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Application of X-ray Reflection Interface Microscopy in Thin-film Materials *

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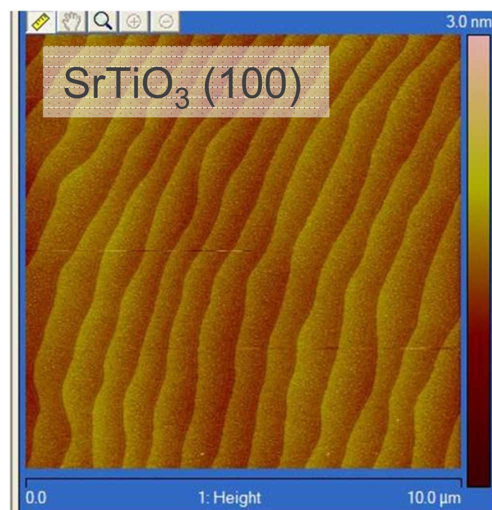
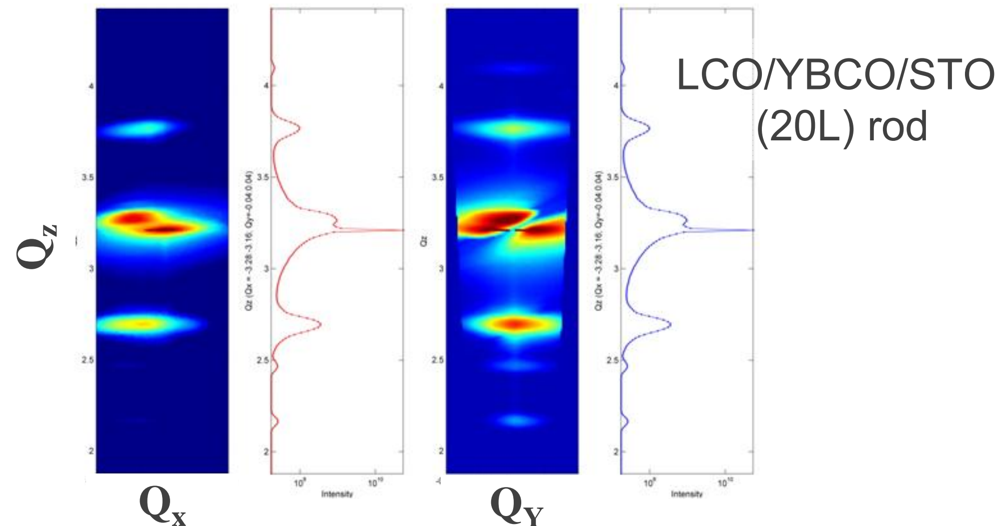
Outline

- Introduction
- X-ray reflection Interface Microscopy (XRIM)
  - Basics
  - Setups
- Examples
  - $SrRuO_3/SrTiO_3$
  - $EuTiO_3/DyScO_3$
  - Bi_2O_3 on STO
- Summary

Introduction

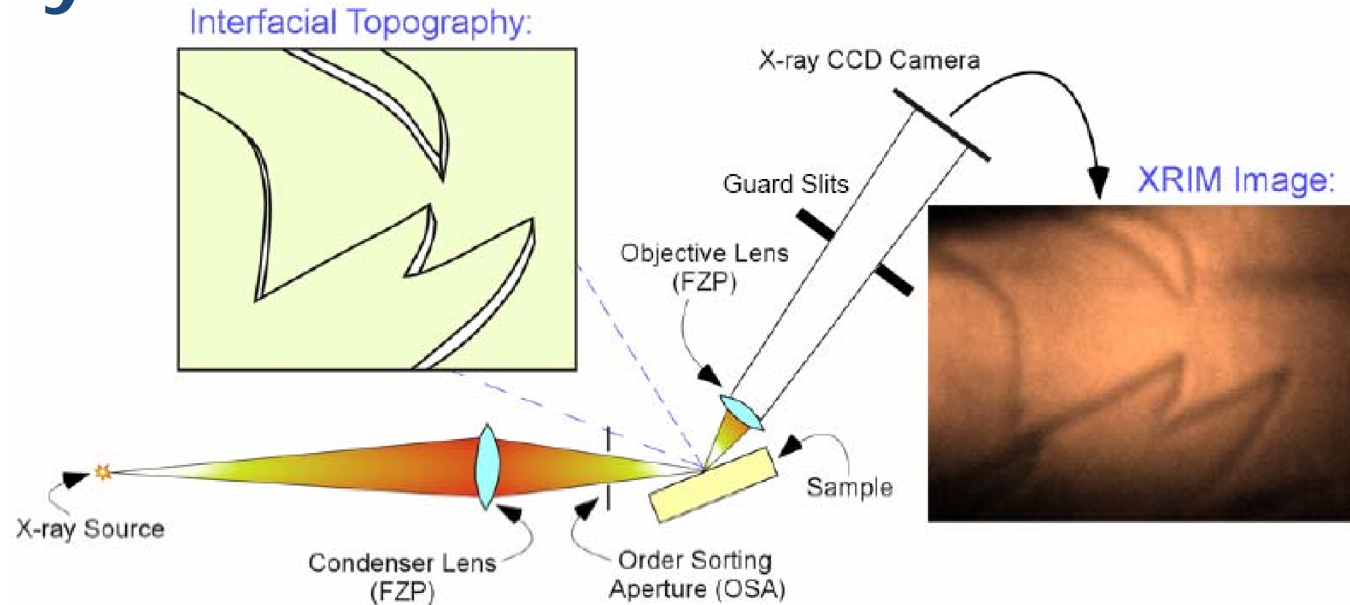
- Imaging & scattering at surfaces and interfaces
  - Microscopy methods normally focus on topographical information
  - Scattering methods normally focus on structural information
  - Combination of the two methods could probe both at the same time



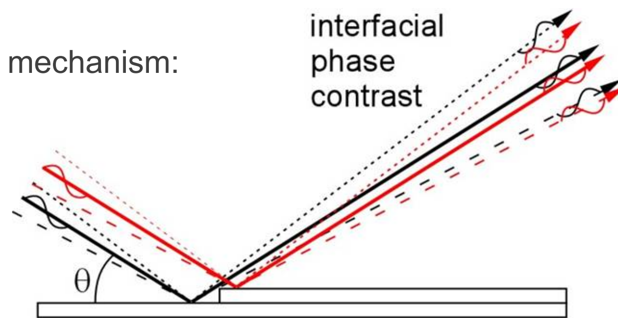


- Advantages of X-ray reflection surface/interface imaging
  - In-situ, real time measurements; probing buried interfaces, etc
  - Structure sensitive and potentially, element, valence state sensitive.
  - Quantitative analysis possible

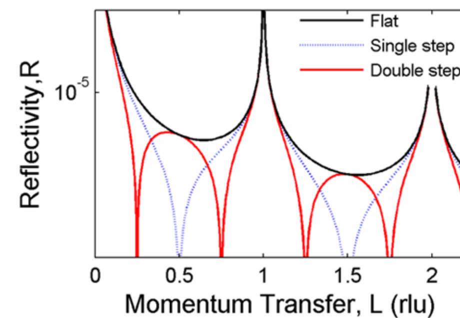
X-ray Reflection Interface Microscopy



Phase contrast mechanism:



Intensity contrast at defects:



