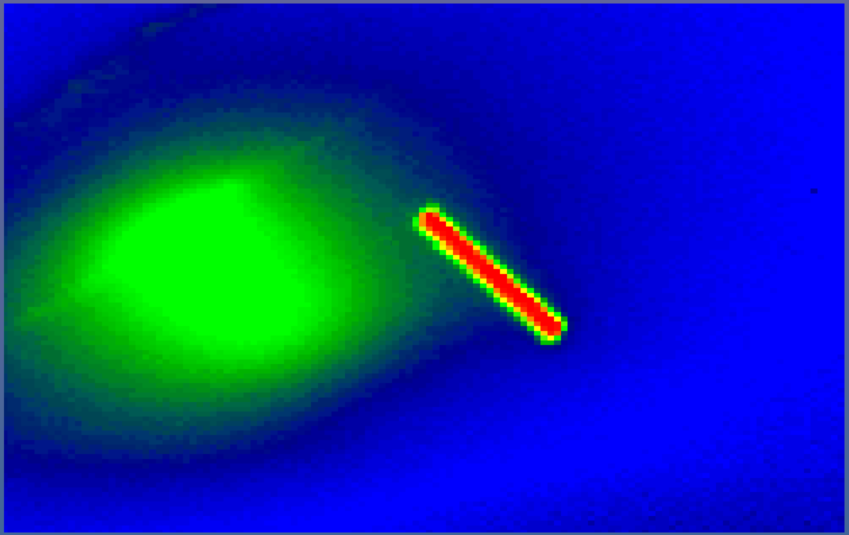
A new era in surface diffraction – pulsed laser deposition of complex metal oxide thin films



Phil Willmott, Christian Schlepütz, Roger Herger,
Oliver Bunk, and Bruce Patterson

Beamline X04SA Materials Science, Swiss Light Source

ERL Workshop 3: "Almost Impossible Materials Science"
June 16 - 17th, 2006

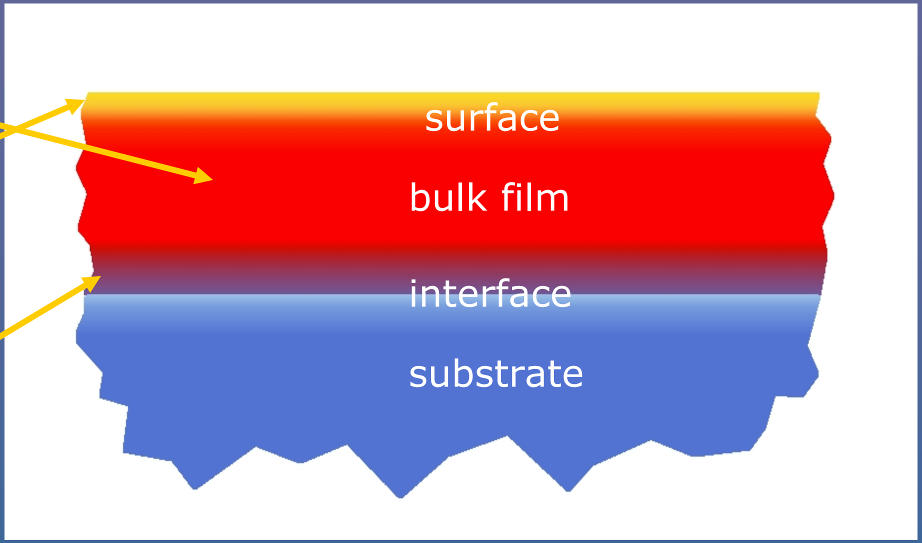
Motivation

- Strongly correlated electron systems
  - Perovskites ABO_3
- Size effects (cation/anion ratio)
  - Rotation of O-octahedra
  - Mott-Hubbard model [U (Coulomb) v W (bandwidth)]
- Choice of cation (valence), oxygen vacancies
  - Vary dimensionality and doping
- Jahn-Teller distortions
- Heteroepitaxial strain (films)

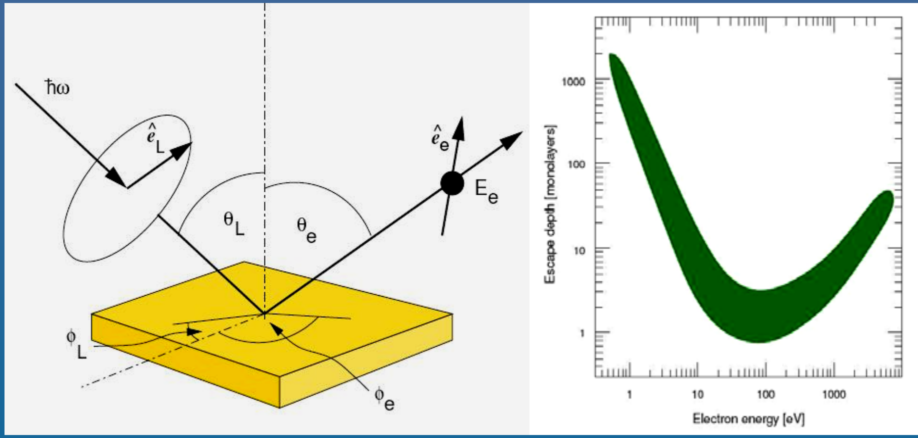
Subtle structural differences at the surface and/or film-substrate interface, due to relaxations/reconstructions, can lead to fundamental changes in the physical properties!!

Motivation

- Downsizing
- Surface/interface effects
  - e.g., FE-STO surface
    D.D. Fong *et al.*, Science **304** 1650 (2004)
  - e.g., 2-D e^- gas, interface STO/LAO
    A. Ohtomo and H.Y. Hwang, Nature **427** 423 (2004)

