# X-ray Scattering Studies of Pulsed Laser Deposition

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# Acknowledgements

Thanks to organizers

**Contributors:**

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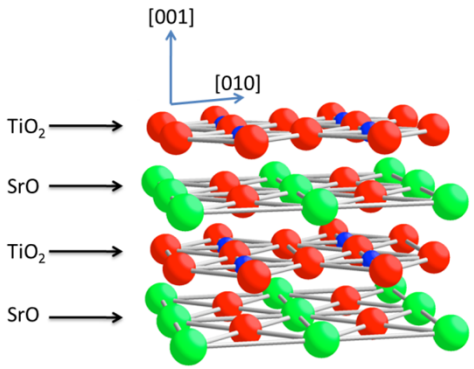
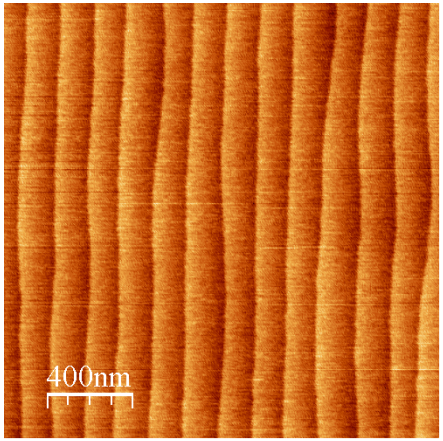
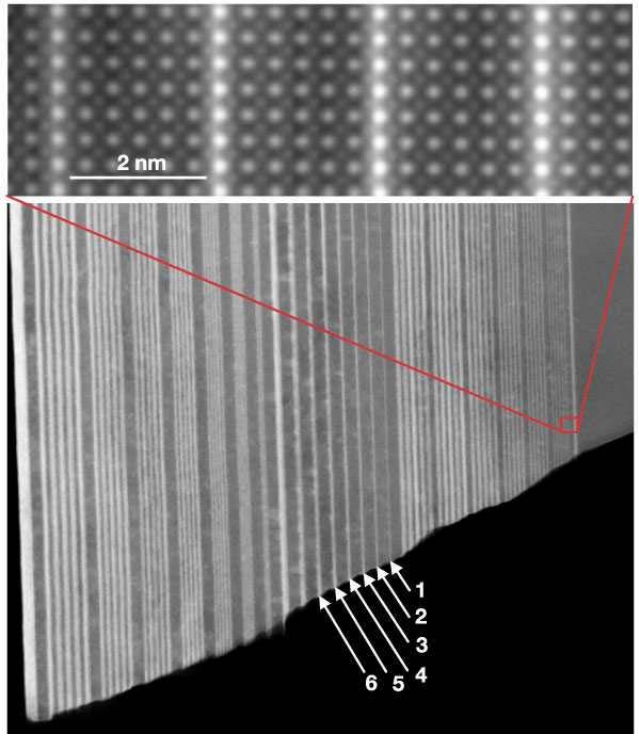
  - Andy Siliciano
  - Dr. Aaron Fleet
  - Dr. John Ferguson
  - Dr. Hui-Qiong Wang
  - Dr. Yongsam Kim
- Prof. Yuri Suzuki
- CHESS Staff
  - **Dr. Arthur Woll, CHESS**
  - Dr. Darren Dale, CHESS

