Ordering in Hybrid Silicate-Oligo (*p*-phenylene vinylene) Nanocomposite Thin Films by X-Ray Scattering

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Motivation

•Characterize nm-scale structure of nano-composite self-assembled film with interesting electro-optical properties

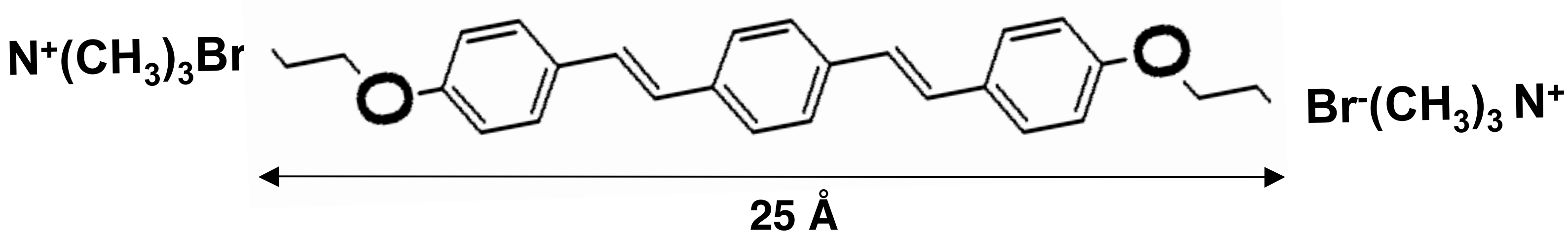
Outline

- Specimens: spin-coated Silicate-OPV thin-films on glass

- X-ray characterization tools used:
  — Specular X-Ray Reflectivity (XRR) with point detector
  — Grazing incidence x-ray scattering (GIXS) with 2D detector

Material & Experimental

OPV molecule (Oligo *p*-phenylene vinylene):



Film Preparation <-- Spin coating on float glass mirror

1 TEOS* : 0.15 OPV : 200 MeOH : 8.3 H_2O : 2.5 HCl
Or
1 TEOS : 0.15 OPV : 400 MeOH : 8.3 H_2O : 2.5 HCl

→ Spin coating on float glass 1000-3000 rpm → Vacuum Anneal 40°C 12 hours

↓

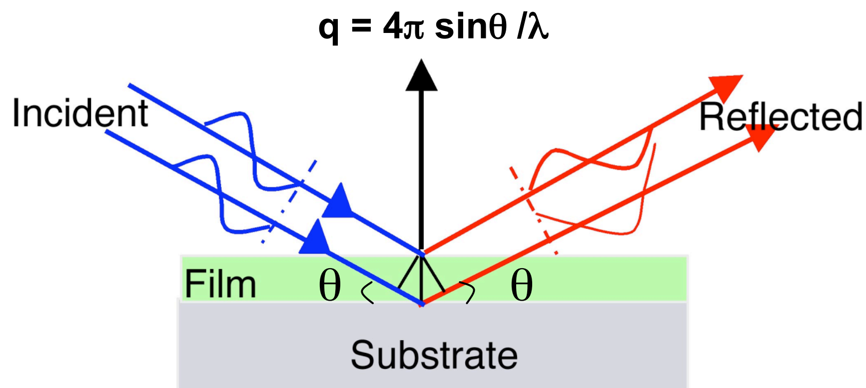
Samples A,B,C,D with various film thickness

* TEOS = tetraethyl orthosilicate: $Si(OEt)_4$. Formula: $C_8H_{20}O_4Si$

Material & Experimental

X-Ray Reflectivity (XRR) --> e^- density profile along surface normal

Performed at DND-CAT 5BM-D station: E = 10.00 keV



Kinematical approach:

$$\frac{R(q_{fz})}{R_F(q_{fz})} = \left| \frac{1}{\rho_\infty} \int_{-\infty}^{\infty} \frac{d\rho(z)}{dz} \exp(iq_{fz}z)dz \right|$$

