X-ray Scattering of Thin Films of Organic Semiconducting Materials

Michael L. Chabinyc
PARC

Alberto Salleo
Stanford
Flexible Displays and Imagers

electrophoretic medium

printed backplane

Photosensor array

Flexible backplanes with a-Si and organic TFTs and photosensors
Thin Films of Organic Semiconductors

**Uses:**
- Electronics: displays (TFTs)  
  biosensor devices (TFTs, LEDs)
- Energy: Photovoltaics  
  Solid-state lighting (LEDs)

**Characteristics:**
- small molecules or rigid-rod,  
  conjugated polymers
- hole and electron conductors
- amorphous to semicrystalline films
- polymers form gels in solvent

**Devices:**
- thin films (< 100nm)  
  single, multi-, or blended layers

**Thin-film transistor**
- $V_D$ $\sim 100$ nm
- $V_G$
- On

**Photovoltaic cell**
- $V_{oc}$
- light

Examples of organic materials:
- P3HT
- F8T2
- PQT-12
- pentacene
- oligothiophenes
Conduction in thin-film transistor (TFT) occurs within 1-2 molecular layers of the dielectric.

Interfacial interactions between semiconductor and dielectric critical to operation.
Charge transport linked to the microstructure

Semicrystalline structure

Transport

Mobile states depend on:
- unit-cell structure
- crystalline order

Trap distribution depends on:
- grain-boundary structure
- crystalline texture
- mosaicity
- amorphous states

Factors affecting microstructure in thin films:
- substrate roughness, surface energies, thermal processing, solvent, etc.
Difficult to study bulk polymer and interfacial structure separately.
Thermal Transitions in Semiconducting Polymers

**PBTTT**
- highest field-effect mobility for polymers
- LC mesophase above ~140° C
- annealing improves mobility and device performance

McCulloch, et. al. Nat. Mater. 2006

**X-ray data from 11-3 using image plate detector (typically ~300 s exposures)**
Lamellar Order: Domain Growth

Annealing improves order and orientation of crystalline domains.

Annealed film

as-spun film

180° C

thickness ~ 300 Å

thickness ~ 1100 Å

(200) log scale

Counts (arb)

qz (1/Ångstrom)

Counts (arb)

qz (1/Ångstrom)

1000 Å

(200) log scale
**In-situ** Studies of Thin Film Crystallization

(100) specular peak

= fast cooling

PQT-12

Sidechain rigid-rod polymers have layered microstructure

in-situ studies can examine crystallization and phase behavior of these materials
Future Needs

Environmental Control
- most polymers degrade in air & room light & high intensity x-rays appear to ablate material
- inert atmosphere helpful to preserve sample during run
  (currently using a He-filled plastic bag…)
- ability to swell polymer with solvent atmosphere might be interesting,
  e.g. examination of gel form

Hot Stages for Crystallization studies
- melt-recrystallization studies are important
  350° C will cover most materials (typical decomposition temp)
- for many systems, dynamics are fast - e.g. response < 1 minute
- Faster temperature stages would be useful to minimize time required to reach temperature for scans; rapid cooling would be useful for quenching structures
- 2 or 3 T/Cs to ensure that the sample stage and sample surface are at the desired temperature.
- Cooling stage to go below RT
Future Needs

Data Acquisition
- convenient to do survey scans with area detector and then high-res scan on same beamline
- array detector for higher resolution grazing scattering (7-2)
- more rapid detection in area scans: it would be much better to be able to do rocking rapidly at different temperatures rather than the "panoramic shot" of reciprocal space

Data Processing
- image analysis (difficult currently during run)
  in-house processing software, e.g. Fit2D replacement