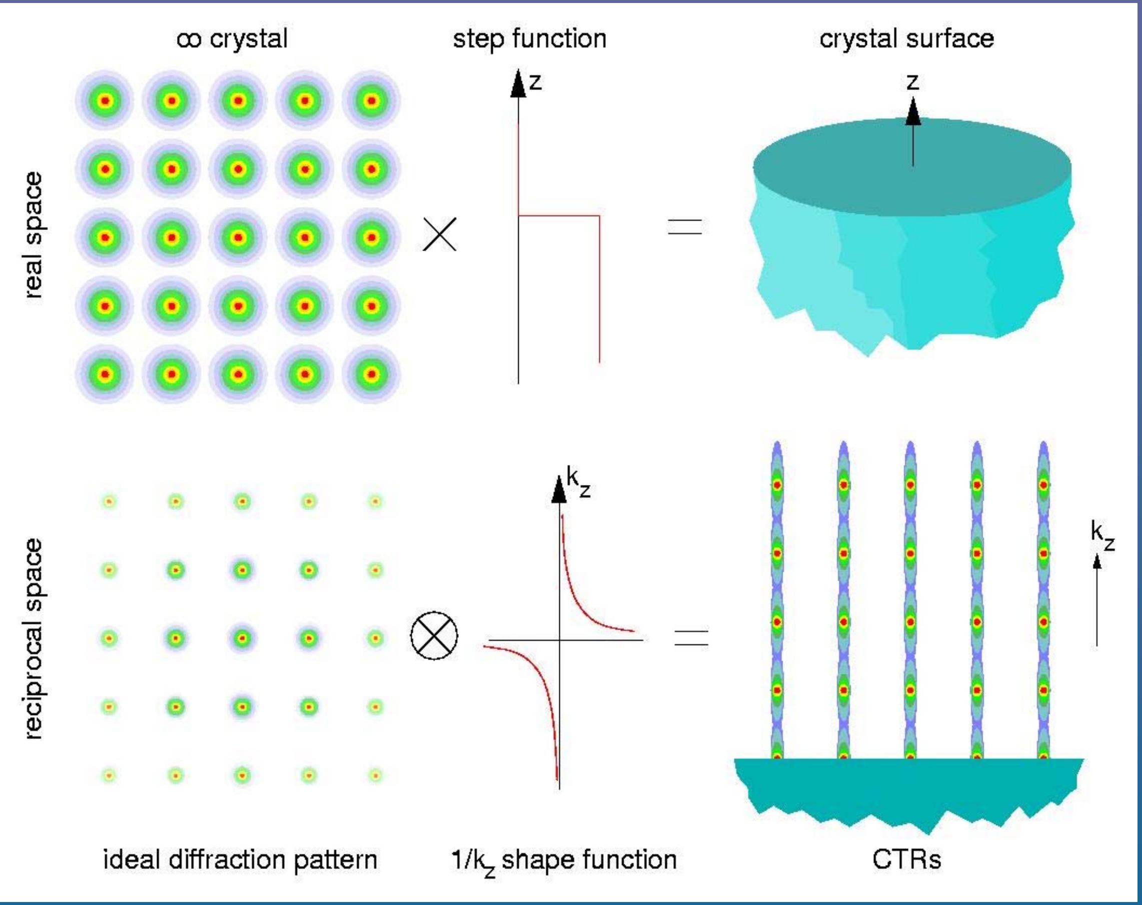


- Bandstructure determination photoelectron spectroscopy
  - universal curve (e^- escape depth) ~ 5 ML
  - Depth of surface ~ 5 ML
  - Measuring bulk properties?
    H.Dulli *et al.*, Appl. Phys. Lett. **77** 570 (2000)

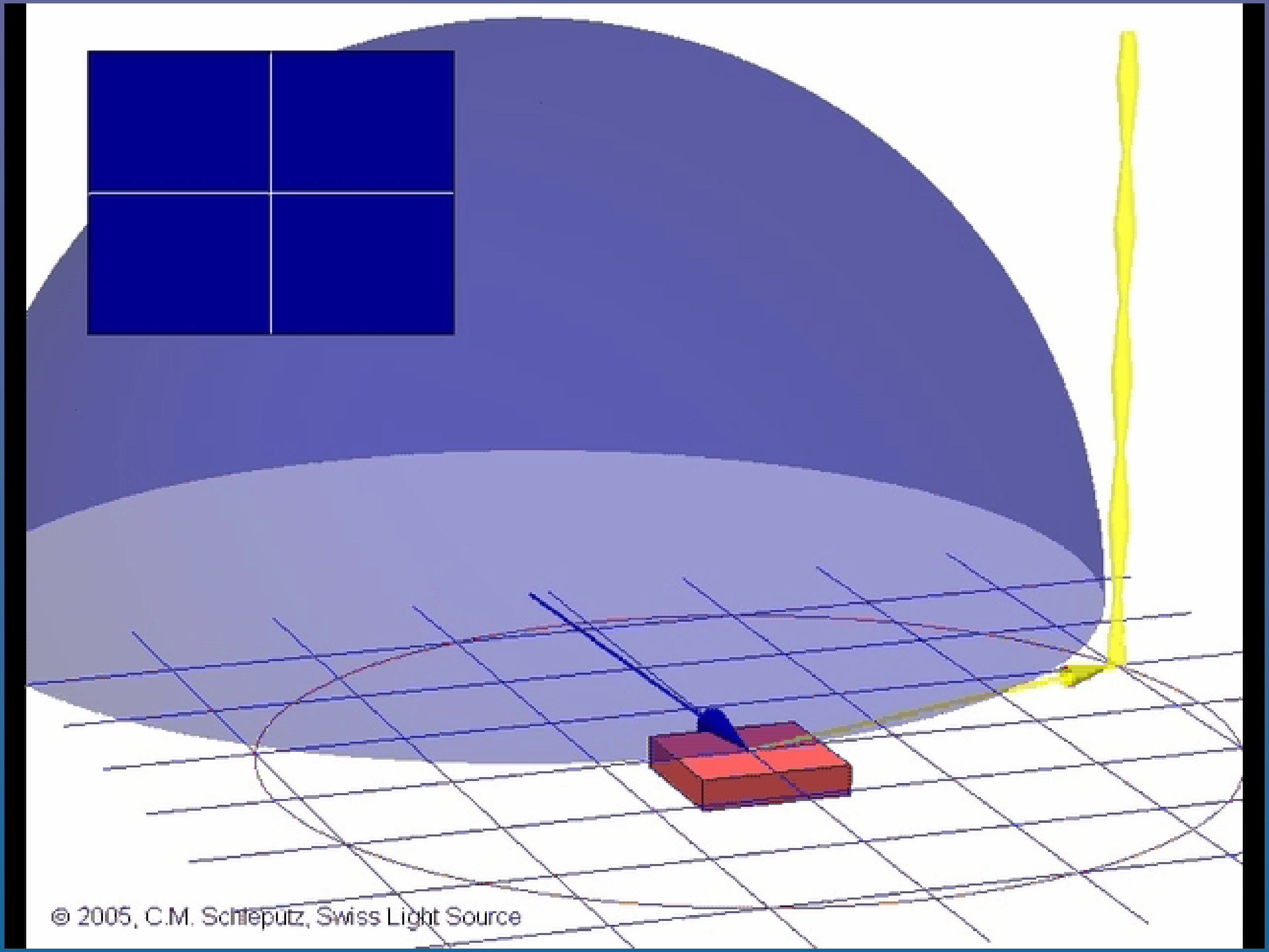


Surface X-Ray Diffraction

- SXRD requires:
  - Atomically flat surfaces
  - High photon flux (SR)
  - Minimization of background signal
  - A very good x-ray detector (weakest part of signal generally the most important!!)