Normalized reflectivity

$$q_{fz} = \sqrt{q_z^2 - q_{fc}^2}$$

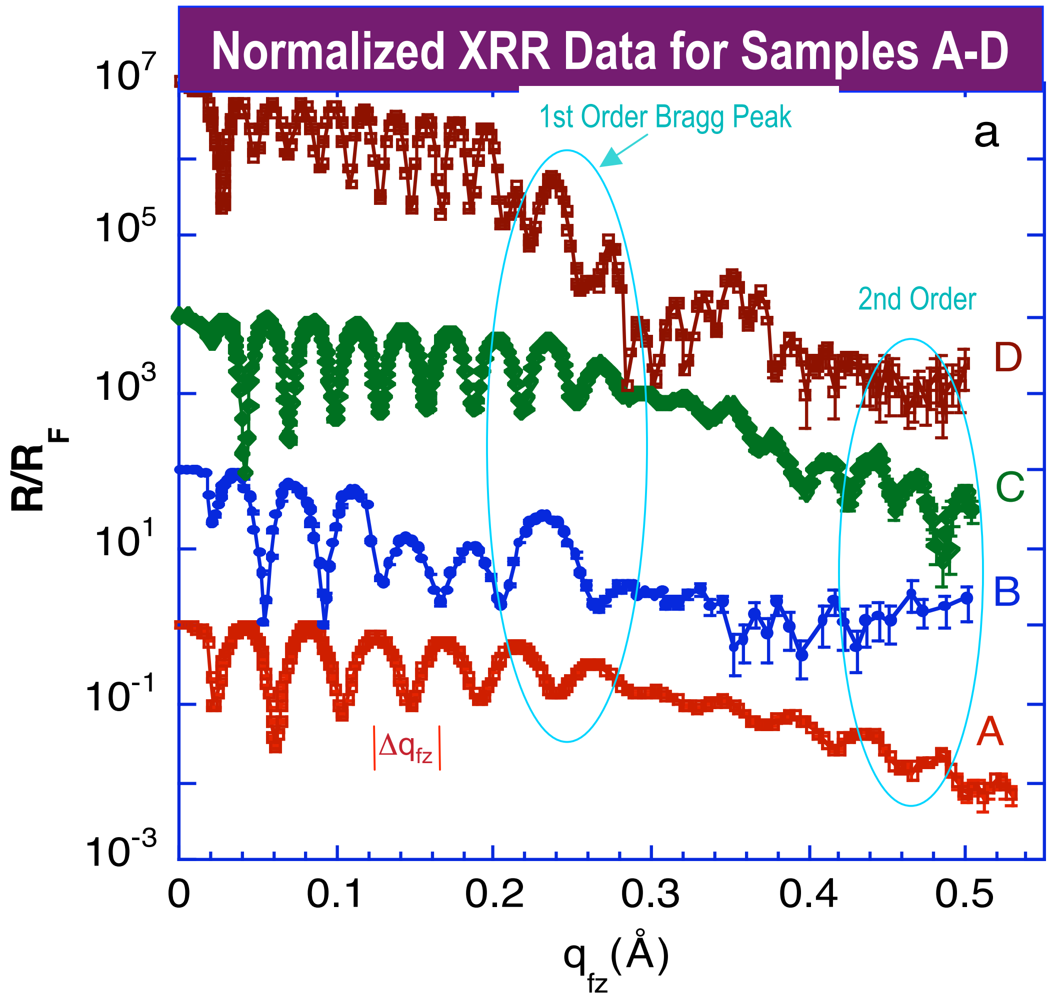
Film refraction correction, q_{fc} = 0.027 Å^{-1} for OPV film

$$R_F(q_{fz}) = \frac{q_{fz} - \sqrt{q_{fz}^2 - q_c^2}}{q_{fz} + \sqrt{q_{fz}^2 - q_c^2}}$$

Fresnel reflectivity for ideal flat surface, q_c = 0.032 Å^{-1} for float glass

XRR of OPV-Silicate Films

APS DND/5BM-D station: E = 10.0 keV



Two features:

- **Quasi-Bragg peaks** -->
The presence of periodic structure in the surface normal direction.