# PLD: Atomically Precise Growth of Epitaxial Perovskite Films




**Etched & Annealed Starting Surface**

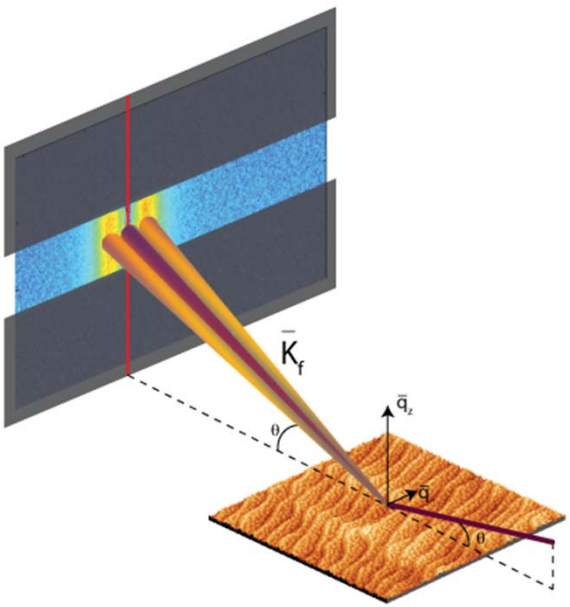


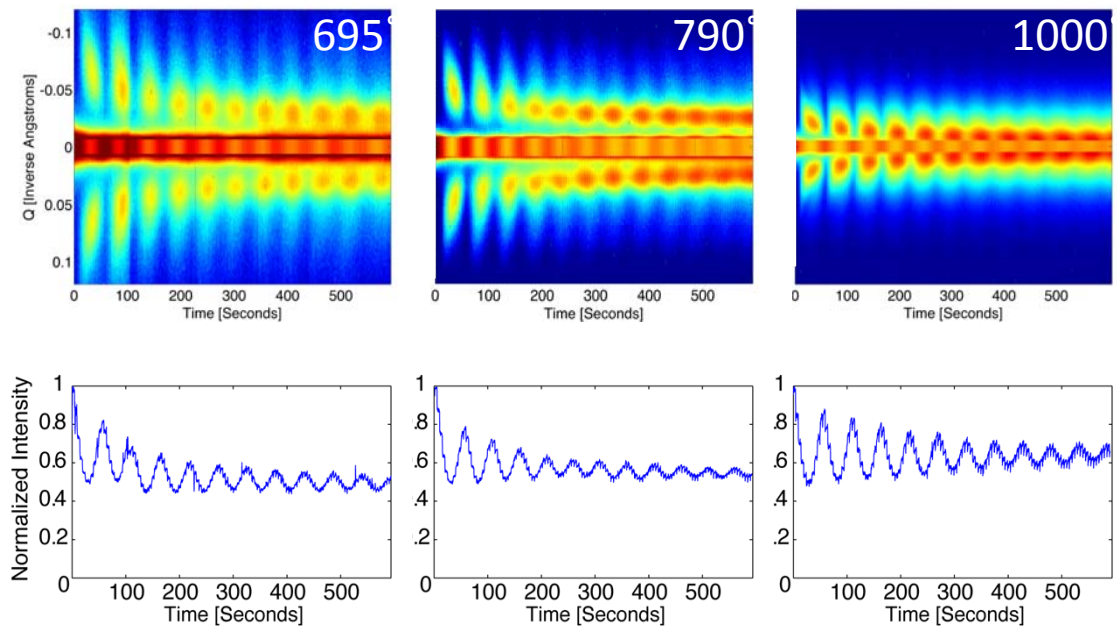

**Ohtomo, A.; Muller, D.A.; Grazul, J.L.; Hwang, H.Y. *Nature,* 419, no. 6905, (26 Sept. 2002) : 378-80 Nature (UK)**

# Two Types of Questions:

- How/why does PLD work so well?
- Can we develop new materials and/or heterostructures?

# Time-Resolved X-Ray Studies: Reflectivity ($q_\perp$) and Diffuse Scattering ($q_\parallel$)



PRL **94,** 036102 (2005) PHYSICAL REVIEW LETTERS week ending 28 JANUARY 2005

# Observed Effects of a Changing Step-Edge Density on Thin-Film Growth Dynamics

Aaron Fleet,[1,2] Darren Dale,[3,2] Y. Suzuki,[4] and J. D. Brock[1,2]
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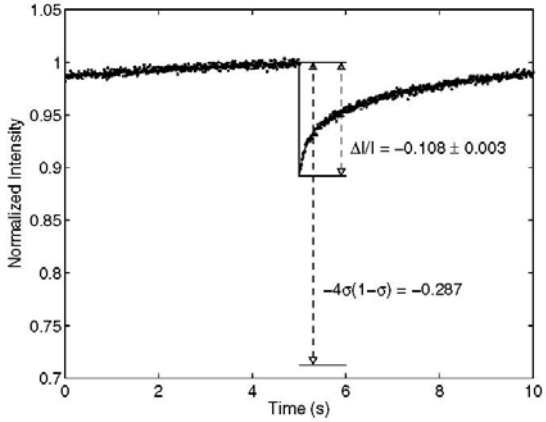
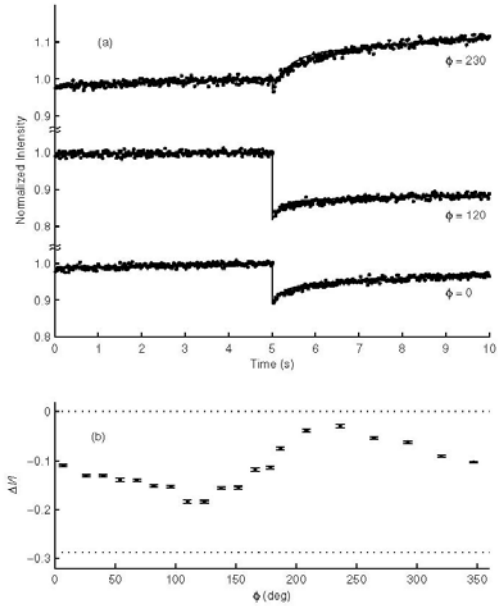
(Received 31 August 2004; published 25 January 2005)