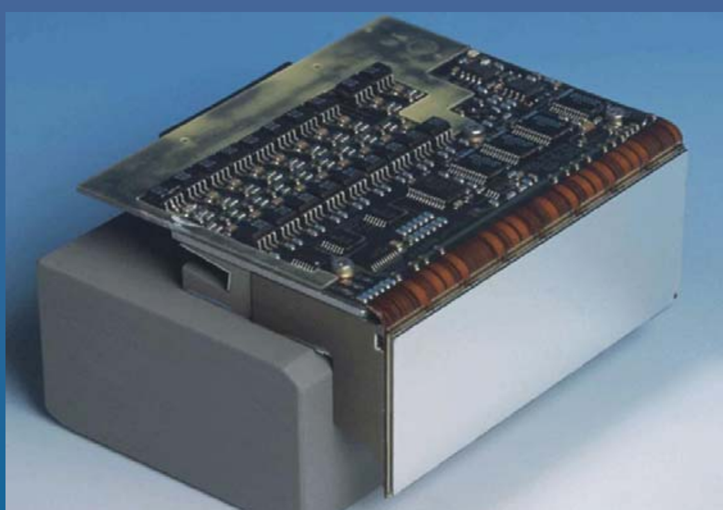


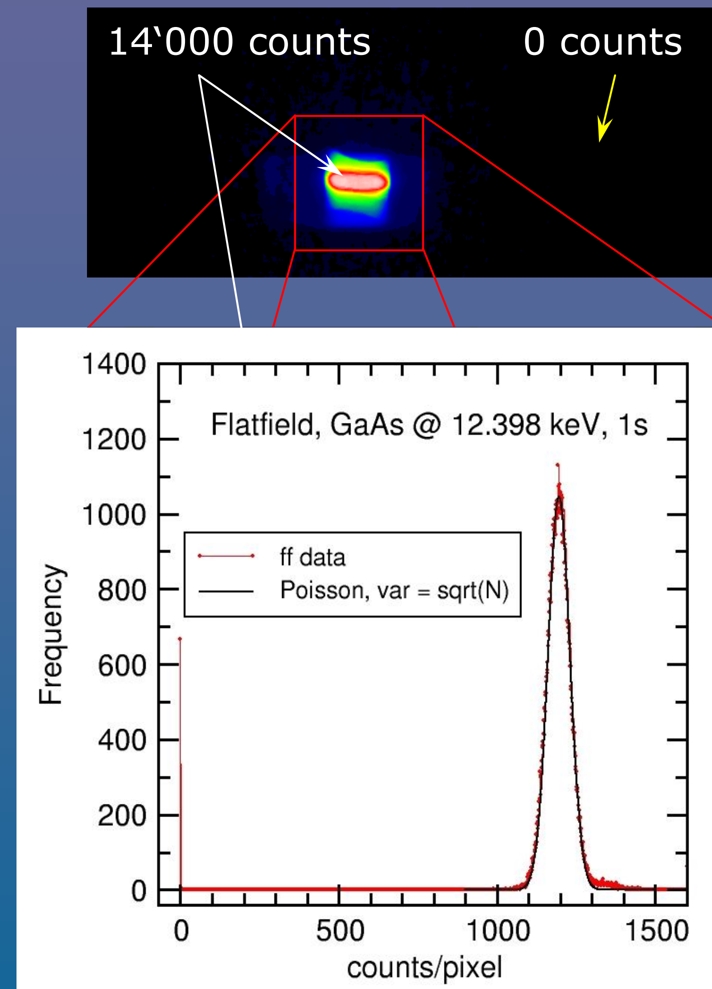
Recording CTRS and FORs



The PILATUS II pixel detector

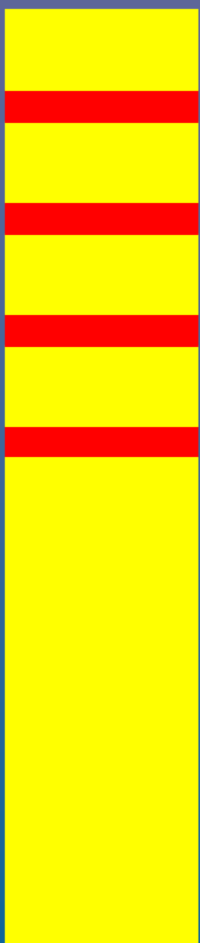
- 20 bit counter/pixel → accumulates > 10^6 cts before saturation
- Linear counting rates up to 10^6 cts/s
- 487×195 pixels, 172×172 μm^2 each
- Single-photon counting technology, no dark-noise, < 0.1% dead pixels
- Up to 100 frames/second





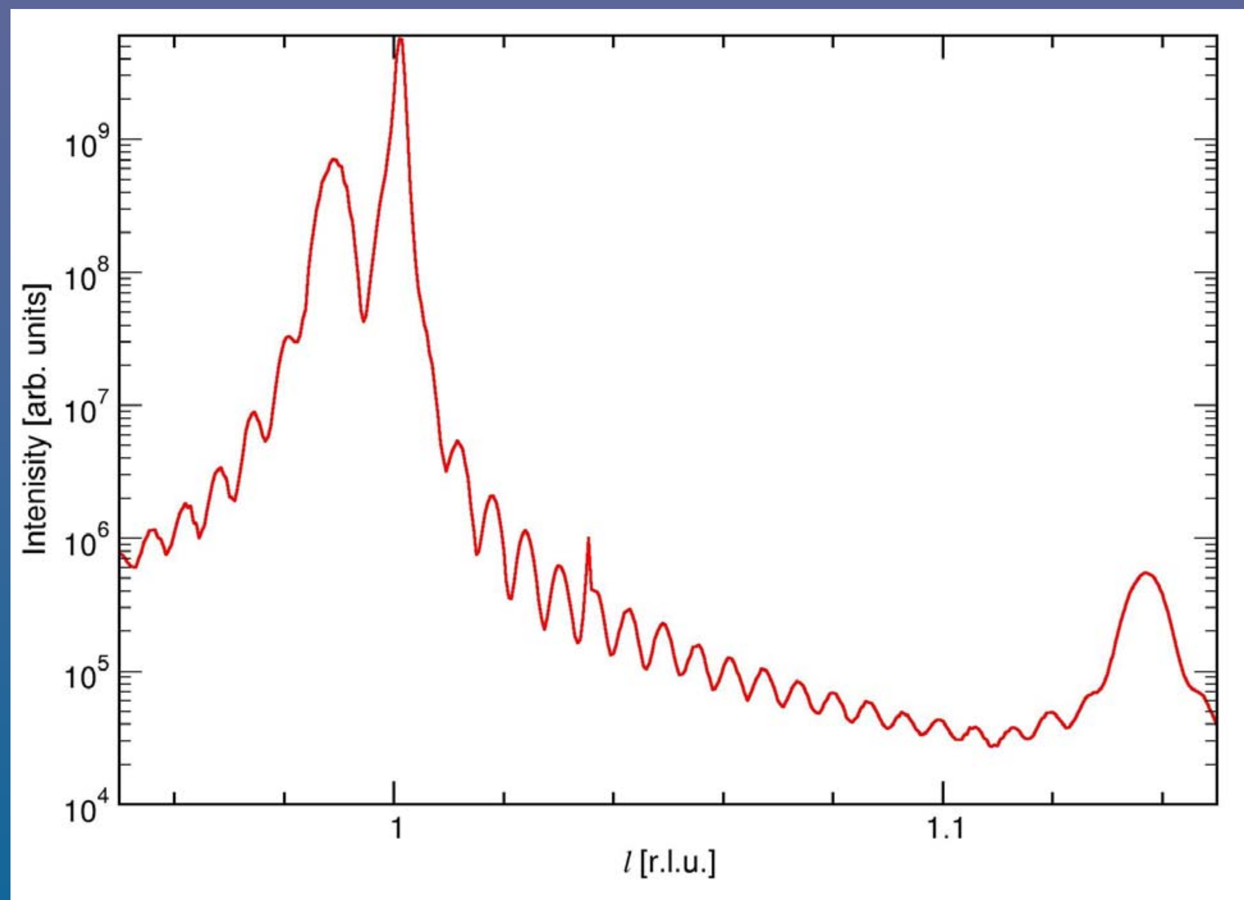
Results using P-II

- Raw data: Dawber, Lichtensteiger, *et al.* (Uni Geneva)