- The period $d_{\perp} = 2\pi/q^{B}_{fz}$, where q^{B}_{fz} = Bragg peak position.

- Kiessig fringes /modulations related to film thickness -->
Overall film thickness is
$t_f = 2\pi/\Delta q_{fz}$

XRR Analysis by Inspection of fringes and peaks

Table 1. Film thickness t_f, period $d_\perp$ and number of layers N calculated from the XRR results

Sample	t_f (Å)	$d_\perp$ (Å)	N
A	143	29.4	5
B	167	27.3	6
C	214	26.7	8
D	314	26.2	12

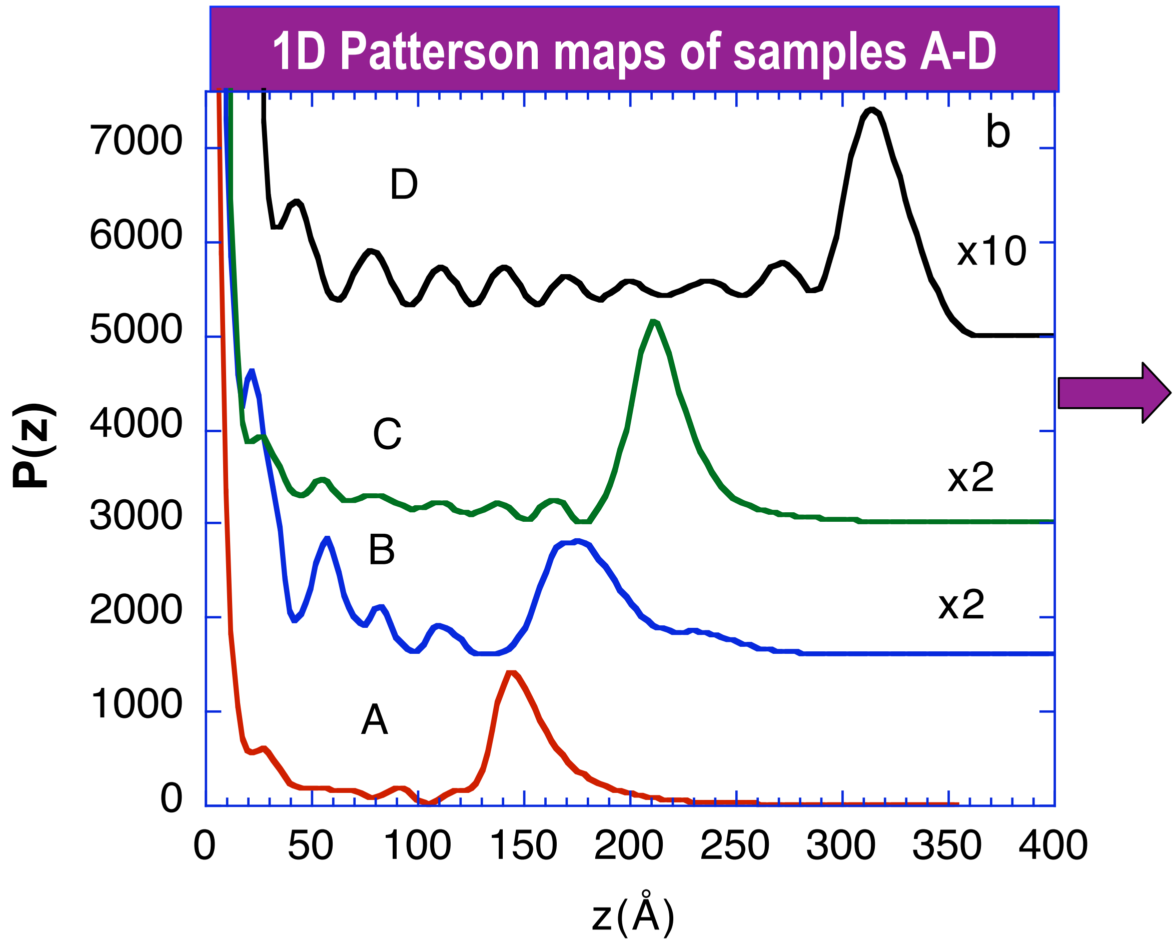
XRR Analysis by Fourier Inversion

- 1D Patterson Map P(z) = Inverse Fourier transform of the normalized reflectivity

$$P(z) = \frac{1}{2\pi}\int |\Phi(Q)|^2 e^{-iQz} dQ = \frac{1}{\rho_\infty^2}\int <\frac{d\rho(s)}{ds}><\frac{d\rho(s+z)}{ds}> ds$$

