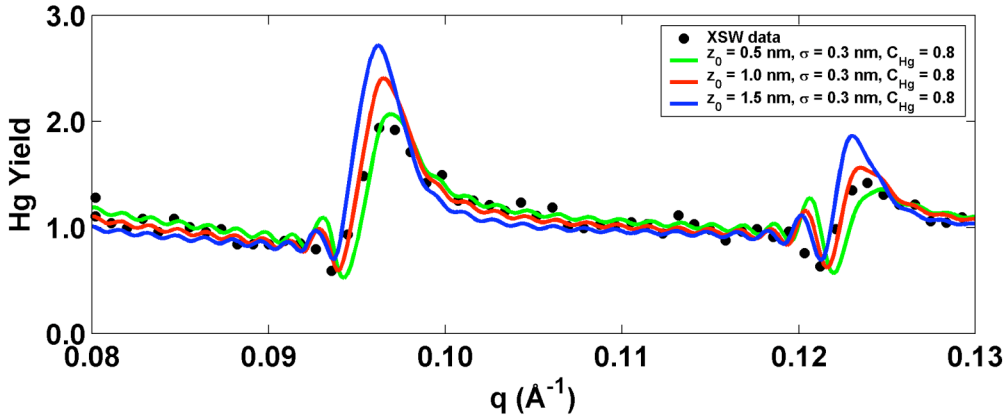
Ex situ

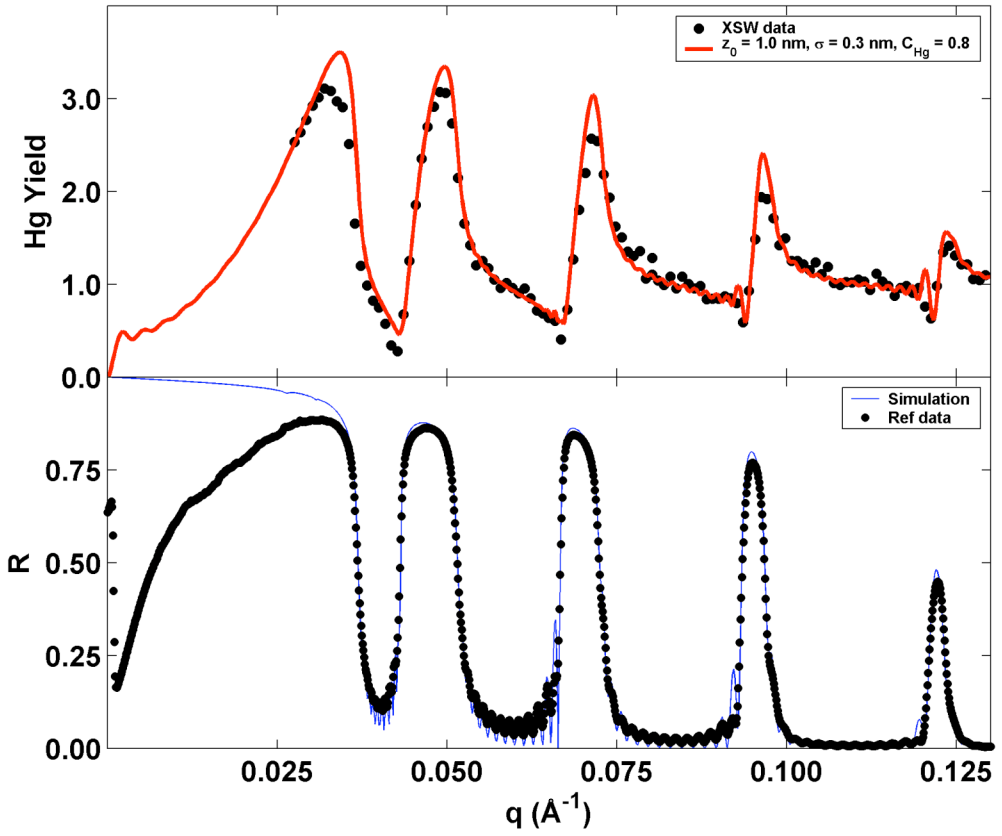


Case 1:
Hg-Poly(U) adsorbed to NH_3^+ terminated surface

0.5 nm Resolution