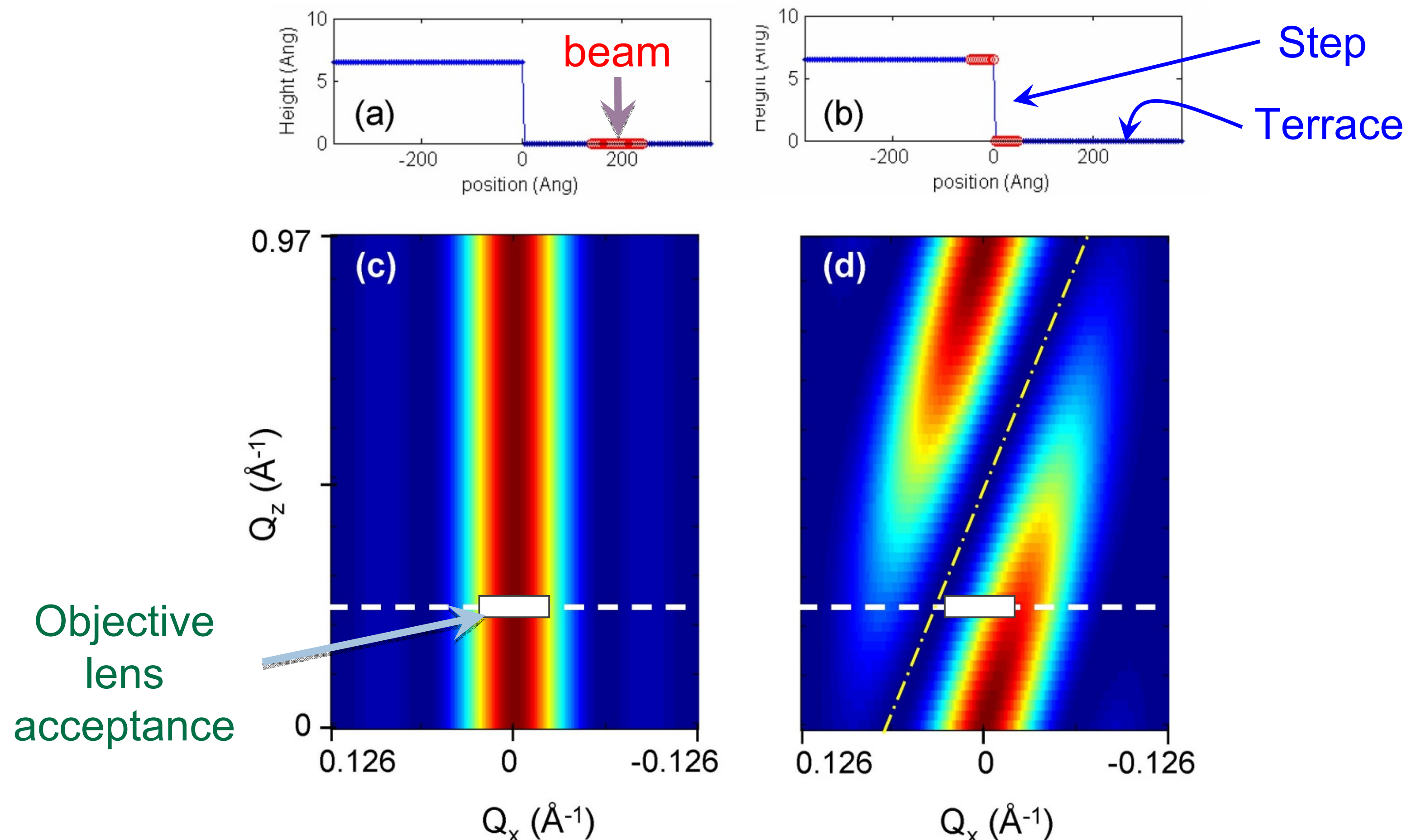
Characteristics:

⟶ Strong contrast (~100%), but weak reflected beam intensity ($R < 10^{-5}$)

⟶ Sub-nm vertical sensitivity, but modest lateral resolution (~100 nm),

Fenter et al., *Nature Physics* 2(10) 700-704 (2006)

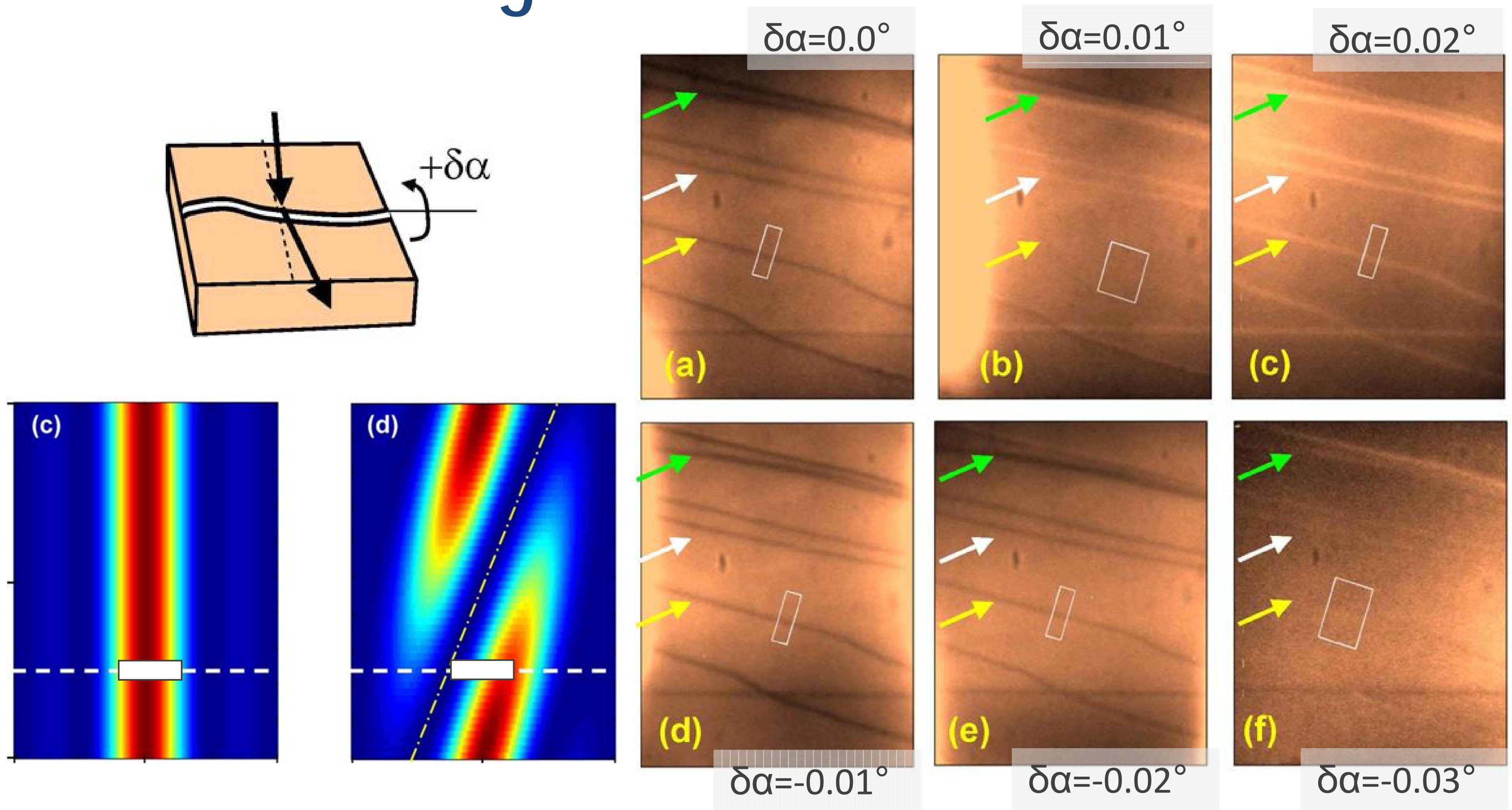
XRIM—Scattering View of Contrast Mechanism



- When the beam is on the terrace, the scattering intensity will all be accepted by the objective lens, i.e., the bright background;
- When the beam is over the step, some of the scattered intensity falls outside of the objective lens, i.e., the dark line appears.