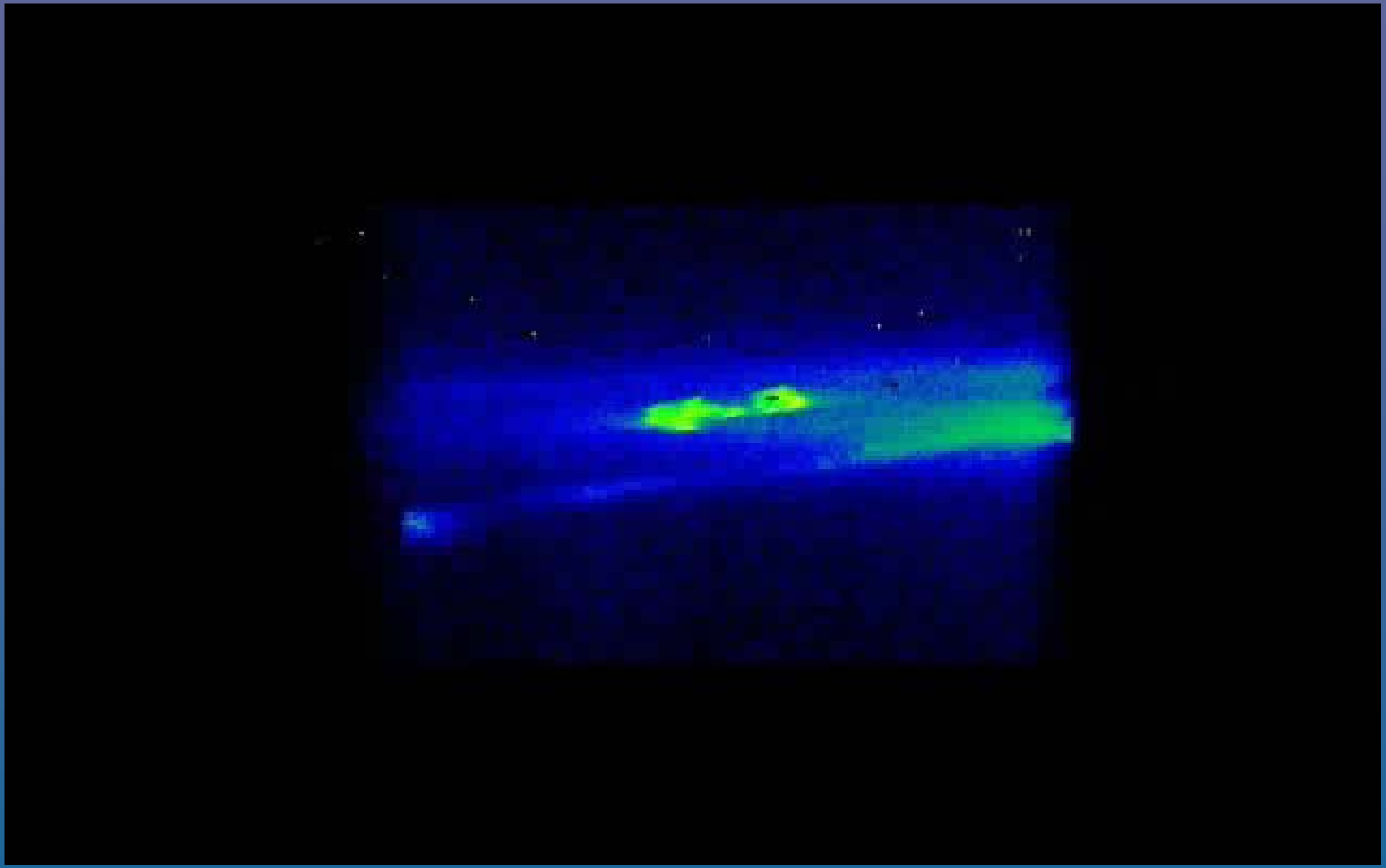


24 x
(5 ML
$SrTiO_3$
+ 2 ML
$PbTiO_3$)