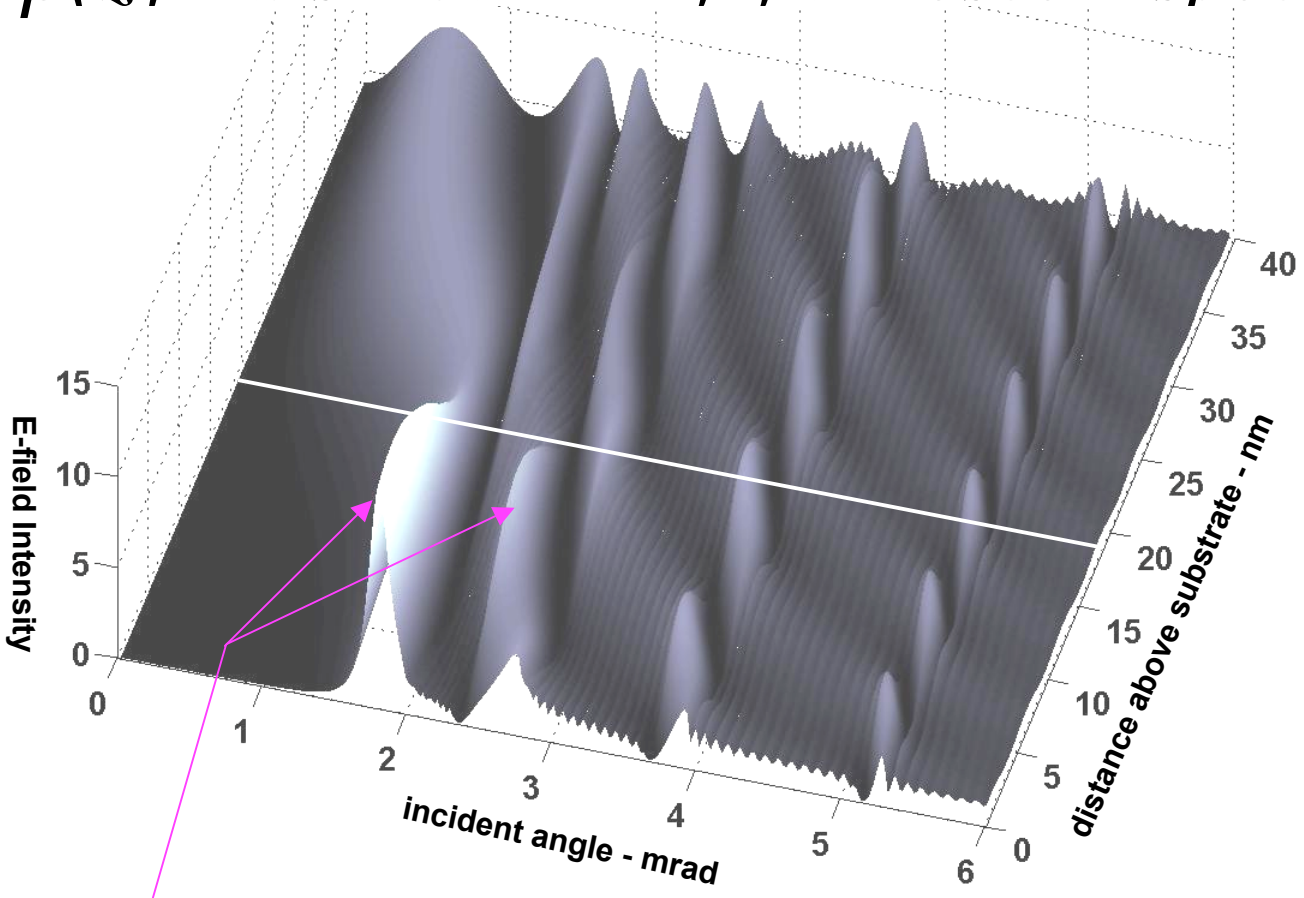




X-ray E-field Intensity Surface

$$XSW\ \ Fluorescense\ Yield : Y(\theta) = \int_0^t I(\theta, z)\ \ \rho(z)\ \ dz$$