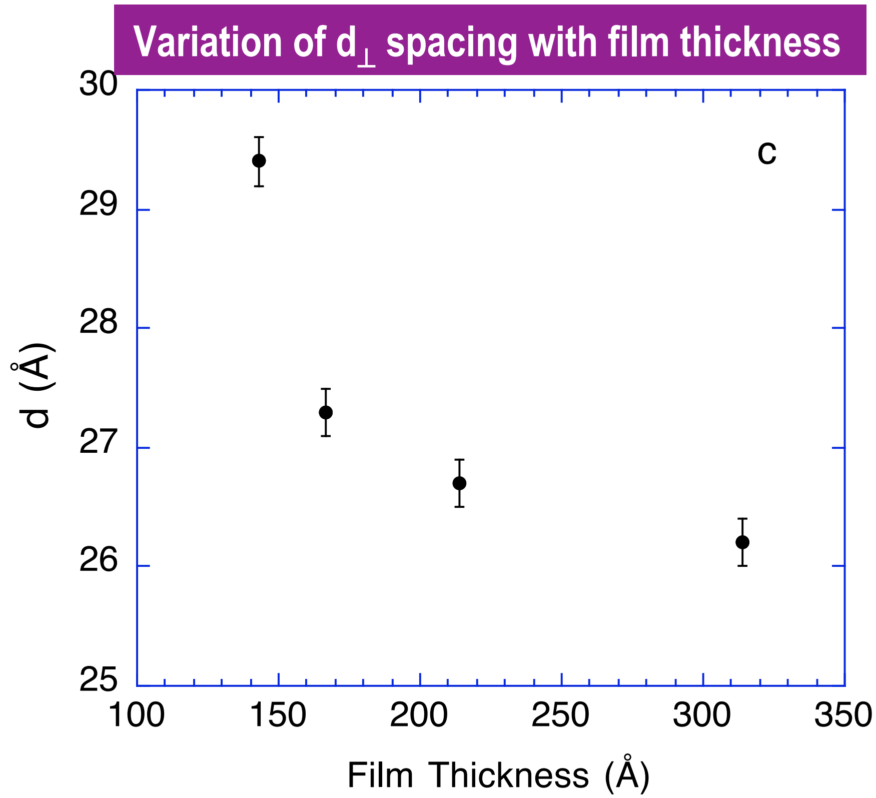
- Peaks in P(z) mark separation distances between any two interfaces which are sensed by a change in electron density.

Fourier Inversion of XRR Data from OPV-Silicate Films



- The large primary peak --> Overall film thickness
- The secondary maxima --> electron density variations inside film --> layered ordering along the surface normal direction
- The t_f and $d_\perp$ observed from P(z) agrees with those from XRR results