$SrTiO_3$
substrate

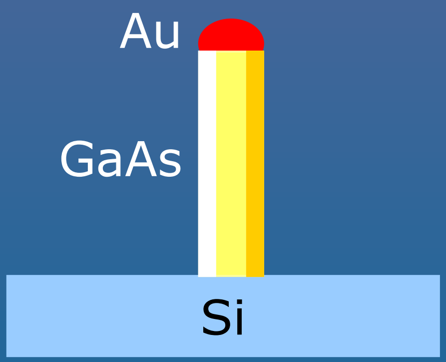


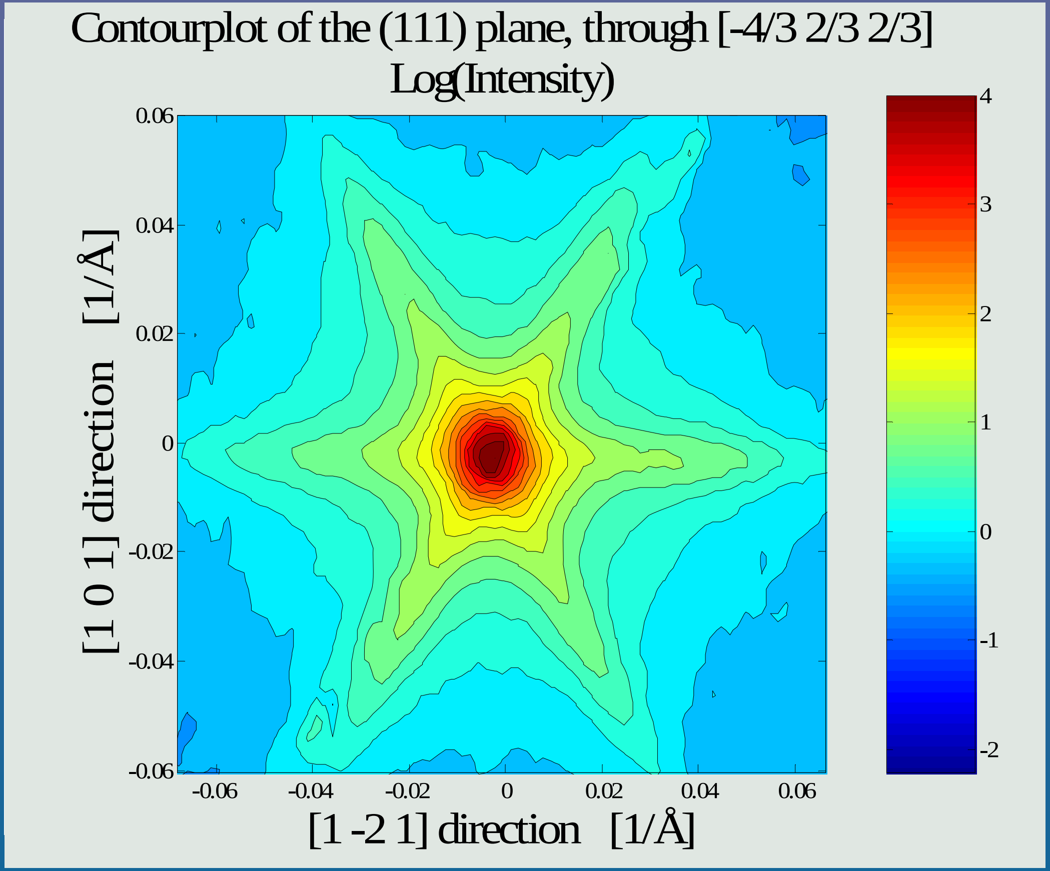
And how it looks



GaAs nanorods

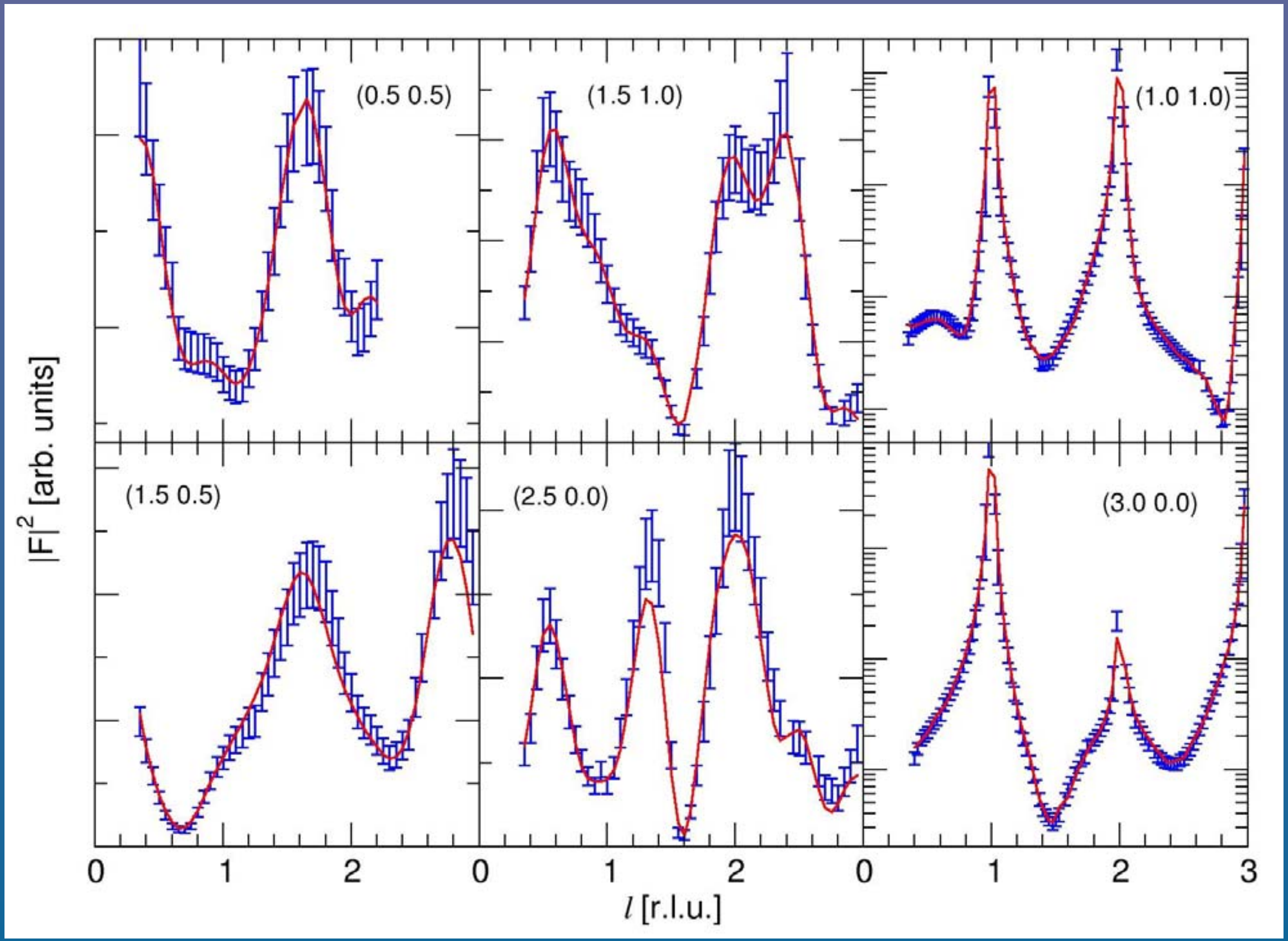
- R. Feidenhans'l and S.O. Mariager (Uni Copenhagen)
  - Au/GaAs rods have hexagonal cross-section on Si(111)
  - 6 CTRs
  - 15 mins, PII
  - c.f. 4 hours, pt. det.





Strontium titanate

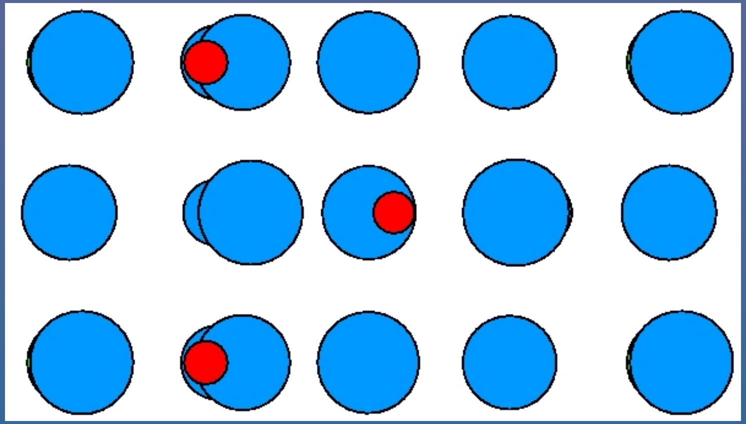
- 1800 independent structure factors: 9 CTRs, 17 FORs
- (2x2), (2x1), (1x1) domains



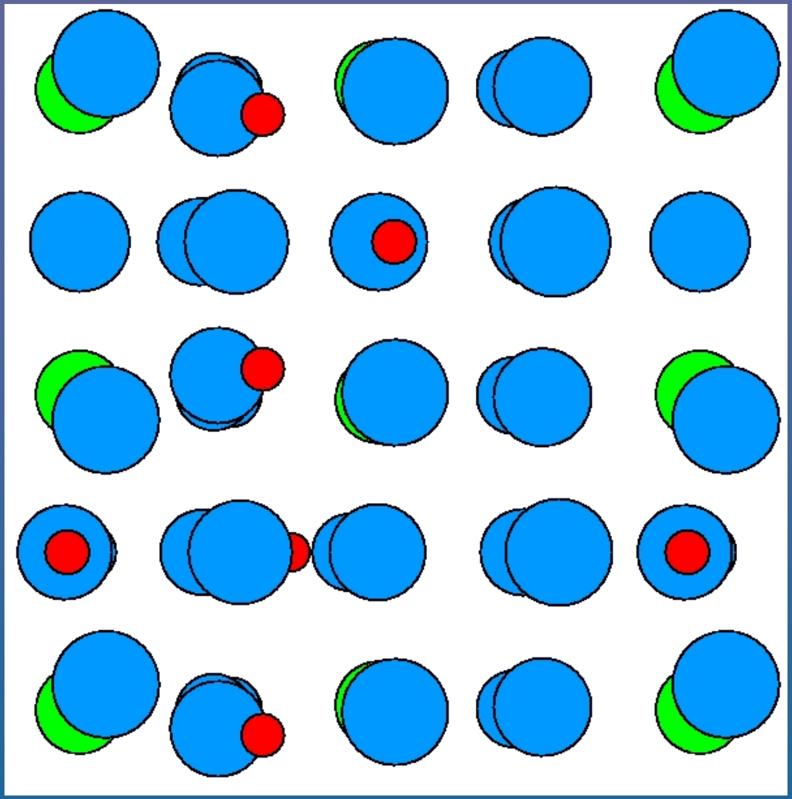
- $\chi^2_{red} = 0.99$

Strontium titanate

- Models



(2x1)



(2x2)

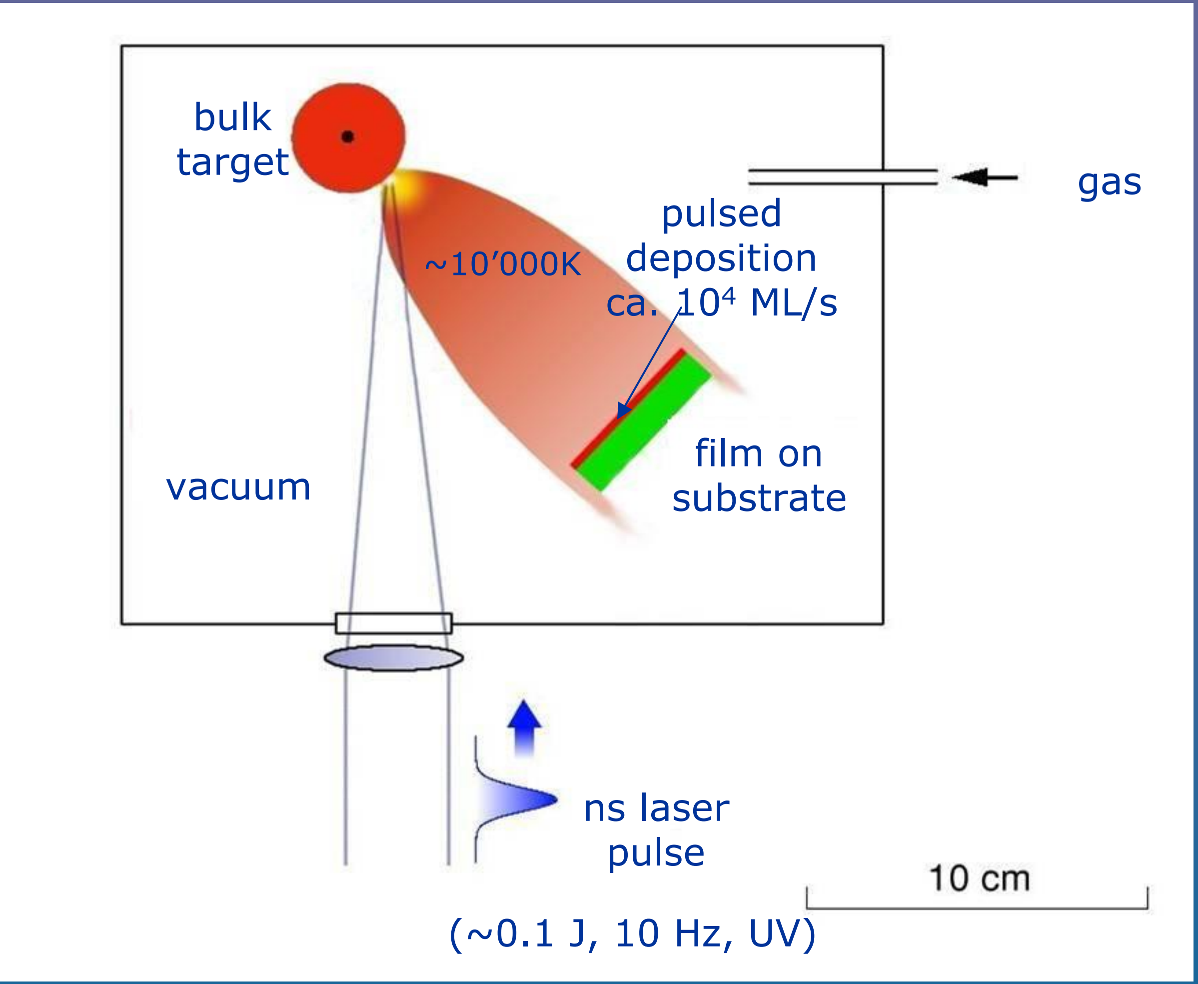
- Hard work modelling – see later!