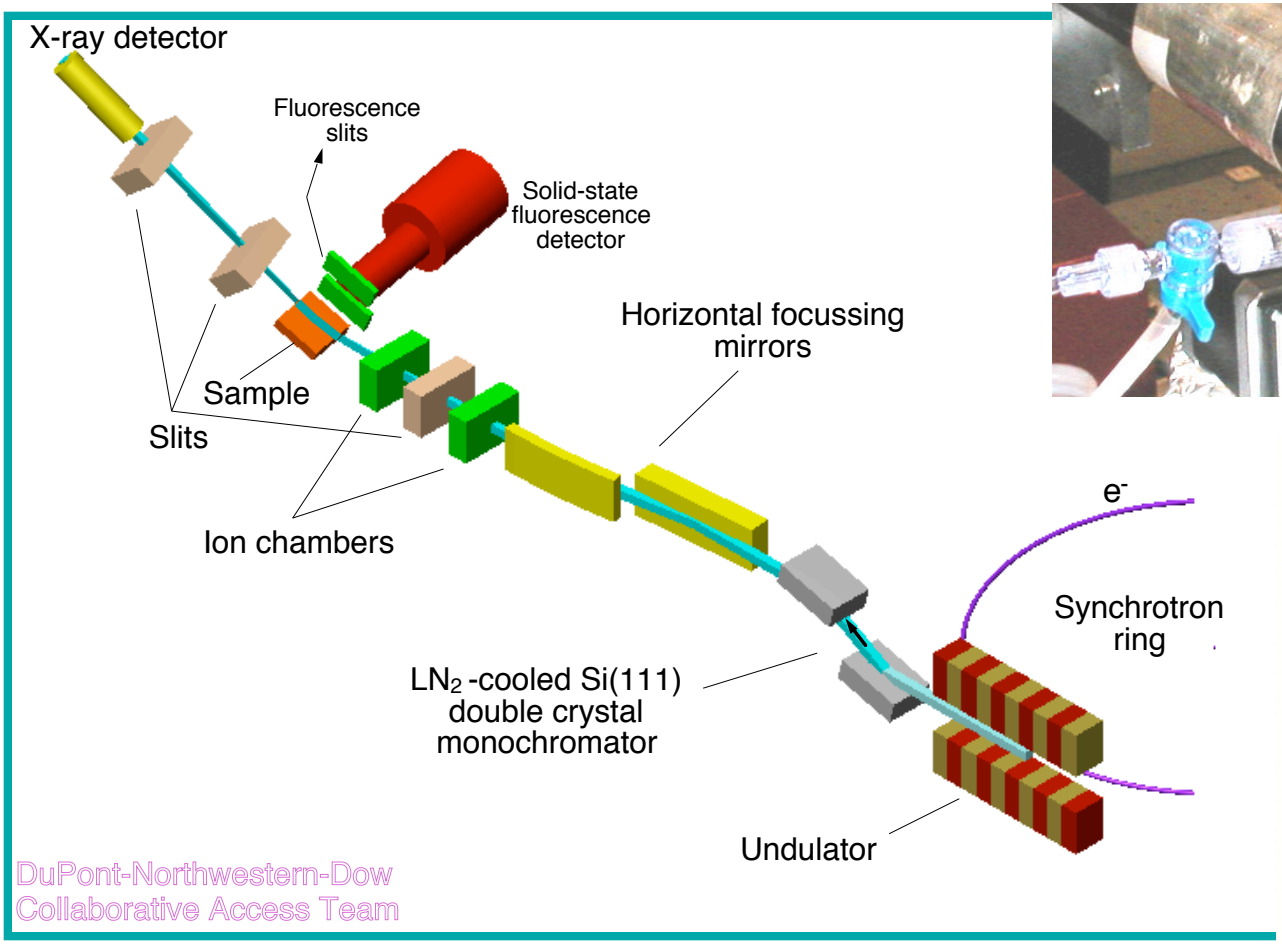
$$\rho(z) = distribution\ of\ \ fluorescent\ species$$