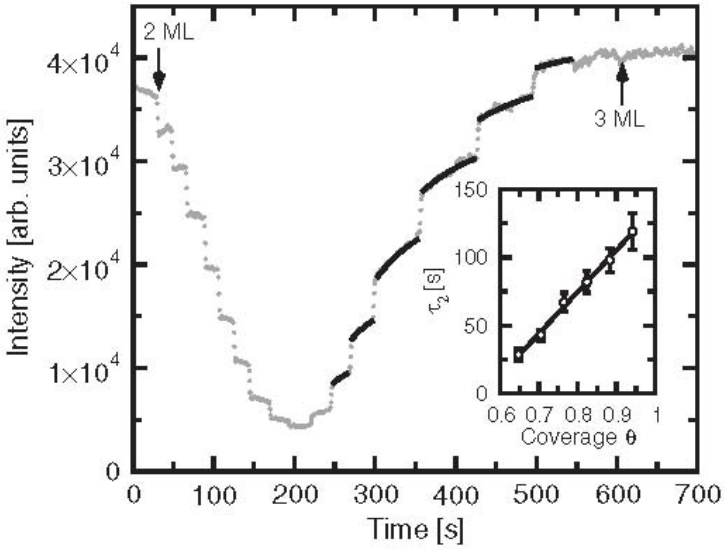



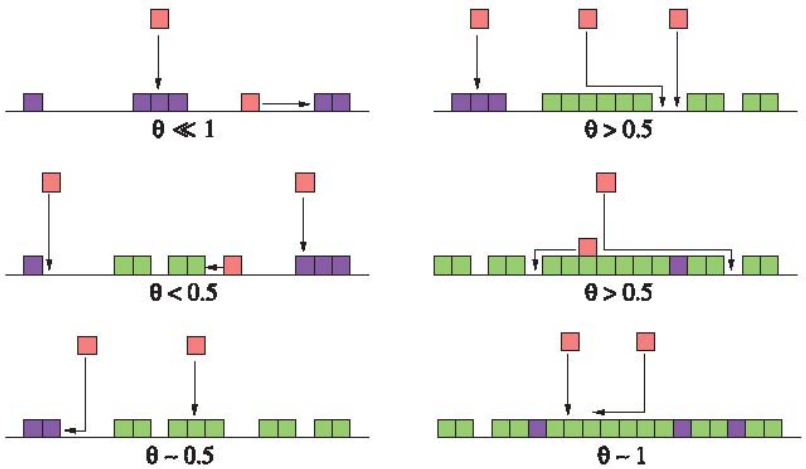

Experiment is inconsistent with simple impulse approximation. Smoothening process is faster than time resolution of experiment.

PRL **96,** 176102 (2006) PHYSICAL REVIEW LETTERS week ending 5 MAY 2006

# Energetic Surface Smoothing of Complex Metal-Oxide Thin Films

P. R. Willmott,* R. Herger, C. M. Schlepütz, D. Martoccia, and B. D. Patterson
*Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
(Received 19 January 2006; published 2 May 2006)




Again smoothening is faster than experimental resolution. On basis of the slow observable kinetics, argue that "island break up" by energetic plume is responsible for smooth growth during PLD.

PRL **96,** 226104 (2006) PHYSICAL REVIEW LETTERS week ending 9 JUNE 2006

# Nonequilibrium Interlayer Transport in Pulsed Laser Deposition

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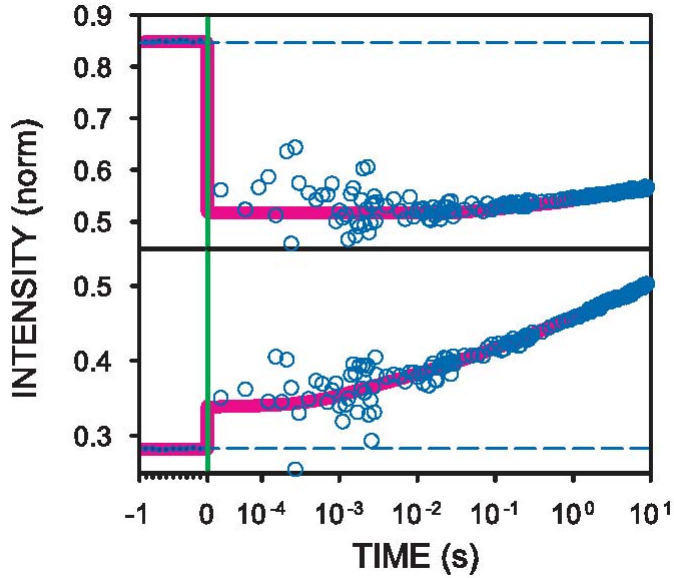
(Received 28 February 2006; published 6 June 2006)