Preparing surfaces

- Single crystal available as bulk?
  - High quality?
  - Atomically flat?
- Cleaving plane?
  - (quasi-)cubic – NO!
  - Interest in other plane?
- Problems with the above?
- Thin films!
- Pulsed laser deposition (PLD)

- P.R. Willmott, Prog. Surf. Sci. **76** 163 (2004)

PLD at the Swiss Light Source



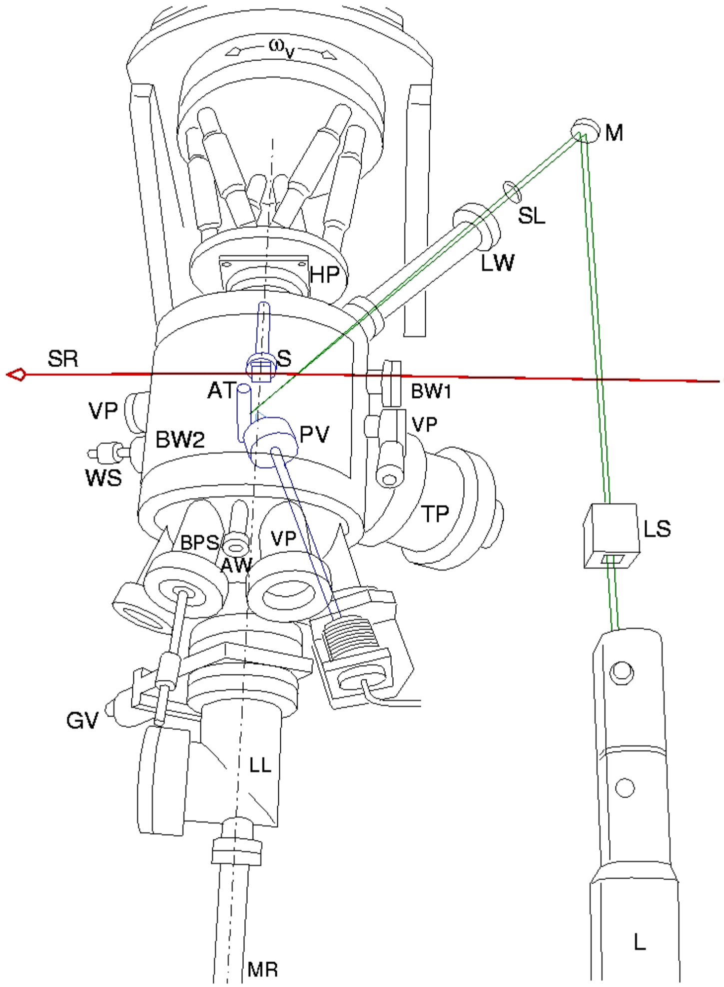
P.R. Willmott and J.R. Huber, Rev. Mod. Phys. **72** 315 (2000)

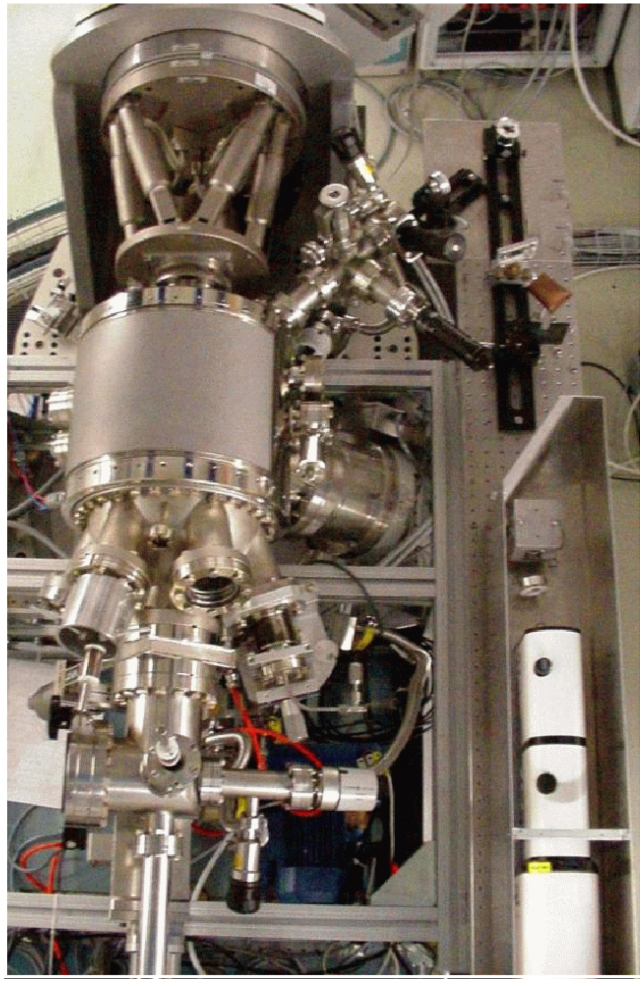
PLD@SLS - unique features

Synchronized gas pulse

Rapid target movement - alloys

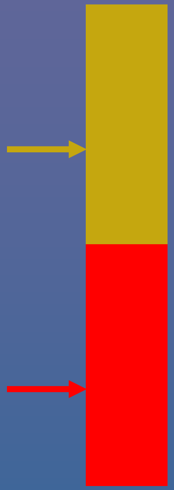
SXRD and in-situ PLD – the perfect marriage?