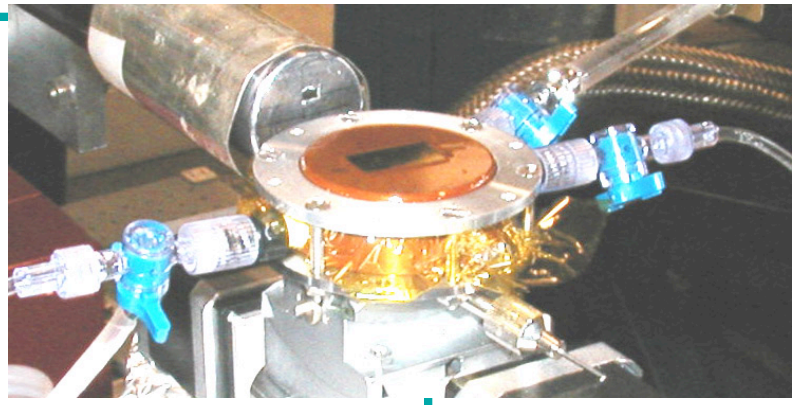


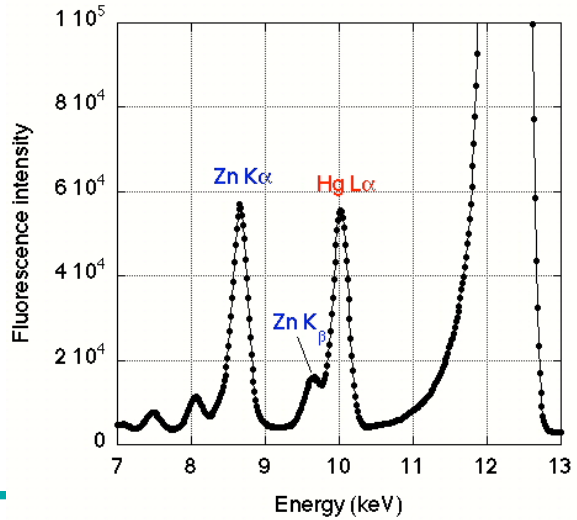
resonant cavity
E-field enhancement
EFI > 4