Fenter et al., *Journal of Synchrotron Radiation*, ***15****, 558-571 (2008)*

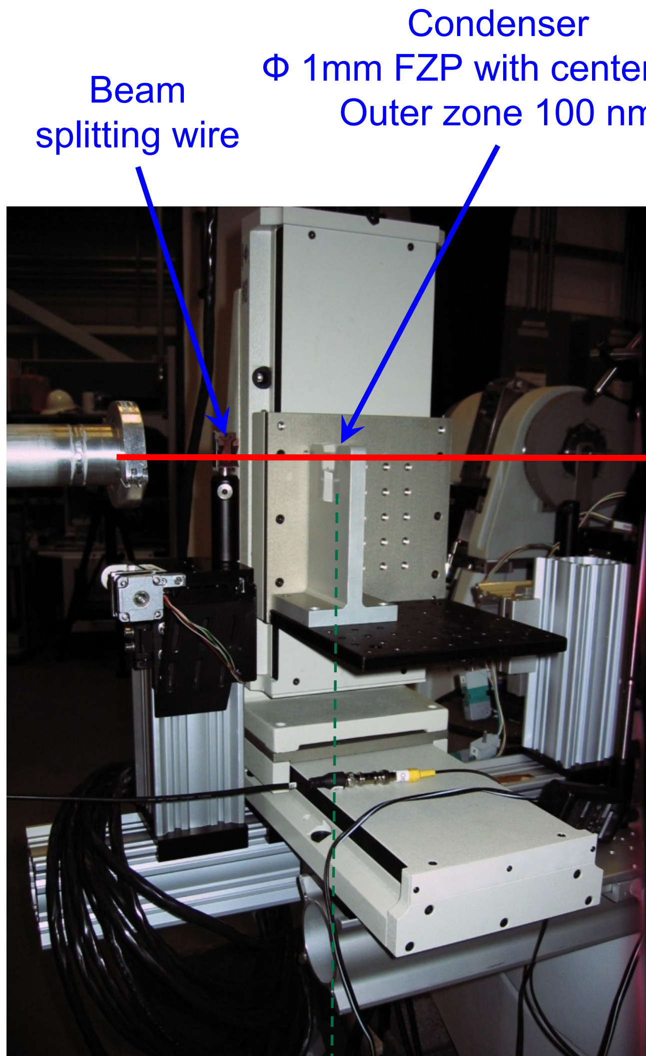
XRIM—Tuning the Contrast

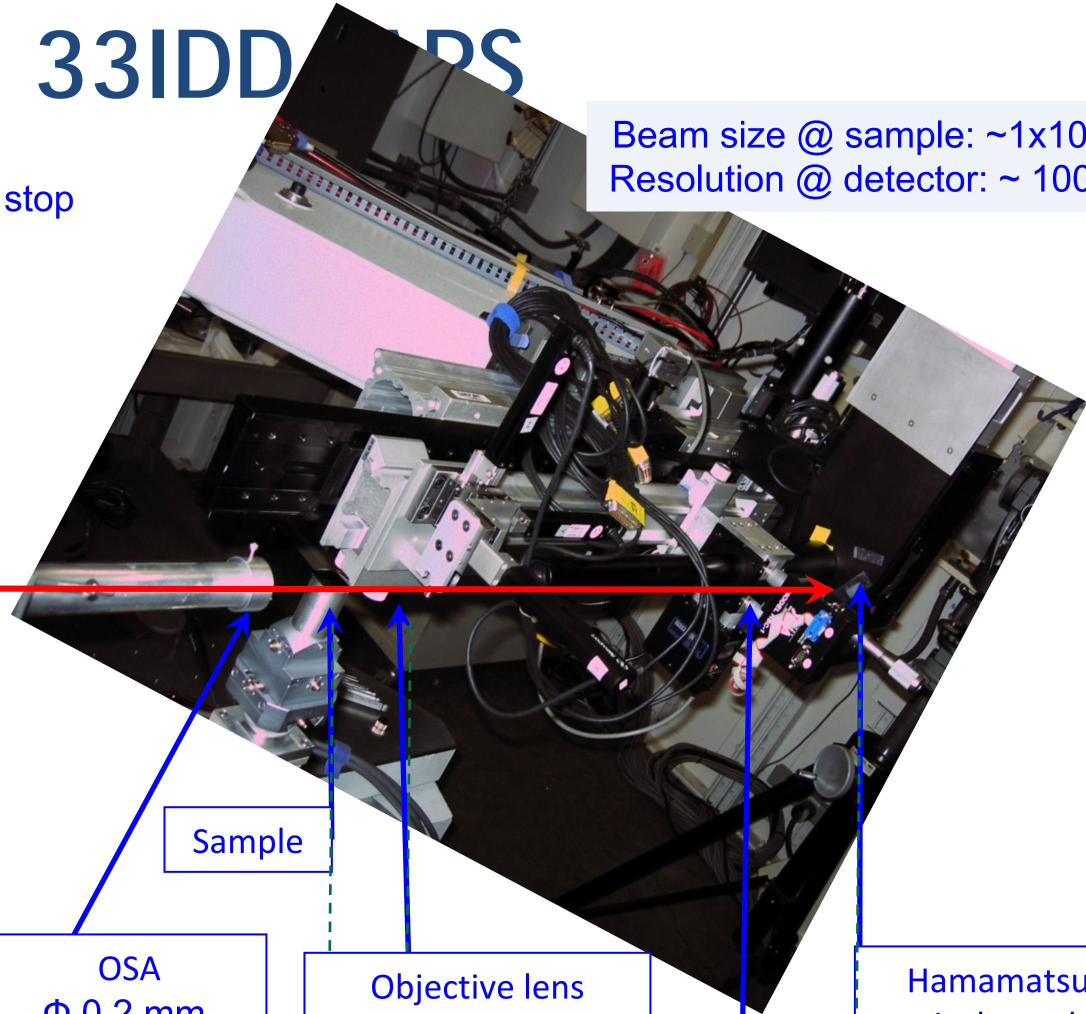


The offset angle from the specular condition, δα, controls the contrast between the terrace and the steps.