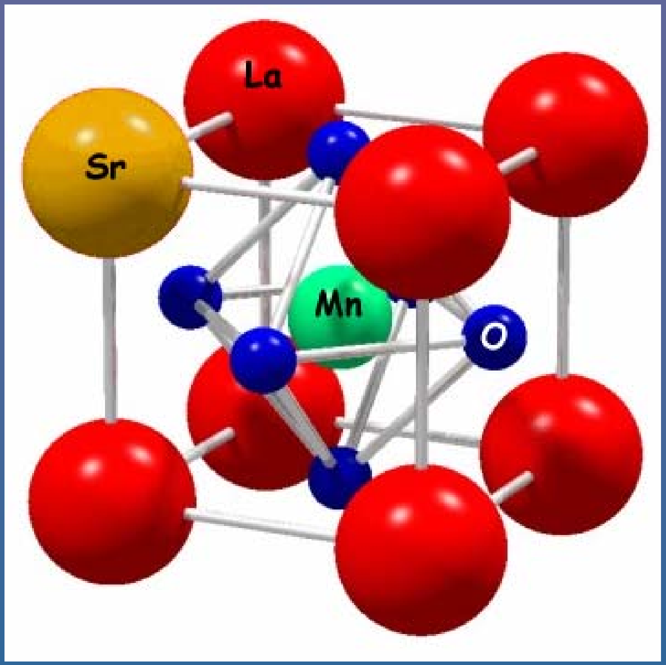




$La_{1-x}Sr_xMnO_3$ thin films

- Ablate $LaMnO_3/SrMnO_3$ rod
  - Any choice of x!
- > 100 nm growth
  - Still 2-D (RHEED)
  - High crystalline quality (channeling-RBS)
- ML-for-ML studies
  - Grow 1 ML
  - Full SXRD data set
  - Repeat…





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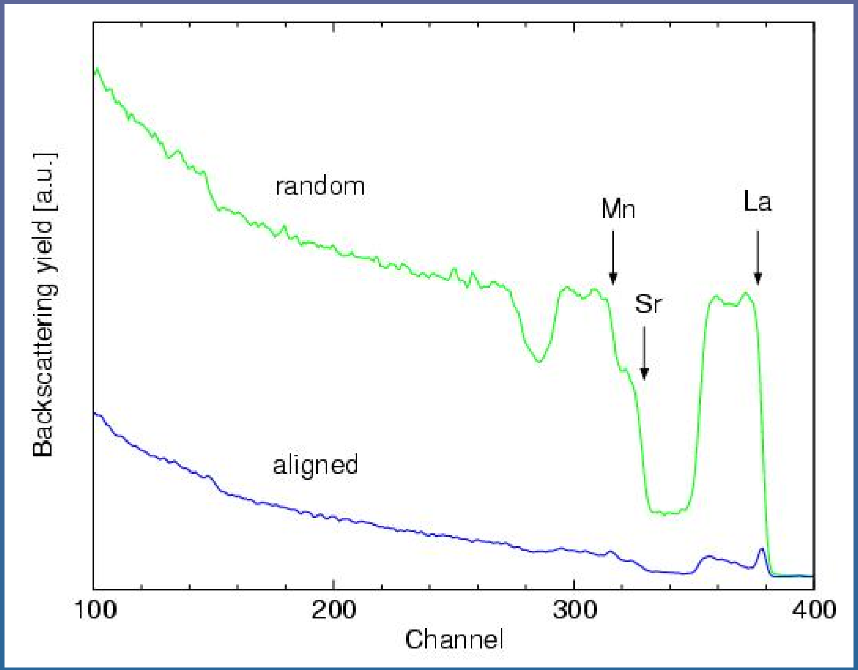

