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

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Almost impossible materials science
Cornell, June 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

- Downsizeing

- Surface/interface effects
  - e.g., FE-STO surface
  - e.g., 2-D e⁻ gas, interface
    STO/LAO

- Bandstructure determination
  photoelectron spectroscopy
  - universal curve (e⁻ escape depth) ~ 5 ML
  - Depth of surface ~ 5 ML
  - Measuring bulk properties?
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

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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 μm² 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.

Contourplot of the (111) plane, through [-4/3 2/3 2/3]
Log(Intensity)
Strontium titanate

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

\[ \chi^2_{\text{red}} = 0.99 \]
Strontium titanate

• Models

(2x1)

• Hard work modelling – see later! (2x2)
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)

PLD at the Swiss Light Source

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P.R. Willmott and J.R. Huber, Rev. Mod. Phys. 72 315 (2000)
SXRD and in-situ PLD – the perfect marriage?
La$_{1-x}$Sr$_x$MnO$_3$ 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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(11l) CTRs

Log(Int)

$L (r/lu)$

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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


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???

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 ⇒ RHEED-like mapping of large chunks of k-space – “parallel processing”

- nm-focussing ⇒ “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)