Fenter et al., *Journal of Synchrotron Radiation*, ***15***, *558-571 (2008)*

XRIM Setups at 33IDD APS

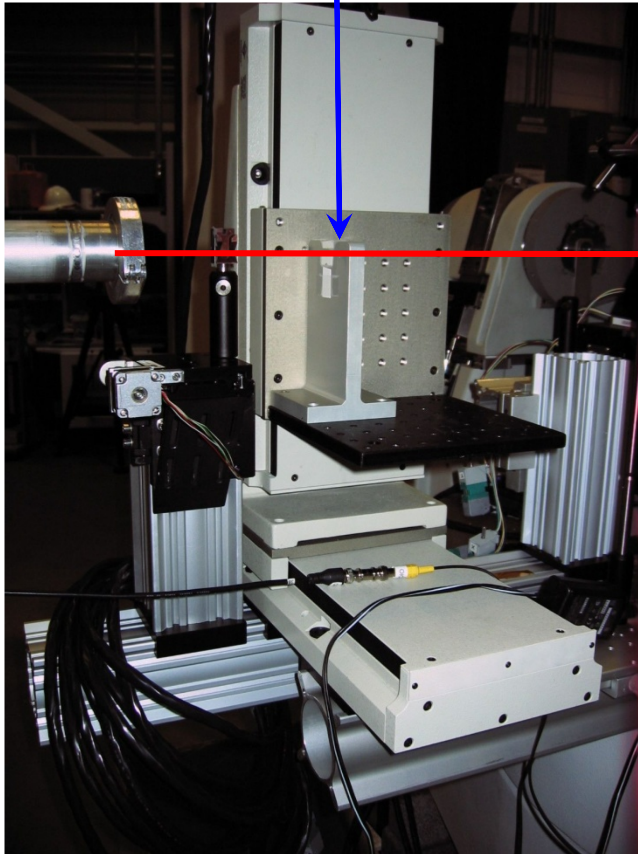


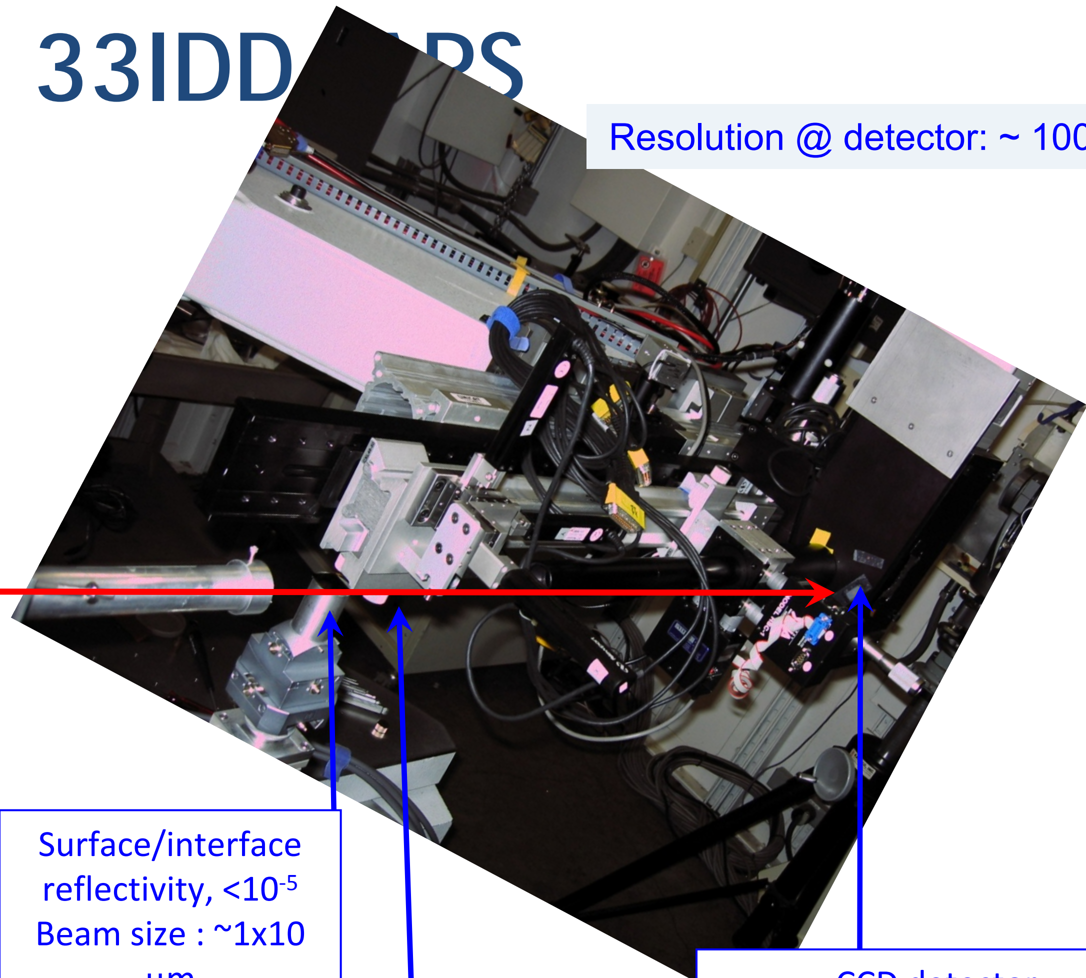


XRIM Setups at 33IDD APS

Resolution @ detector: ~ 100 nm

Condenser FZP
Theoretical efficiency ~30%
Actual efficiency ~ 10%





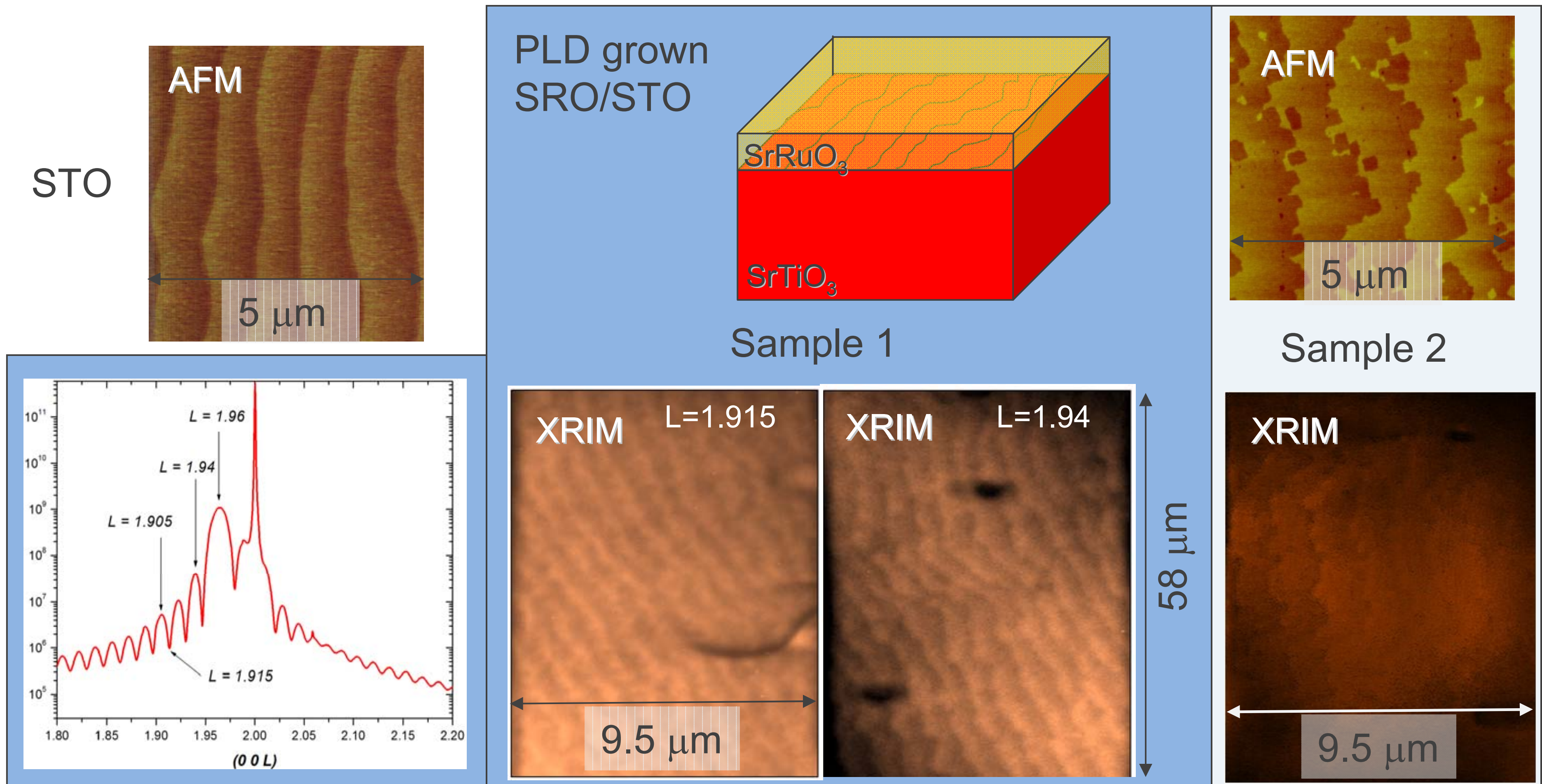
Surface/interface reflectivity, $<10^{-5}$
Beam size : ~1x10 μm

Objective lens
Theoretical efficiency ~ 20%
Actual efficiency ~ 8%

CCD detector
1 X-ray photon ~ 1 count
Count time: 20s – 2000s
Actual resolution : 170 nm

Source size ~16x280 μm, working energy 10keV, flux ~ 10^{12} photon/s

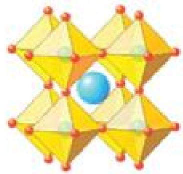
XRIM Measurements I – SRO/STO

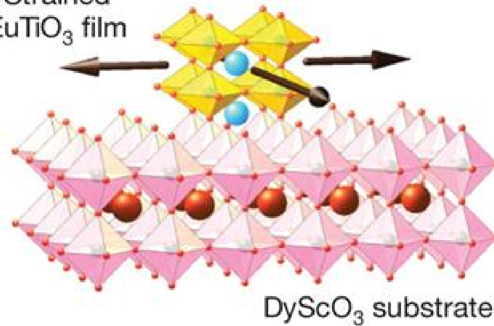


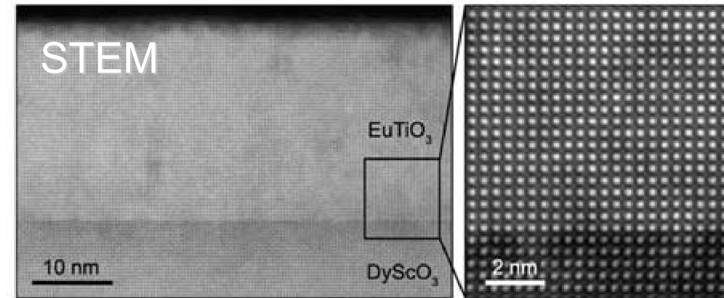
The steps on the STO surface (under ~400 Ǻ SRO film) can be seen on the sample 1, where the surface SRO features are smaller than the XRIM resolution. The zigzag steps on the SRO surface can be seen on sample 2 with XRIM as with AFM.