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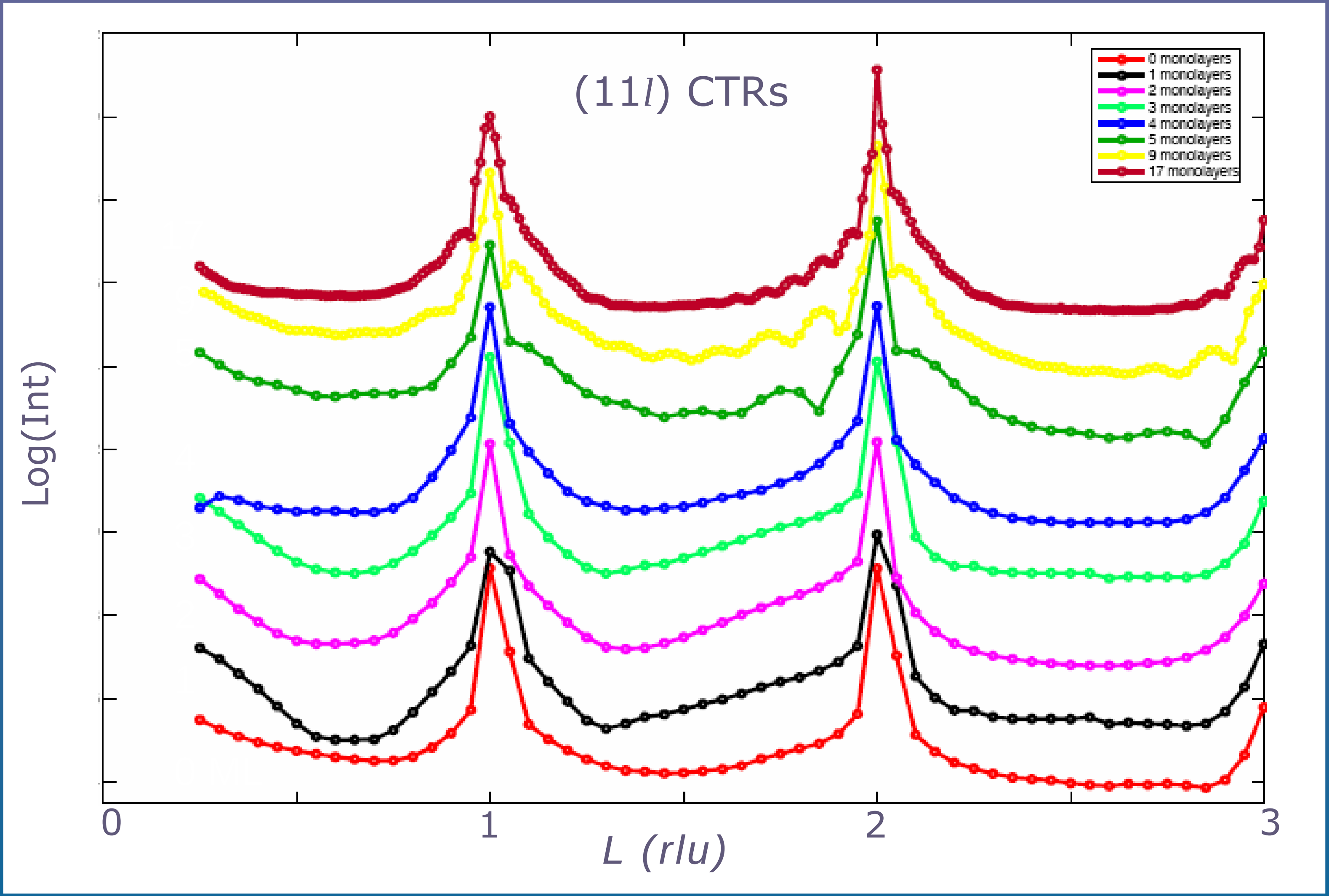
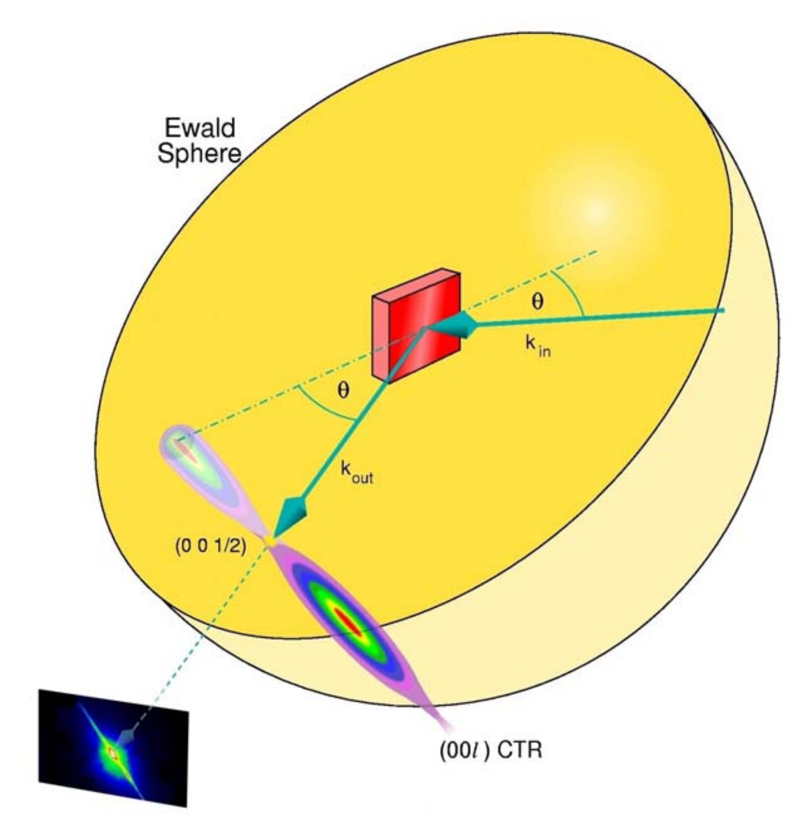
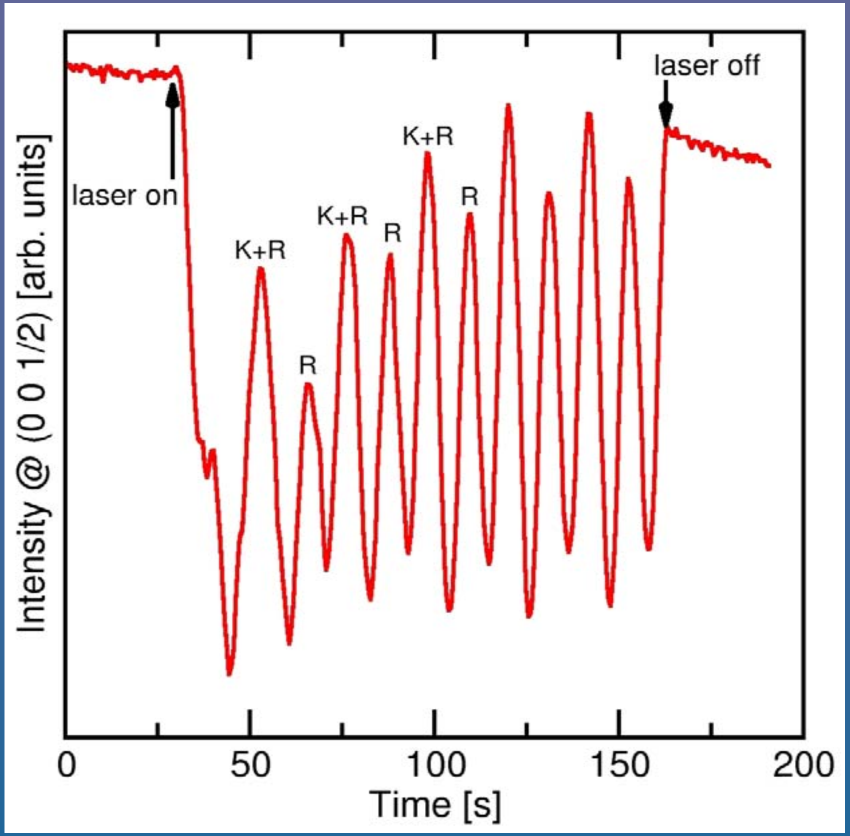
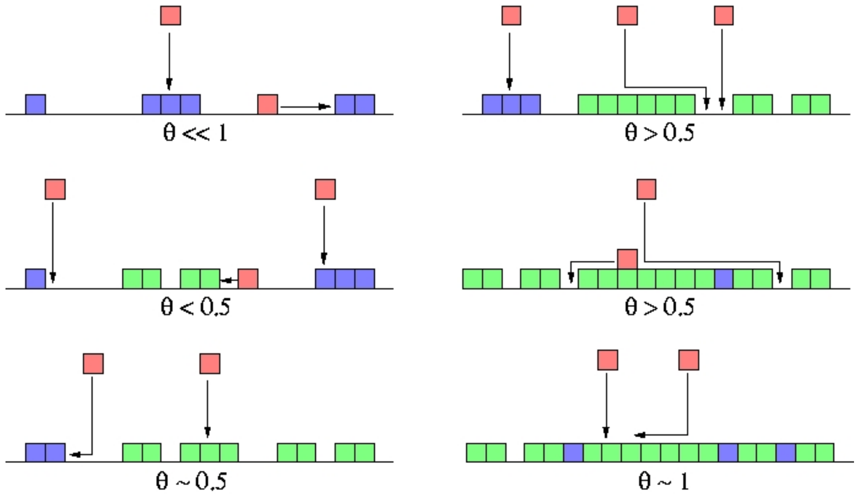


Kinetic studies of LSMO





Kinetic studies – island breakup

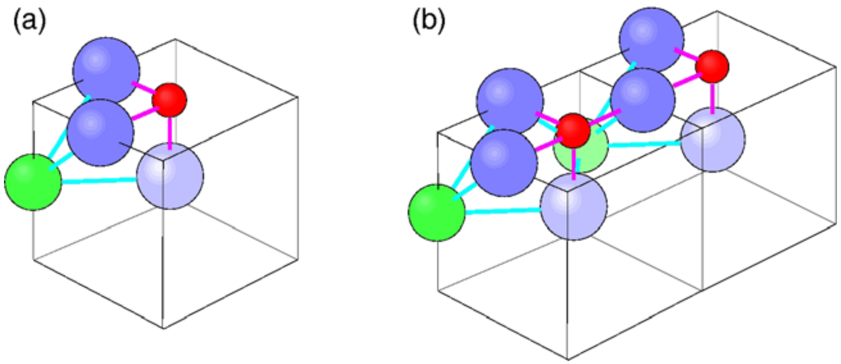


PLD:

- High supersaturation
- High density of small 2-D islands
- Broken up by impinging flux up to $\theta \approx 0.5$

Above $\theta \approx 0.5$, island coalescence
Island breakup suppressed

J.M. Pomeroy *et al.*, Phys. Rev. B **66** 235412 (2002)



Willmott *et al.*, Phys. Rev. Lett. **96** 176102 (2006)

The future of surface diffraction

- Complex systems (e.g., perovskites), thin films (PLD)
  - Unit cell ~ 20 atoms
  - “surface” up to 5 ML depth
- Structural evolution
- Massive data sets! Limited beamtime!
- PILATUS to the rescue
- Modelling – many possibilities, local minima
- Direct methods (c.f. STO!)
  - Phase retrieval
  - Genetic algorithms
  - Light elements (e.g., H); extracting the valence bonds???

J. Ciston *et al*., submitted; L.D. Marks *et al*., Acta Cryst. A**62** (2006)

ERL and surface diffraction

- 1000 x flux/brilliance
  - Full data sets (inc. massive oversampling)
  - Follow structure as fn. of
    - Temp; film thickness; strain; external field; …
- ~1 ps bunches
  - Directly probe PLD/nonthermal processes…
- High energies + large 6M pixel detector $\Rightarrow$ RHEED-like mapping of large chunks of k-space – “parallel processing”
- nm-focussing $\Rightarrow$ “Surface-reconstruction microscopy” (?!) …
- … becomes feasible with ERL!

Thanks to…

- Pilatus detector: Christian Brönnimann and Detector Group, SLS
- Surface diffractometer: Michael Lange, Dominik Meister
- Software: Christian Schlepütz, David Maden
- External users:
  - Robert Feidenhans'l *et al*. (Copenhagen)
  - Matt Dawber *et al*. (Geneva)