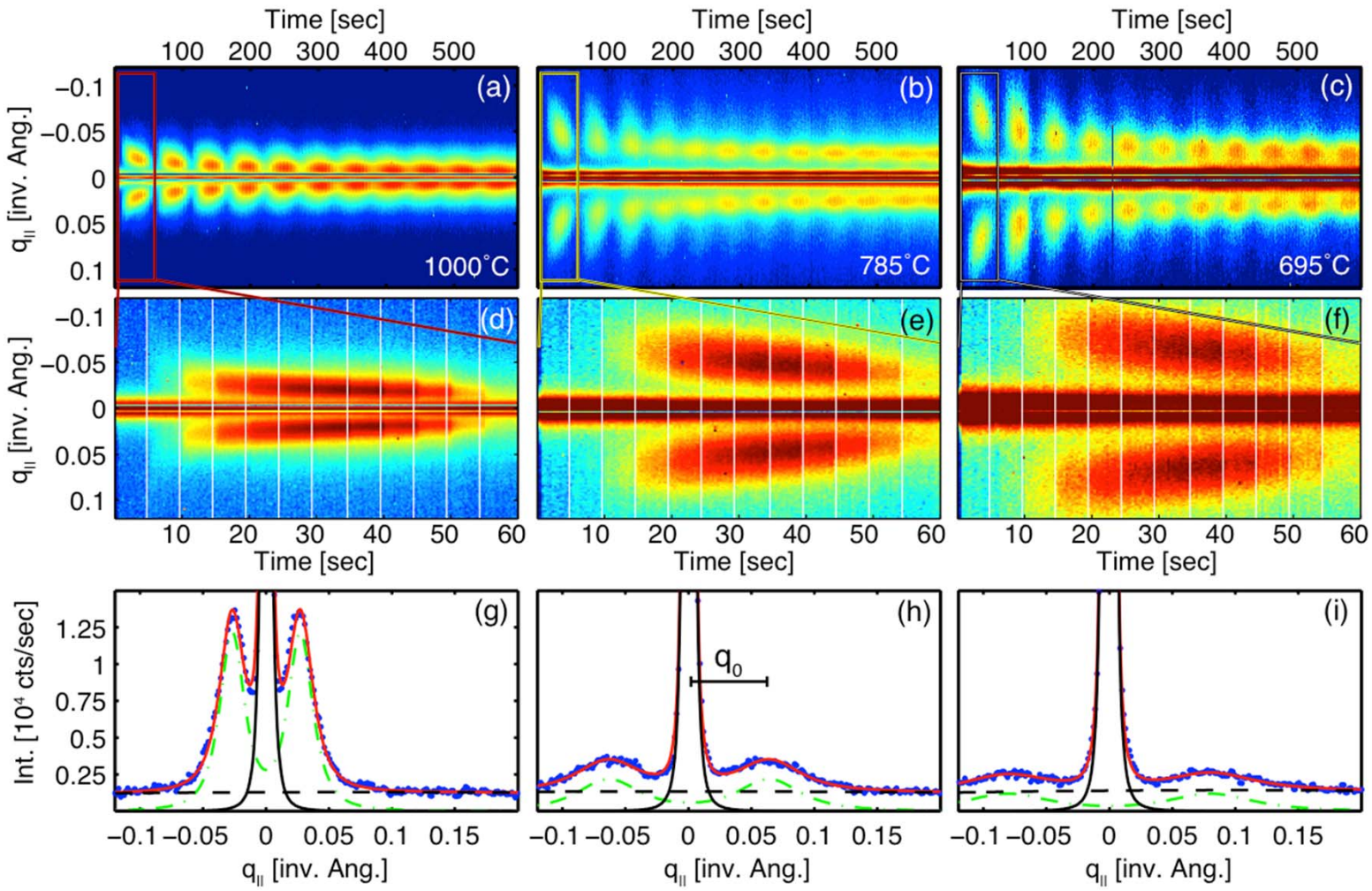



Pushes time-scale down to that of plume width, smoothening still too rapid to observe.

# Time-scales

- Duration of plume
- Repetition rate
- Binning time of detector
- Island Nucleation
- Crystallization
- Aggregation of material
- Intra-layer transport
- Island coarsening
- Inter-layer transport
- Possibly, others…

# Diffuse Scattering

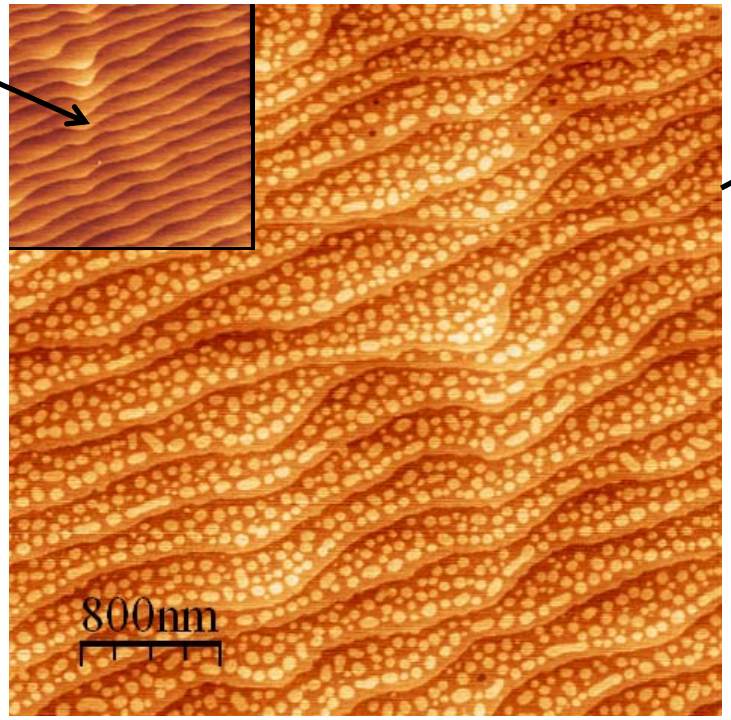


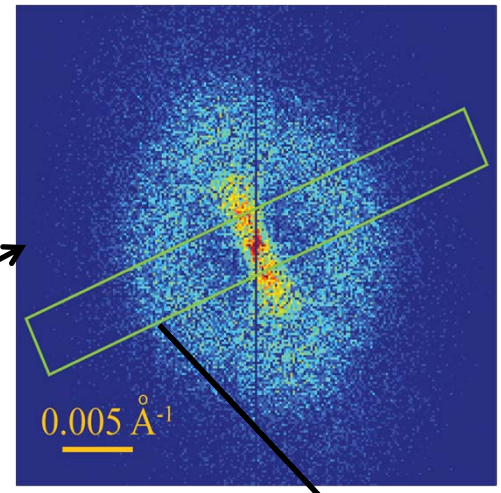

Ferguson, J.D., et. al. *Physical Review Letters* **103**, 256103 (2009).