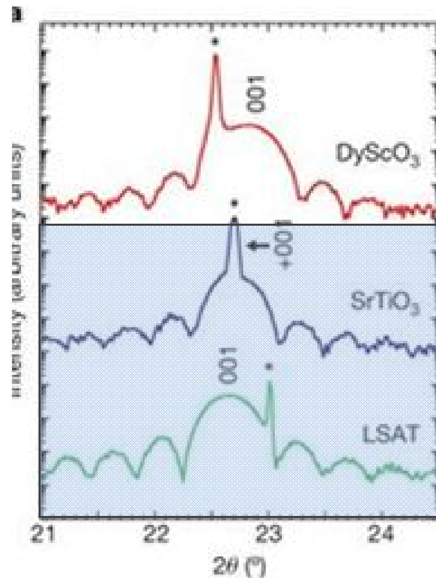
Sample from Gyula Eres, Christopher Rouleau, and Jonathan Tischler(ORNL).

XRIM Measurements II – ETO/DSO







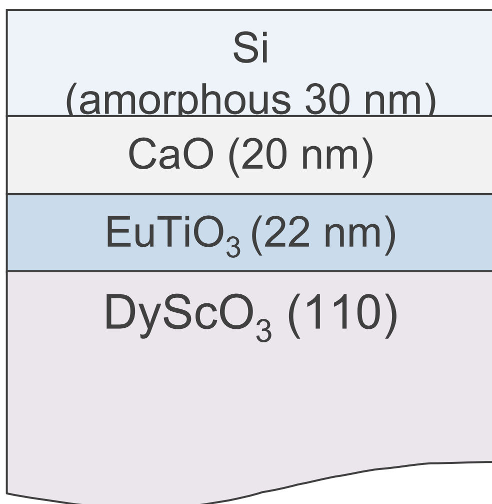


Surface normal direction:
DSO (110): c_{DSC_bulk} = 3.943 Å
ETO (100): c_{ETO_bulk} = 3.905 Å vs. c_{ETO_film} = 3.876 Å

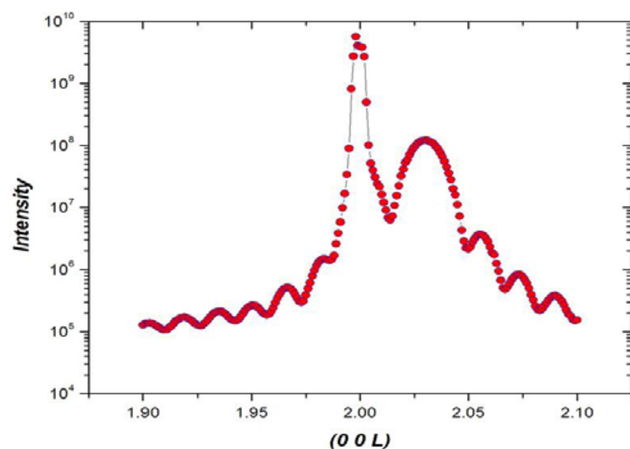
In plane, ETO film is under ~1.1% biaxial tension to commensurate to the DSO substrate. Such ETO film is potentially both ferroelectric and ferromagnetic.

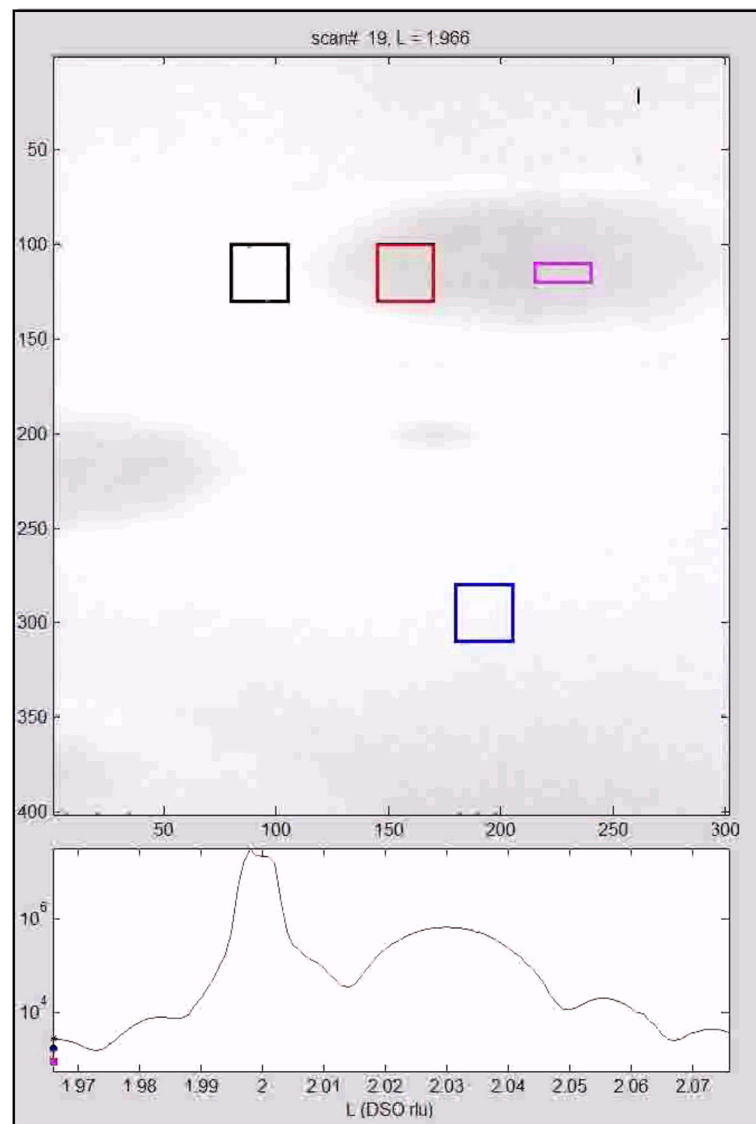
J. H. Lee *et al. Nature* **466**, 954-958 (2010)