X-Ray Reflectivity Characterization



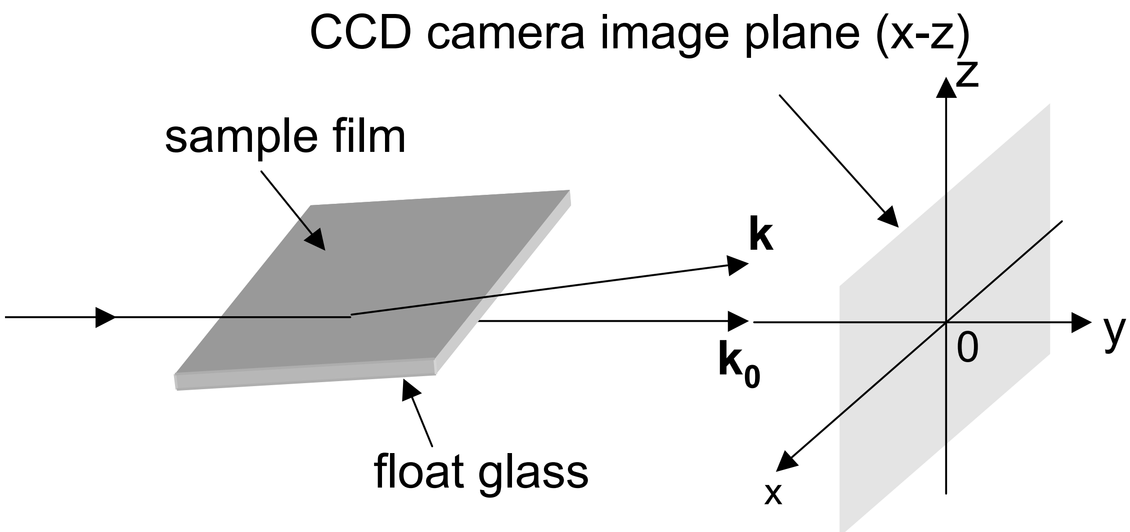
Summary of XRR:

- Silicate-OPV nano-scaled films possess layered ordering along the surface normal direction
- $d_{\perp}$-spacing period decreased with film thickness which may be related to the lower evaporation rate of solvent hence resulting in thinner silicate layers.
- Patterson map approach is suitable for Model-Independent XRR data analysis for layered thin films

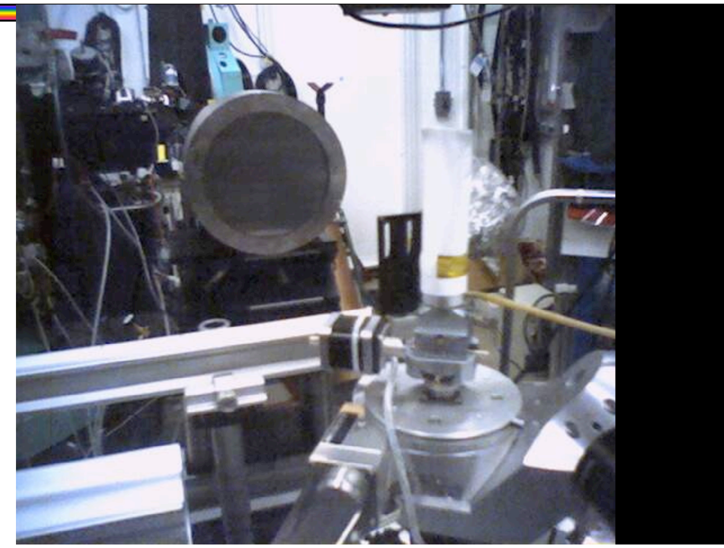
Grazing Incidence X-Ray Scattering (GIXS) --> 3D structure

OPV-Silicate Film / Glass

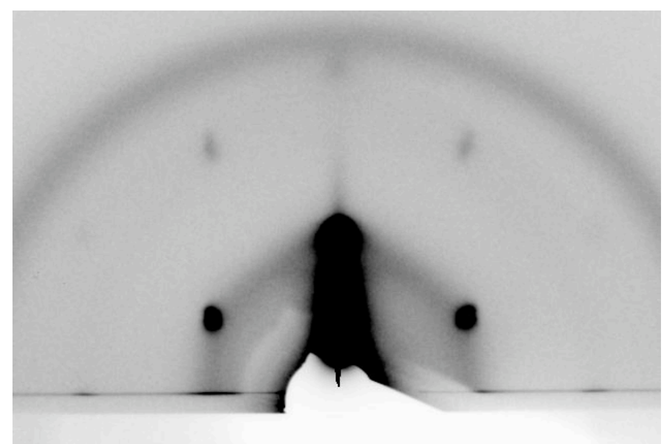
Performed at DND 5ID-C: E = 12.40 keV



Schematic of experimental setup



Looking downstream



Definition of direct space and reciprocal space geometry for GIXS CCD experiments