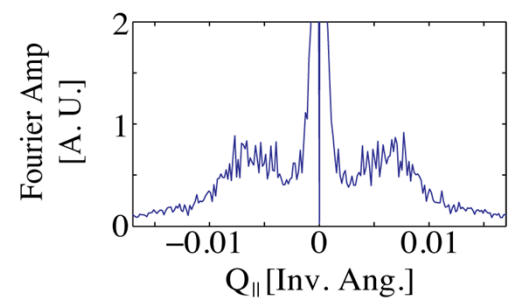
# Atomic Force Microscopy

11.3 Monolayers of $SrTiO_3$

Starting Surface

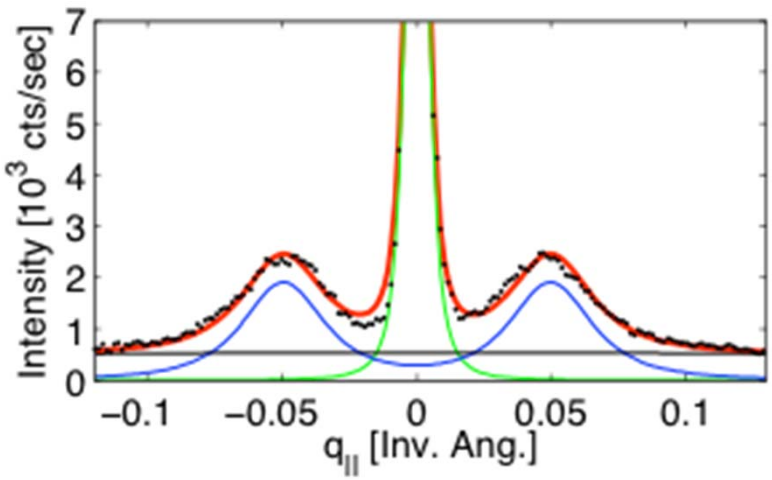



Excellent real space images of small number of stationary islands.

# Modeling the Diffuse Scattering

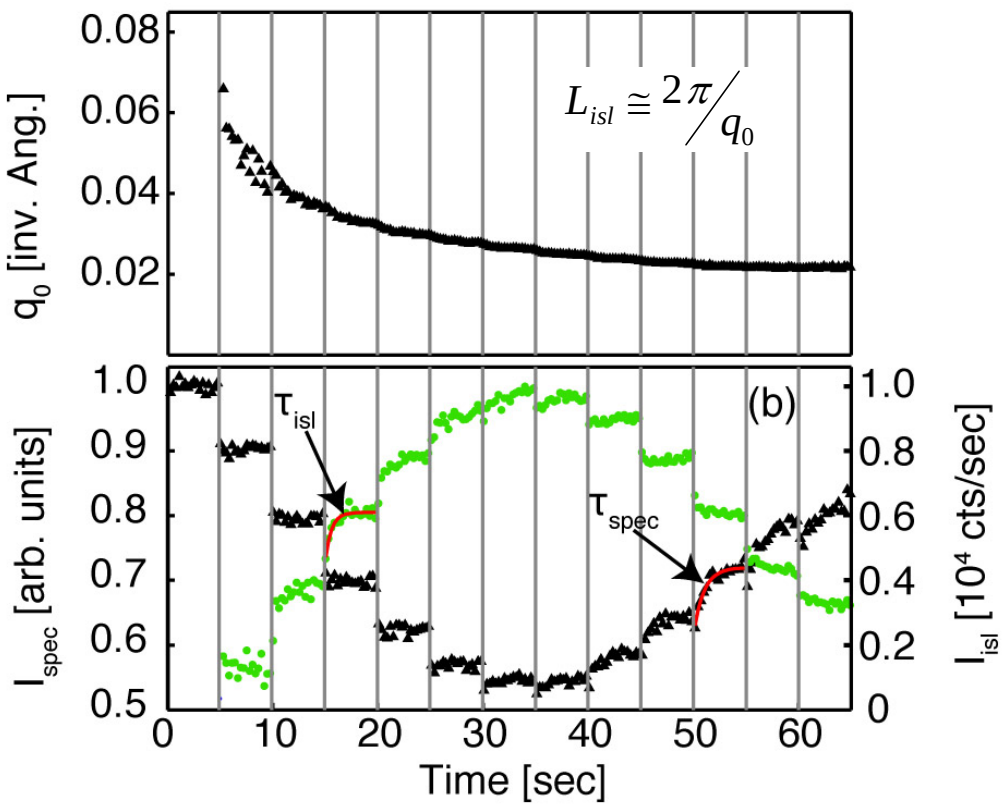



$$I(q) \propto \frac{1}{(1+\xi^2(q-q_0)^2)^{\frac{3}{2}}}$$

**Key Points:**

- **Peak Position** – Distance between island centers
- **Integrated Intensity** – Amount of material in all islands
- **Full Width Half Max** – Island-Island correlation length