XRIM Measurements II – ETO/DSO



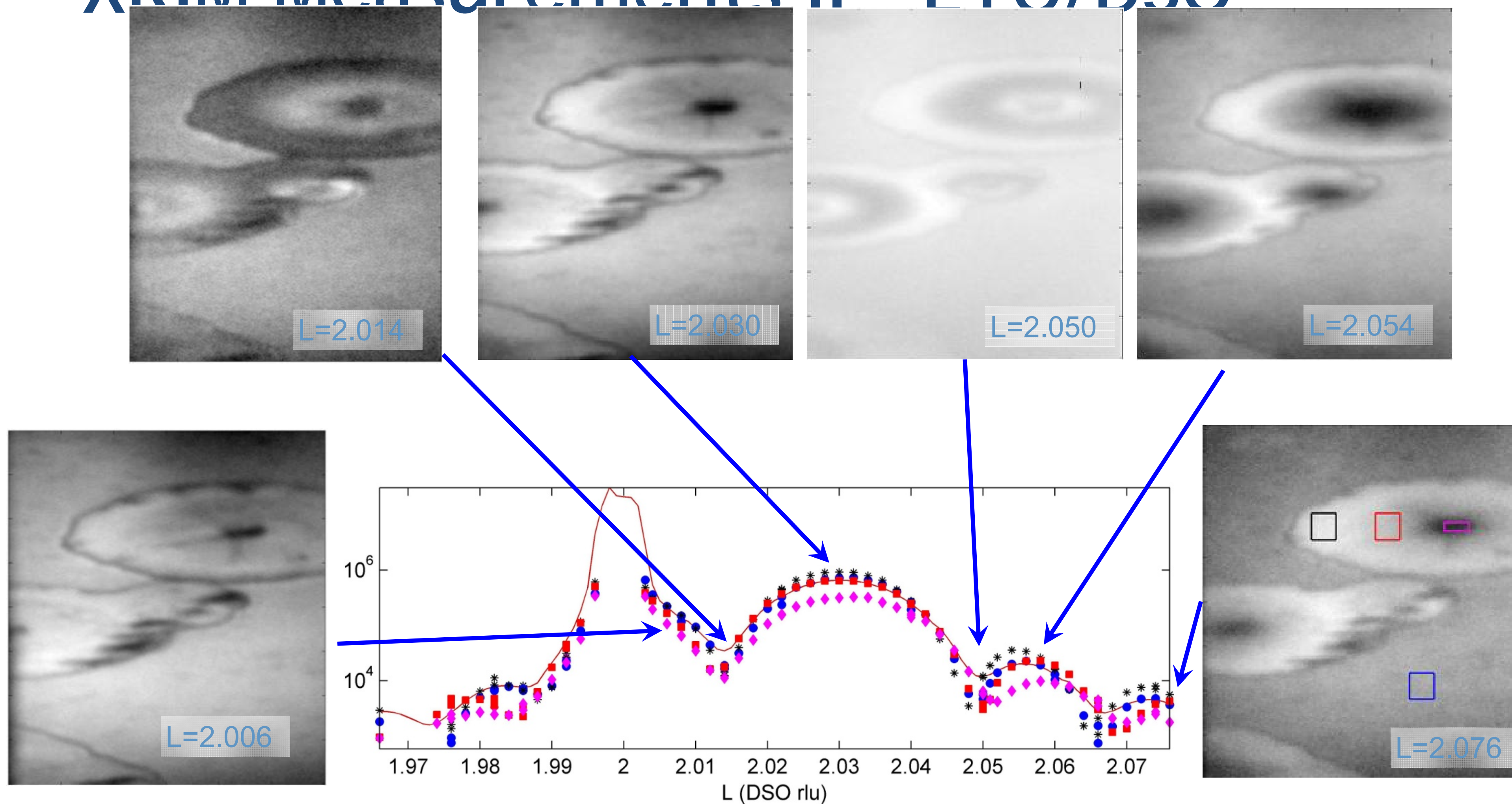
DSO: c_{DSO_bulk} = 3.943 Å
ETO: c_{ETO_film} = 3.884 Å





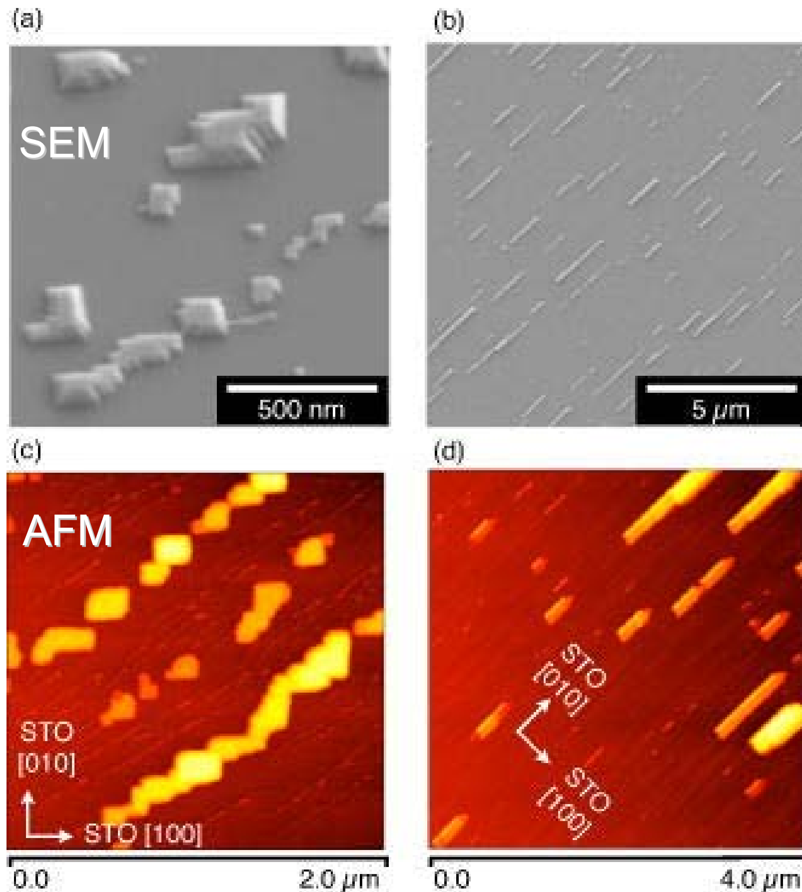
Sample from June Hyuk Lee, Darrell G. Schlom (Cornell), and John W. Freeland (APS, ANL)

XRIM Measurements II - ETO/DSO



The center of the circular structure is thinner. Maybe some growth problem.

XRIM Measurements III – Bi_2O_3/STO

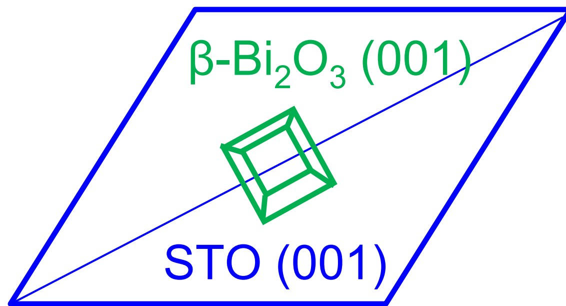


δ-Bi_2O_3 is an important oxide ionic conductor, yet bulk phase is only stable in a narrow temperature range. By epitaxial growth on the slightly lattice mismatched oxide substrate, the δ-Bi_2O_3 nano-structure or thin film can be stable in room temperature.

Images of δ-Bi_2O_3 nanostructures on (001) $SrTiO_3$. (a) and (c), $SrTiO_3$ miscut <0.2°, nanoislands form with {101} side-wall facets and coalesce along the substrate step edges. (b) and (d), On $SrTiO_3$ with 1° miscut along the [100], nanowires form along the step edges. The heights of the nano-structures are around100 nm.

Proffit et al., Applied Physics Letters (96):021905 (2010)

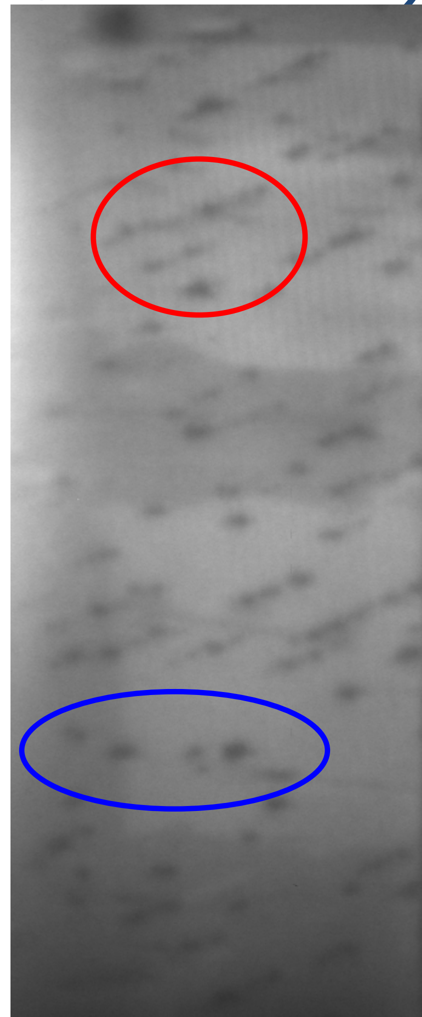
XRIM Measurements III – Bi_2O_3/STO



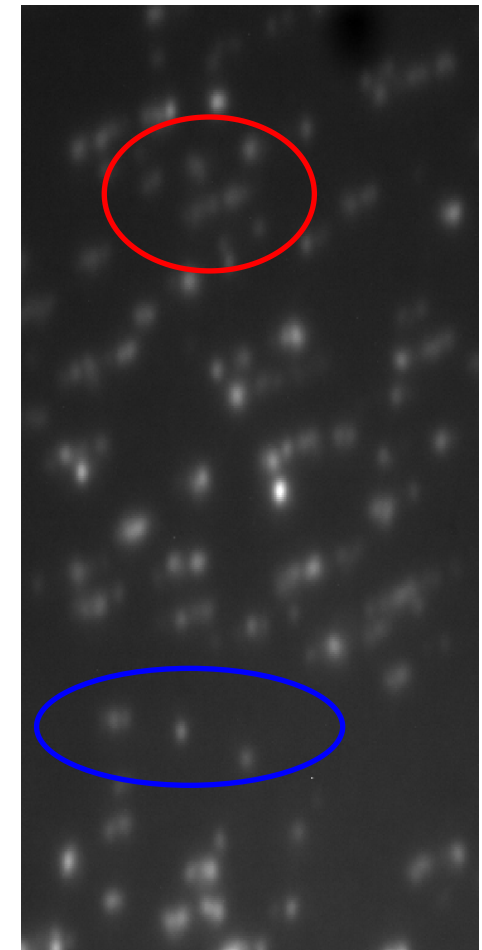
Epitaxial Bi_2O_3 nano dots on STO (001) surface, a mixture of β and δ phases, with ~ 500 nm edge size.