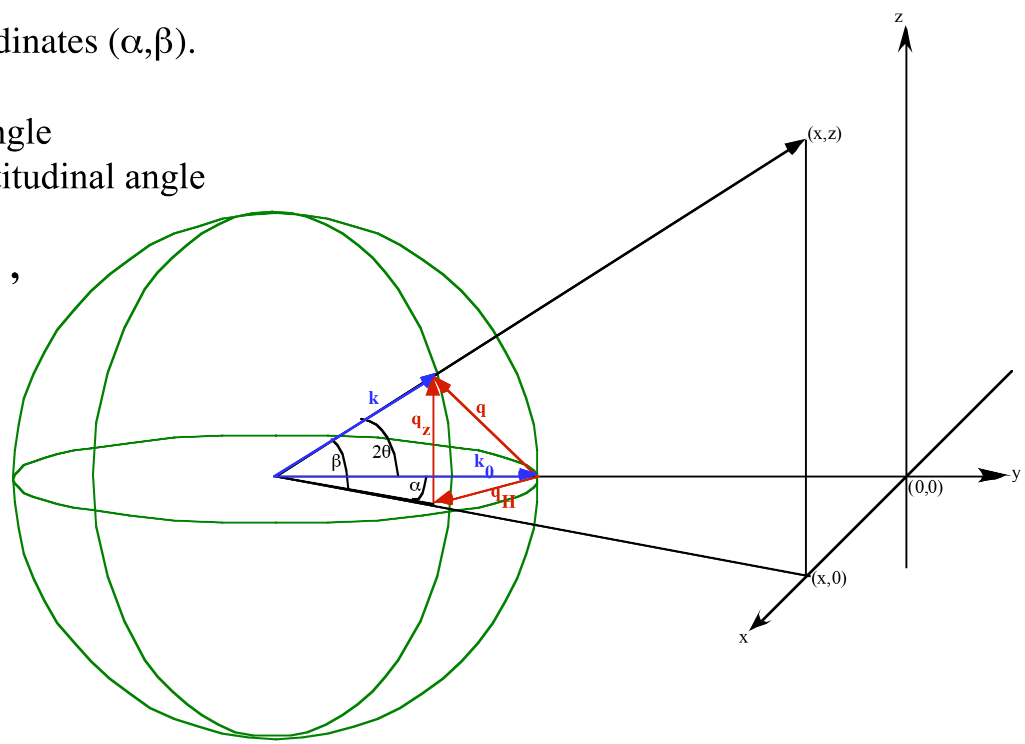
Directions:
y; along incident beam with wave-vector $\mathbf{k_0}$
z: Vertically up
x: right hand rule, horizontal, transverse to incident beam

The CCD image plane is perpendicular to **y**
The image plane is a distance D downstream from the sample / Diffractometer center.
The incident beam intersects the image plane at x=0, z=0 .

A scattered x-ray with direction defined by its wave-vector **k** passes through the mathematical xz image plane at coordinates (x,z), if the scattering angle $2\theta < \pi/2$.

(x,z) can be conveniently transformed into angle coordinates (α,β).

$\alpha = \text{Atan}(x/D)$: In-plane, horizontal , longitudinal angle
$\beta = \text{Atan}(z / (D^2+x^2)^{1/2})$: Out-of-plane , elevation, latitudinal angle



Scattering vector : $\mathbf{q = k - k_0}$, $q = 4\pi\sin({}^{2\theta}/_{2}) / \lambda$,

$\mathbf{q = q_x + q_y + q_z}$, $\mathbf{q_H = q_x + q_y}$

$q_z = {}^{2\pi}/_{\lambda} \sin\beta = {}^{2\pi}/_{\lambda} \, (z / (D^2+x^2+z^2)^{1/2})$,