X-Ray Experimental Setup

5ID-C, DND-CAT Advanced Photon Source, Argonne National Lab

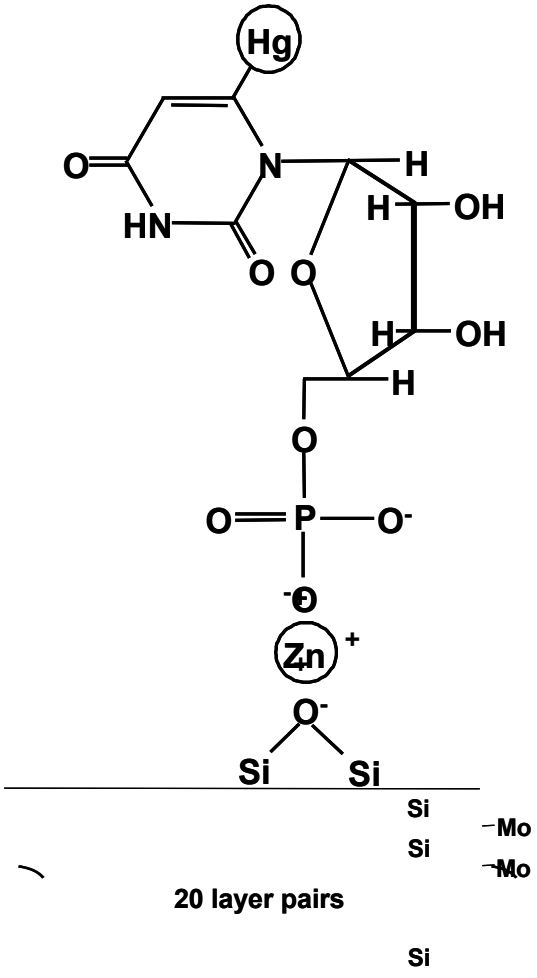




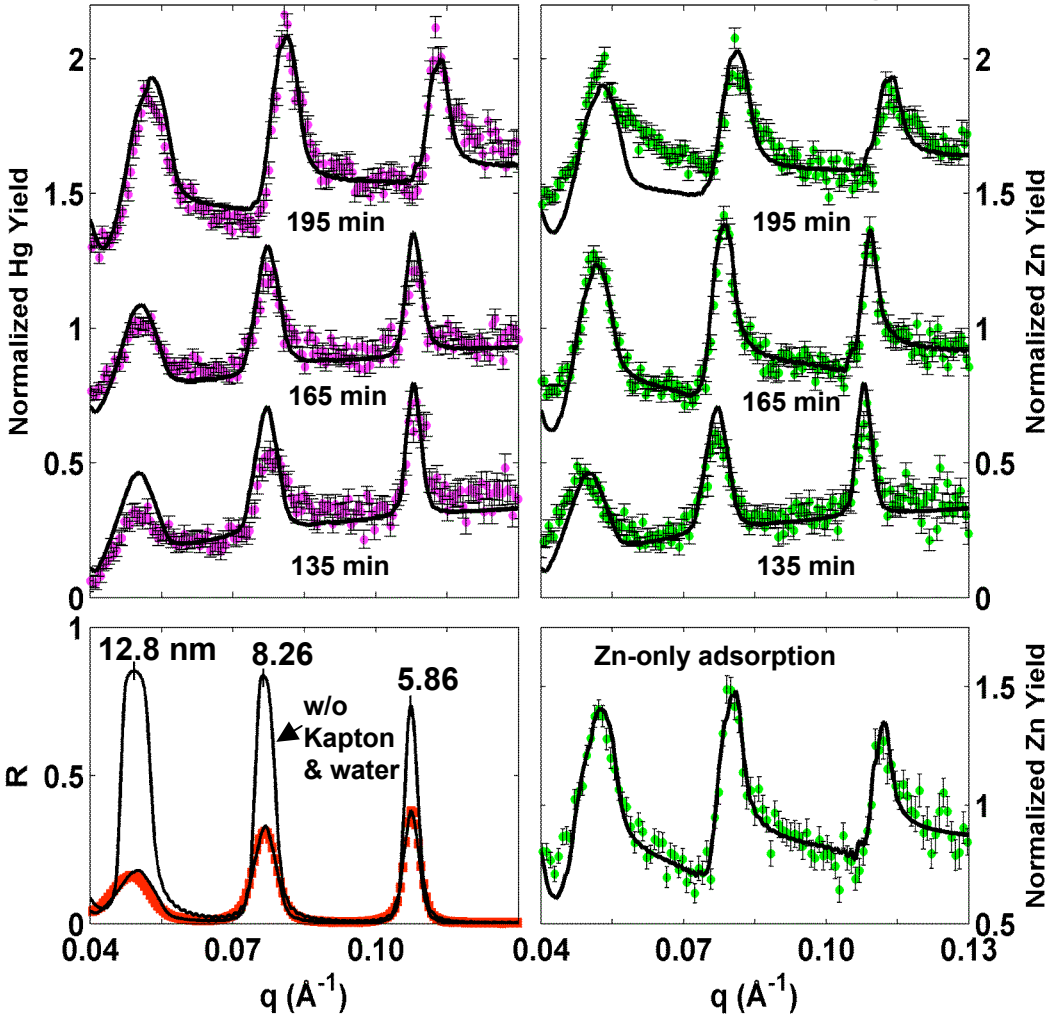


Zn^{2+} Counterion Driven Nucleic Acid Adsorption to a Negatively Charged Hydroxylated Silica Surface

Single monomer of adsorbed Hg-poly(U)