Surface normal direction:
β-Bi_2O_3: c_0 = 5.62 Å
δ-Bi_2O_3: c_0 = 5.531 Å
STO: c_0 = 3.905 Å

- Near STO (002) Bragg peak, the nano dots appear to be dark.
- Near the -Bi_2O_3 (002) Bragg peak, some of the dots light up.



L = 1.992 (STO)



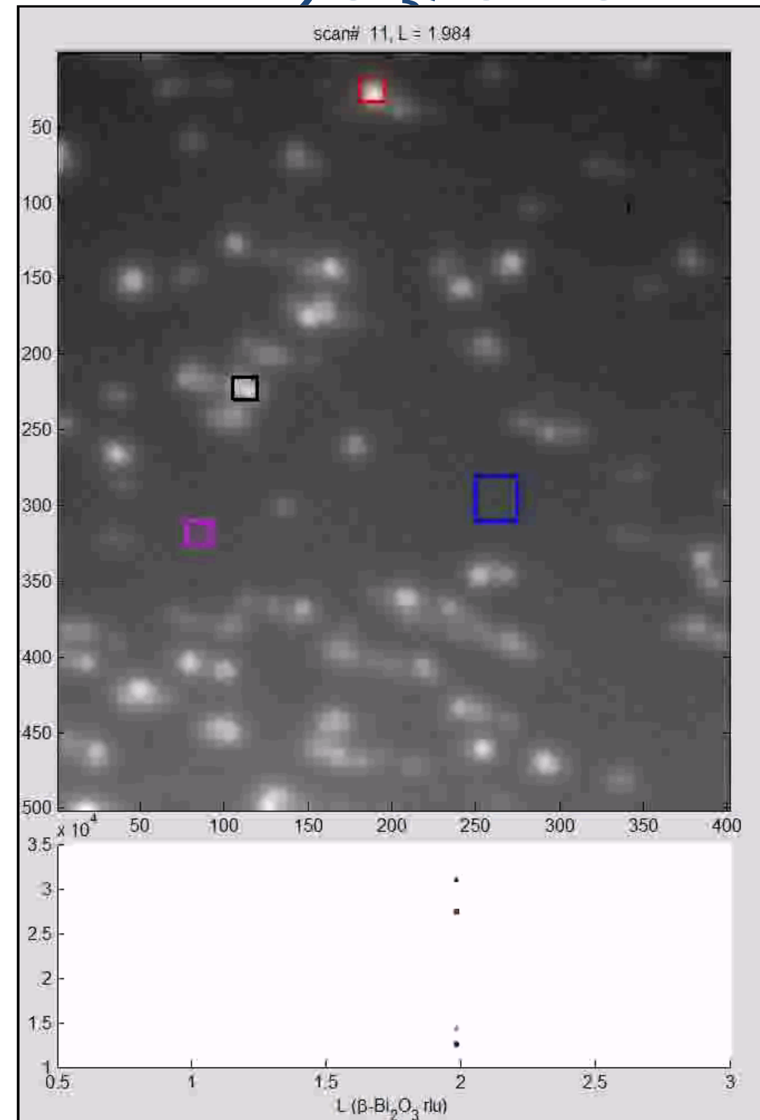
L = 2.002 (β-Bi_2O_3)

Sample from Danielle Proffit (NU & ANL) & Guo-Ren Bai (ANL), et al.