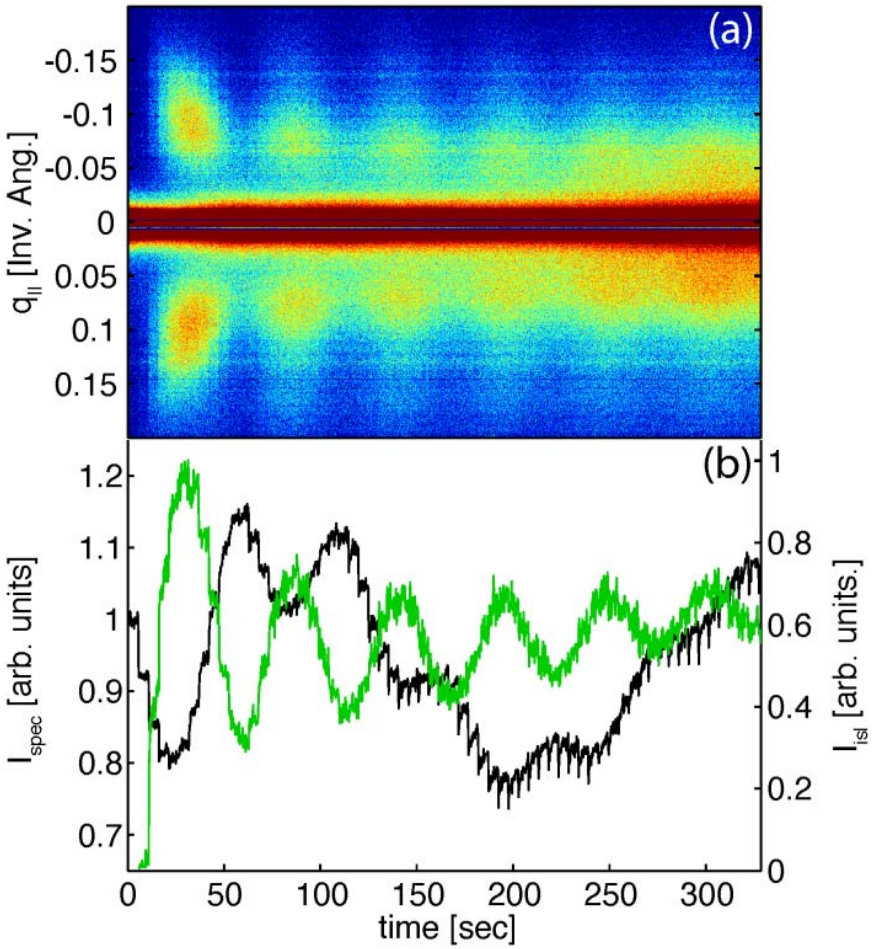
# Best Fit Results to Model

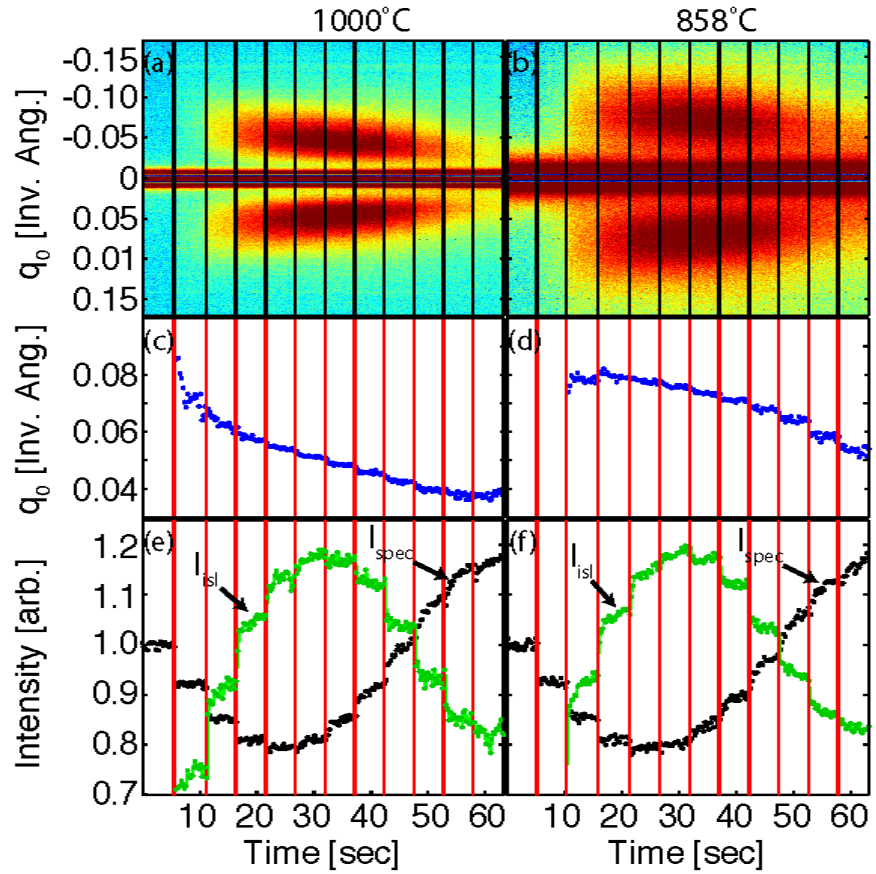



- Island coarsening is significant and occurring on timescale of seconds.
- No additional nucleation of islands after 1st pulse
- Specular and diffuse both show time dependent behavior.
- $I_{tot} = I_{spec} + I_{isl} + I_{sm}$
- Time dependent $I_{isl}$ ➔ mass transfer from smaller to larger islands

Ferguson, J.D., et. al. *Physical Review Letters* **103**, 256103 (2009).

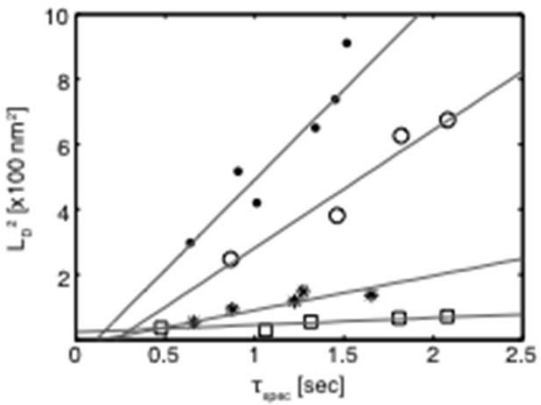
# $LaAlO_3$ on $SrTiO_3$ (001)