Time-dependent XSW Observation of Zn and Hg Atoms



In situ XSW measurements of Biomolecular Adsorption

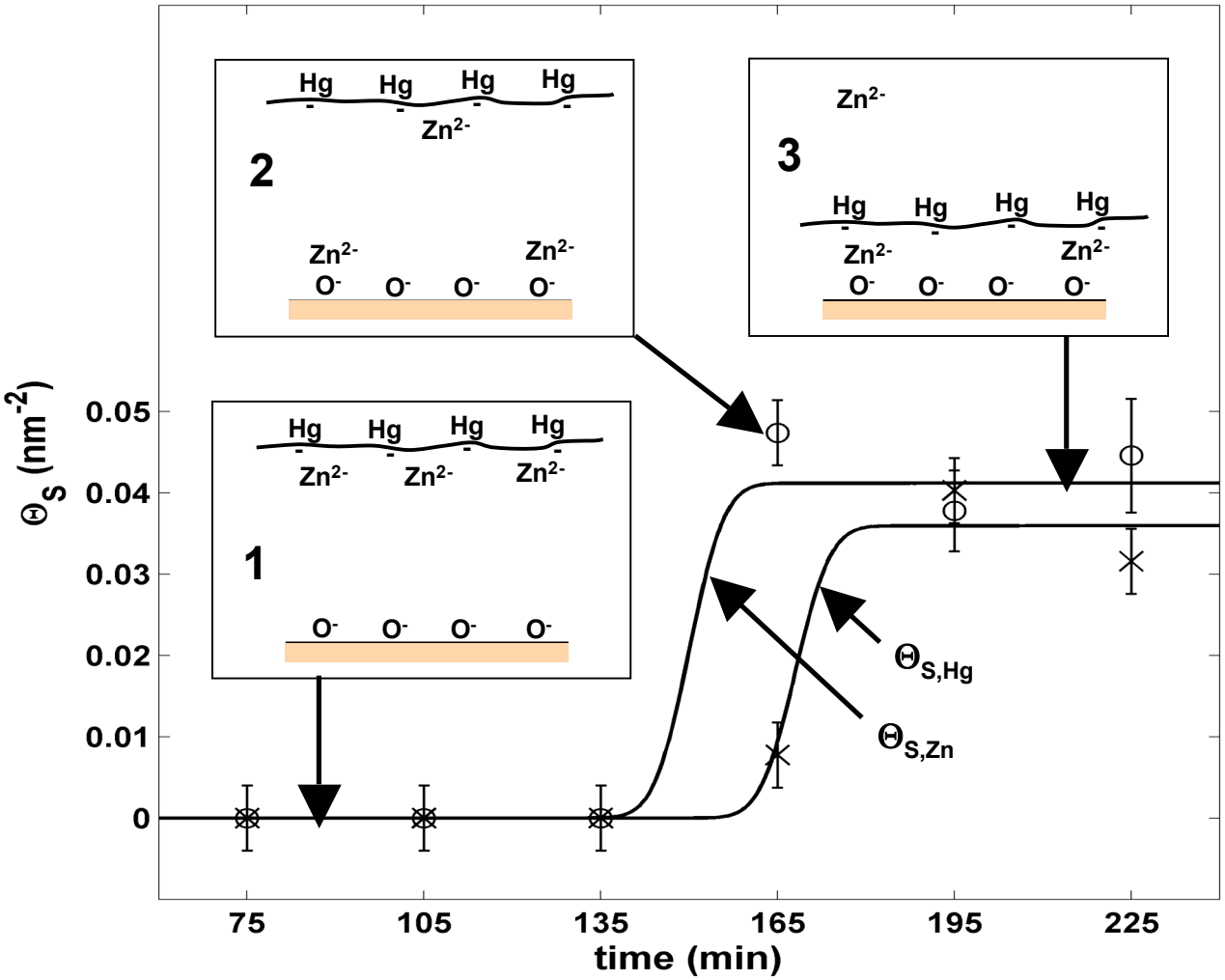
XRR ⇨ t_W Water-Layer Thickness

XRF ⇨ n_T depth-integrated atomic density (tag atoms and counter atoms)

XSW ⇨ t Condensed-Layer Thickness

n_T Condensed-Layer Atomic Density

In-Situ XSW Observation of Zn Induced Adsorption of Poly(U) RNA Molecules to an $SiO_2^-(H^+)$ Surface



Time Sequence:

1 no adsorption of Zn or Hg

2 Zn pre-adsorption

3 Hg-polyU Adsorption

Libera, Cheng, Olvera, Bedzyk,

Summary X-ray characterization of nano materials

- X-ray Scattering is very weak
- X-ray Scattering from molecules, nano clusters, thin films, etc. is kinematical. Simply add up once-scattered wavelets.
- Diffraction pattern is measured in reciprocal space coordinates Q_x, Q_y, Q_z and is directly linked to the Fourier transform of the electron density $\rho(x,y,z)$.
- The unit cell periodicity of the real-space lattice produces a periodicity in the recip-space lattice indexed by hkl.
- The Bragg intensity $I_{hkl} \propto |F_{hkl}|^2$, where F is the FT e- density within the unit cell. The phase of F is lost.
- Specular XRR at low-Q measures the e- density profile $\rho(z)$ at the interface.
- Grazing Incidence can dramatically improve surface sensitivity.
  - GIXRD used to study study 3D structure of nucleated islands, molecular self-assembly, etc.
- X-ray standing wave method solves phase problem and gives element specific structure.
- X-ray methods work in situ (e.g., under water).