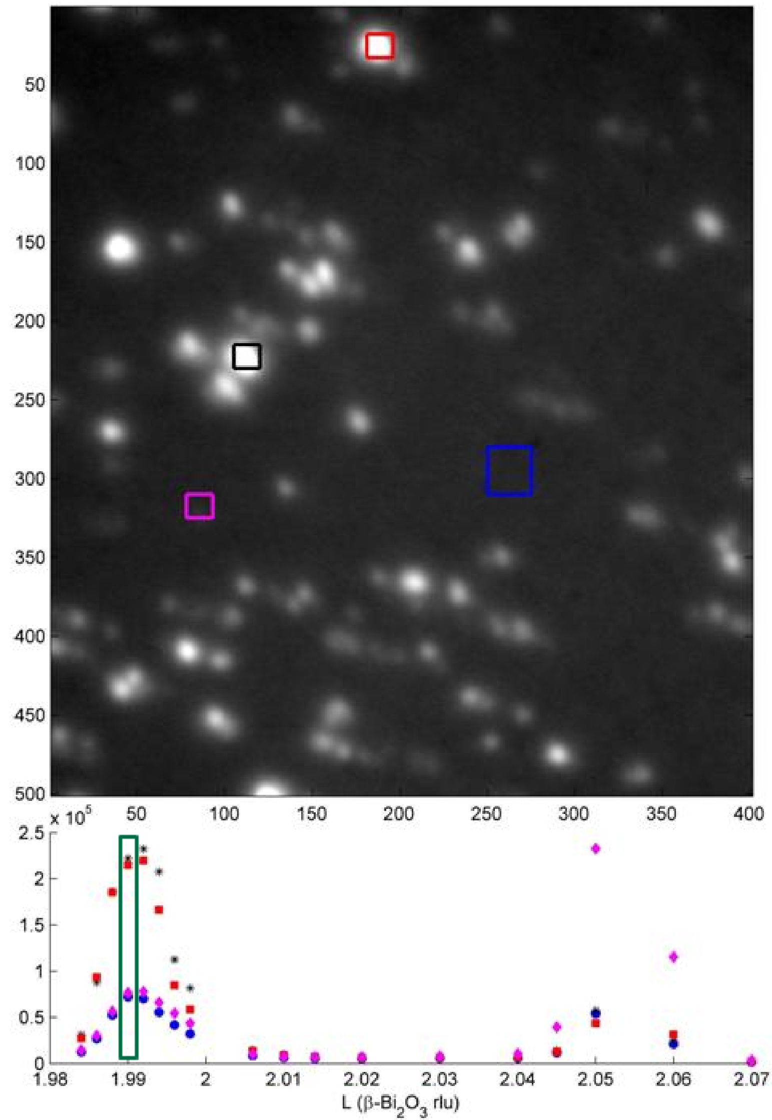
XRIM Measurements III – Bi_2O_3/STO

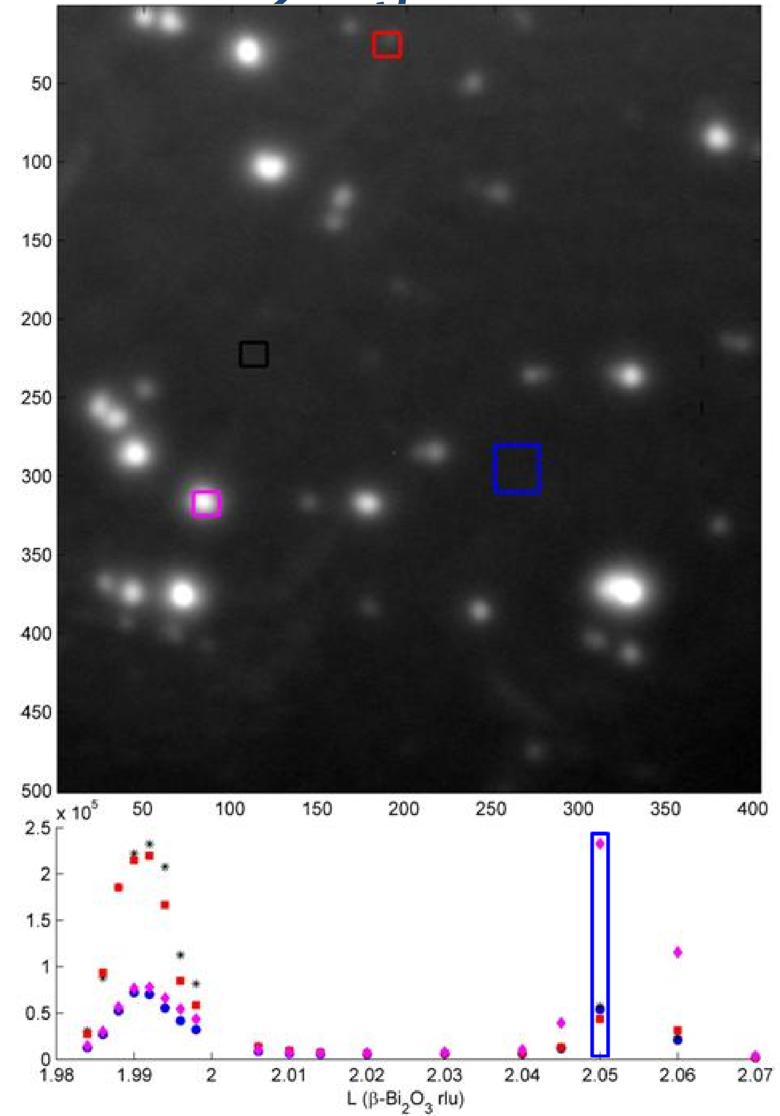
A series of XRIM images are taken along the surface normal direction, swiping through the β-Bi_2O_3 (002) Bragg peak and the δ-Bi_2O_3 (002) Bragg peak. The dots lighting up at the different reciprocal space positions are primarily different phases.

Bottom panel shows the integrated intensities of the boxes marked on the image.



XRIM Measurements III – Bi_2O_3/STO





Summary

- X-ray reflection interface microscopy is capable of imaging the surface, buried interface and thin film topography.
- The information carried in the XRIM images is quite rich. More effort is needed to decode them.
- With improved optics and detector, the in-situ, real time observations of many surface/interface processes, such as the thin film growth, surface dissolution and precipitation, could be realized.
- Combined with the X-ray scattering measurements, both the averaged and the localized information of the surface/interface could be quantitatively revealed.

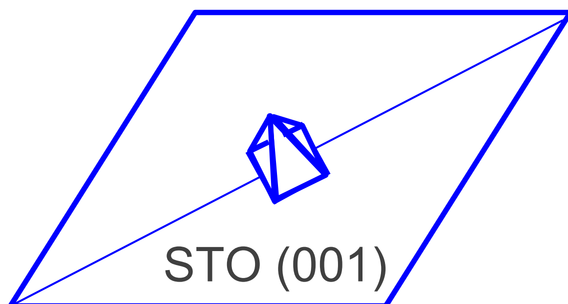
XRIM Further Developments

- In situ measurements (during growth, solid-liquid interface, etc)
- Improve the efficiency of the optics (from <1% → 10-15%)
- Improve the resolution (<50 nm lateral resolution)
- Make it drop-in ready, easier to be combined with scattering measurements in the beamline.

Acknowledgement

- The XRIM data were measured at beamline 33ID at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (contract no. DE-AC02-06CH11357).
- The SRO/STO sample is from Gyula Eres, Christopher Rouleau, and Jonathan Tischler (Oak Ridge National Laboratory).
- The ETO/DSO sample is from June Hyuk Lee, Darrell G. Schlom (Cornell University), and John W. Freeland (APS, ANL).
- The Bi_2O_3/STO sample is from Danielle Proffit (Northwestern University & ANL) and Guo-Ren Bai (MSD, ANL), et al.
- The original development of XRIM was carried out at beamline 12ID, APS, ANL, with the help from Changyong Park, Vaibhav Kohli, and Jeff Catalano (CSE, ANL).

XRIM Measurements II – Bi_2O_3/STO



Nano-pyramid Bi_2O_3 epitaxial on STO (001) surface.
~ 500 nm edge size.

Surface normal direction:
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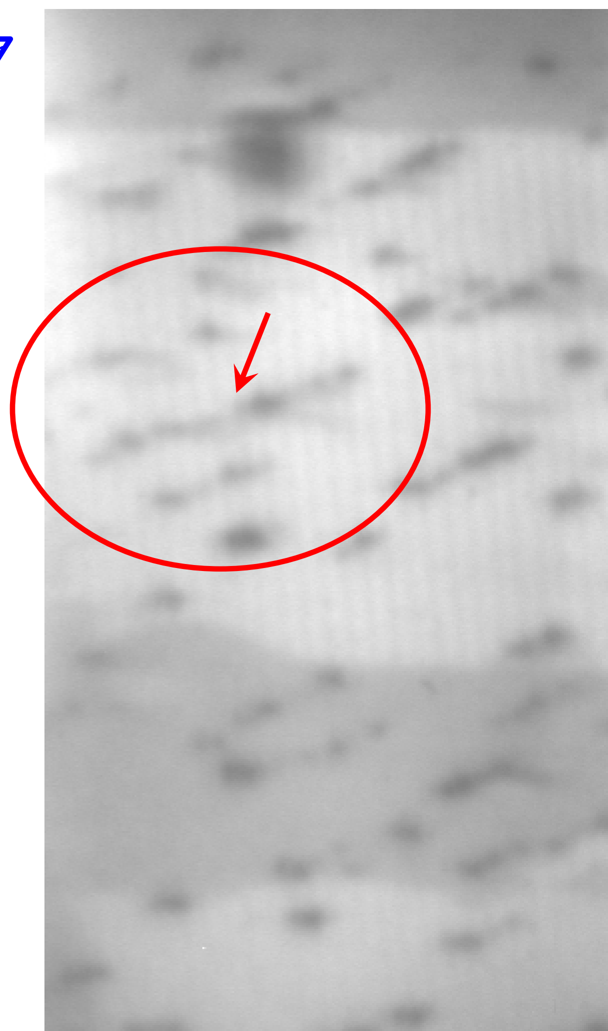
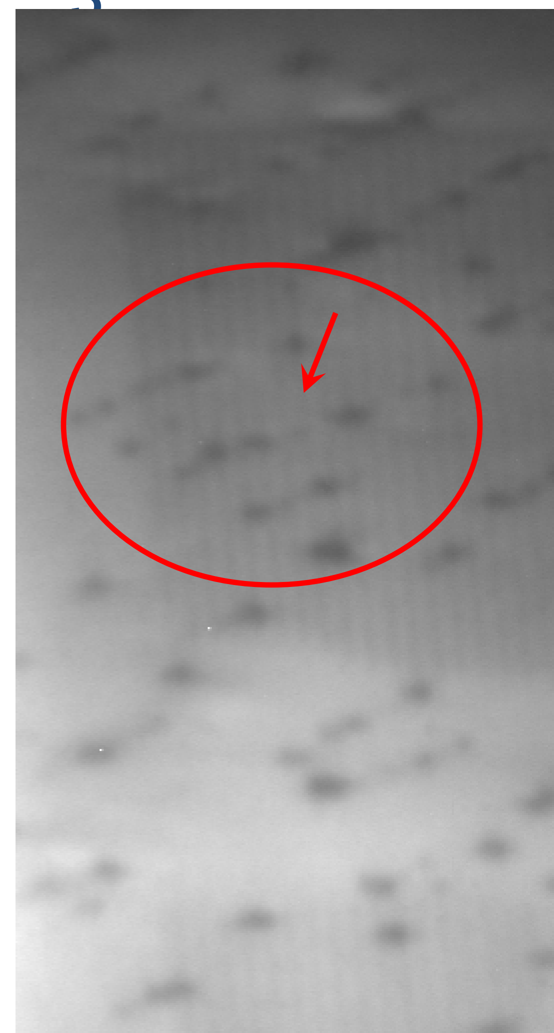


L = 1.99 (STO)



L = 2.01 (STO)