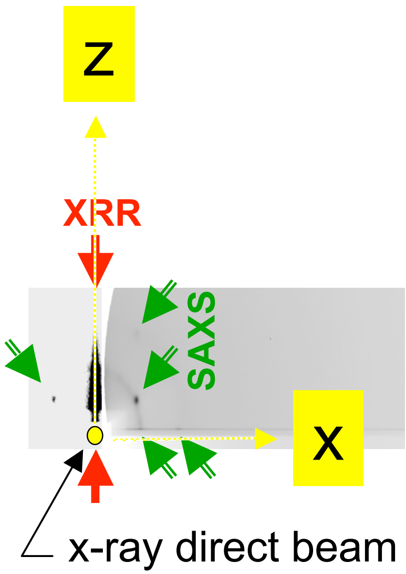
$q_H = {}^{2\pi}/_{\lambda} [2(1 - \cos\alpha \cos\beta) - \sin^2\beta]^{1/2}$,

$q_x = {}^{2\pi}/_{\lambda} \sin\alpha \cos\beta$, $q_y = -{}^{2\pi}/_{\lambda} [1 - \cos\alpha \cos\beta]$

Note that $\cos 2\theta = \cos\alpha \cos\beta = D/(D^2 + x^2 + z^2)^{1/2}$

A Qualitative look at the GIXS 2D Pattern

GIXS geometry
X-ray (λ=1.000 Å) incident angle set near glass critical angle (~0.12°) to enhance scattering from film. Note the Yoneda line.

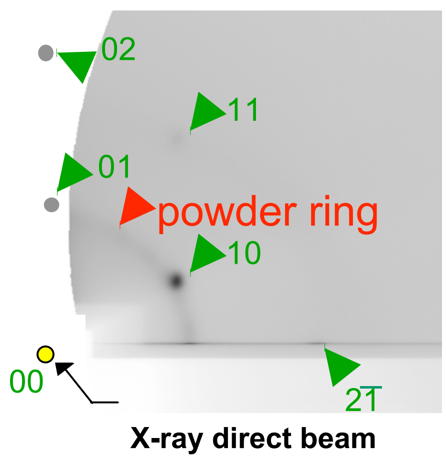


The diffraction pattern (for this case) persists independent of azimuthal rotation angle ϕ about the surface normal. This means that the film microstructure is <u>textured</u>. (The crystal domains have an out-of plane preferred orientation, but in-plane random orientation.) This texturing causes each reciprocal lattice pt. to be smeared out around a ring concentric to the z-axis. A ring intercepting the Ewald sphere causes a diffracted beam, which produces a spot on the detector plane. An ideal random powder microstructure would produce spheres in rel. space and rings on the 2D detector plane.

Specular X-ray Reflectivity (XRR) -> thickness t= 314 Å, d_z=26.2 Å, N=12

Determining the Lattice and Indexing the GIXS Peaks

Nanometer-Scale In-Plane and Out-of-Plane Crystal Structure by GISAXS



GISAX pattern of Silicate-OPV film with t_f = 314 Å

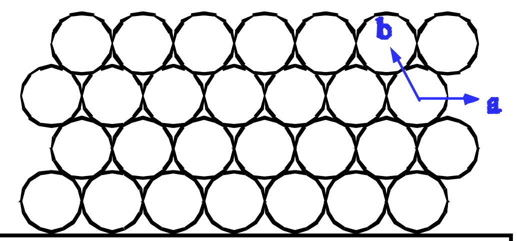
d_{01}=26 Å from XRR

d_{10}=28 Å

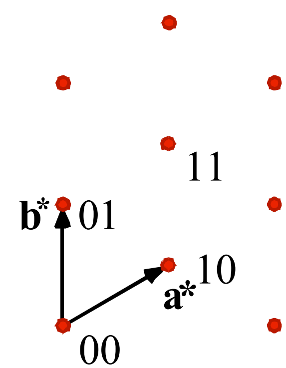
d_{11}=15.2 Å

The fact that d_{01} is slightly less than d_{10} indicates vertically compressive strain in hexagonal stacking of cylinders.

The small-angle Bragg peaks match strained 2D hexagonal packed rods laying down on surface like a pile of logs.