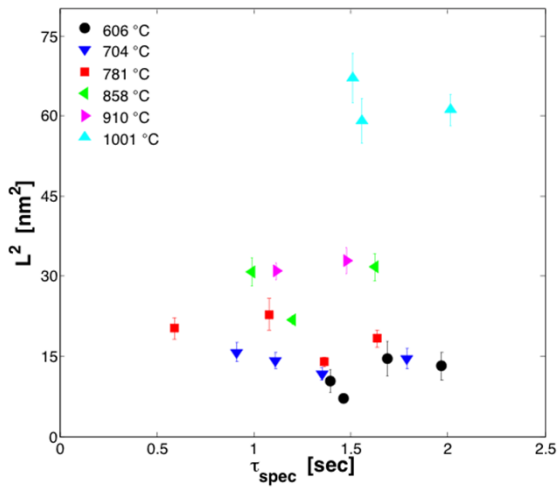



# $L^2$ vs $\tau$

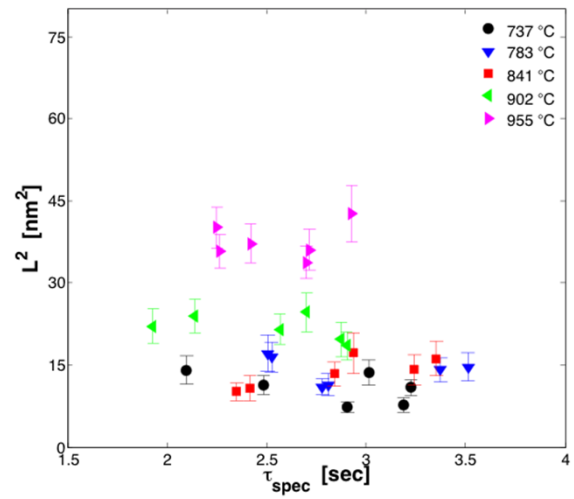
STO on STO




LAO on STO




LAO on LAO




Diffusive

?

?

PHYSICAL REVIEW B **84**, 075479 (2011)

# Quantitative modeling of *in situ* x-ray reflectivity during organic molecule thin film growth

Arthur R. Woll,[1] Tushar V. Desai,[2] and James R. Engstrom[2]
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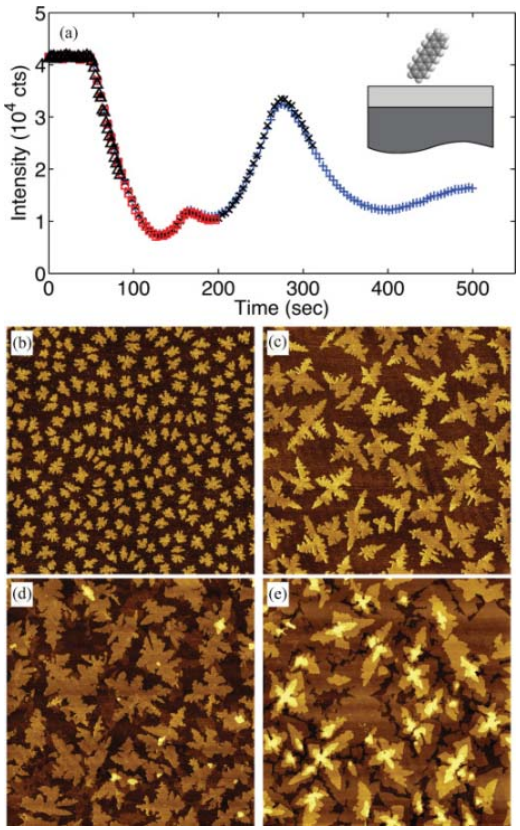
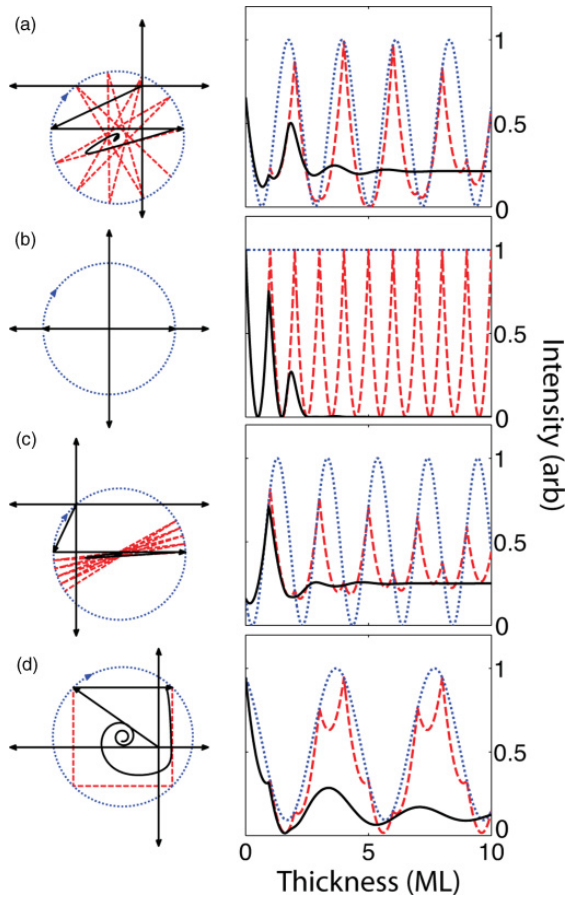
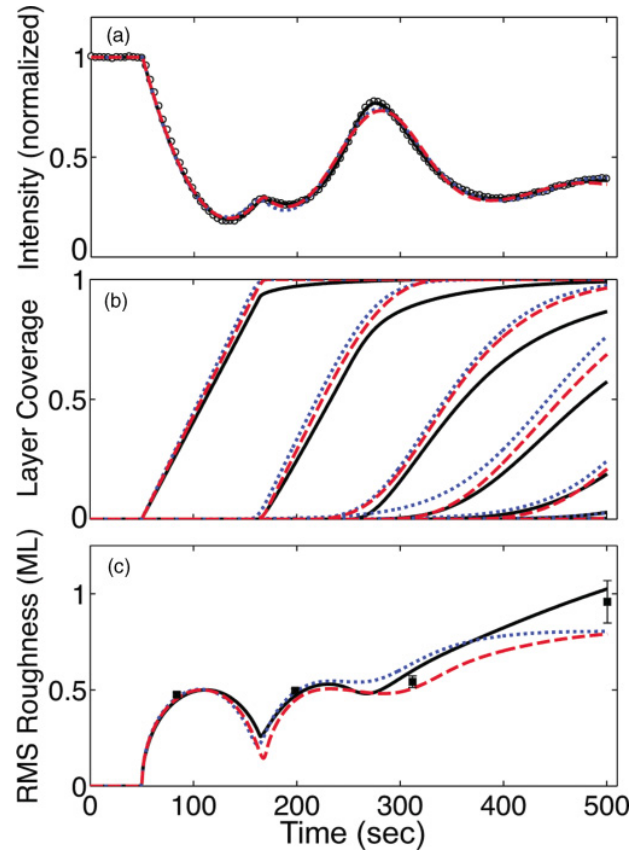
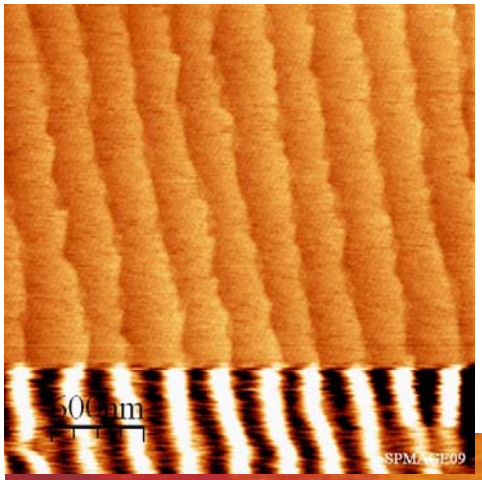
(Received 6 April 2011; revised manuscript received 22 July 2011; published 15 August 2011)