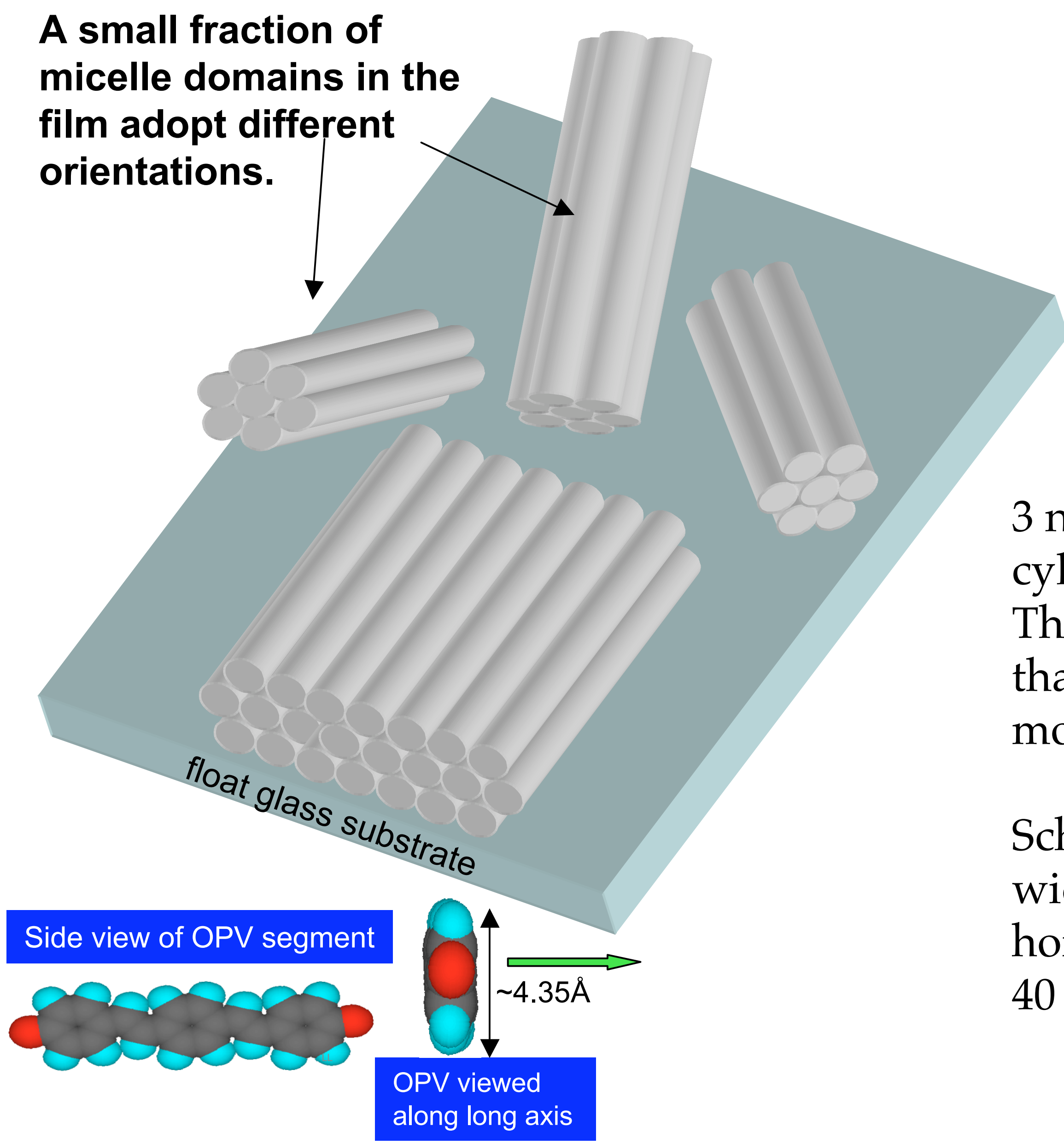


End view of cylindrical micelles lying on substrate surface with hexagonal packing



Powder rings correspond to randomly oriented domains with unstrained hexagonal packing.

Schematic of nm-scale OPV self-assembly from GIXS and XRR



3 nm diameter hex. packed cylindrical micelles.
This diameter is slightly greater than the length of the OPV molecule.

Scherrer formula: From diff. peak widths we get the vertical and horizontal domain sizes. 20 to 40 nm