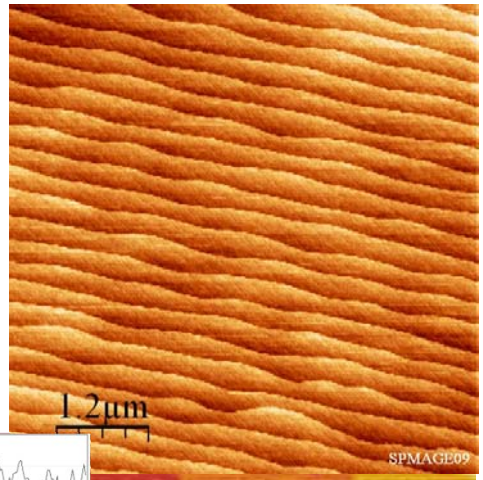



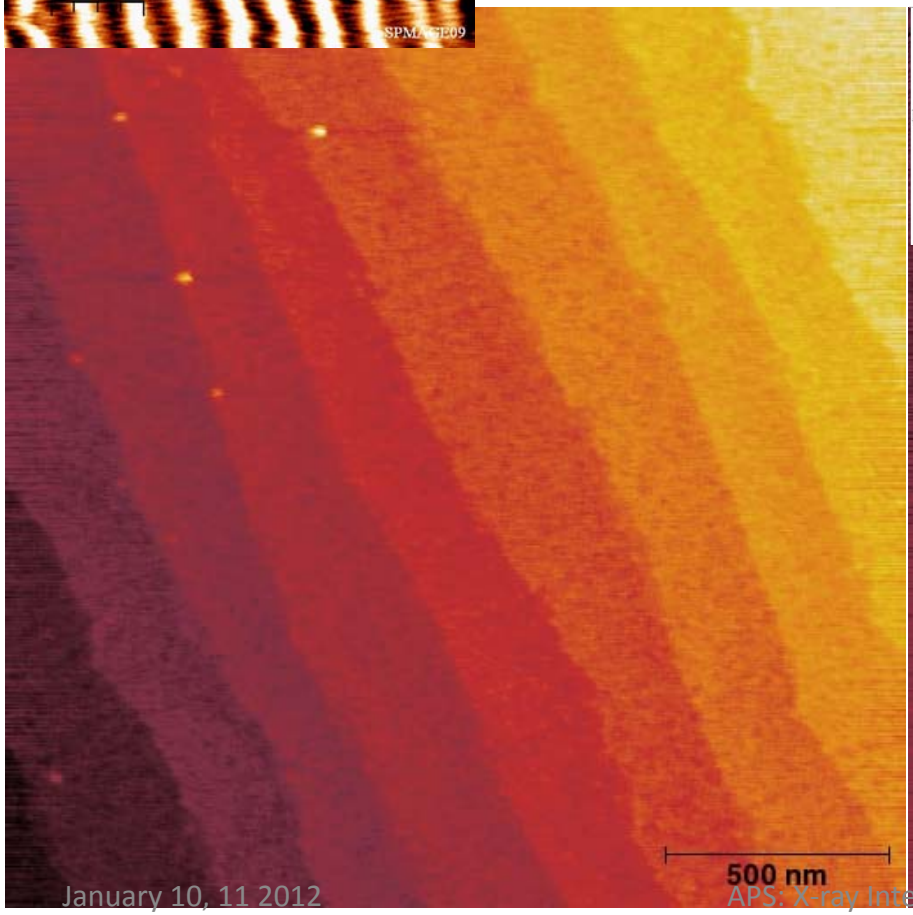



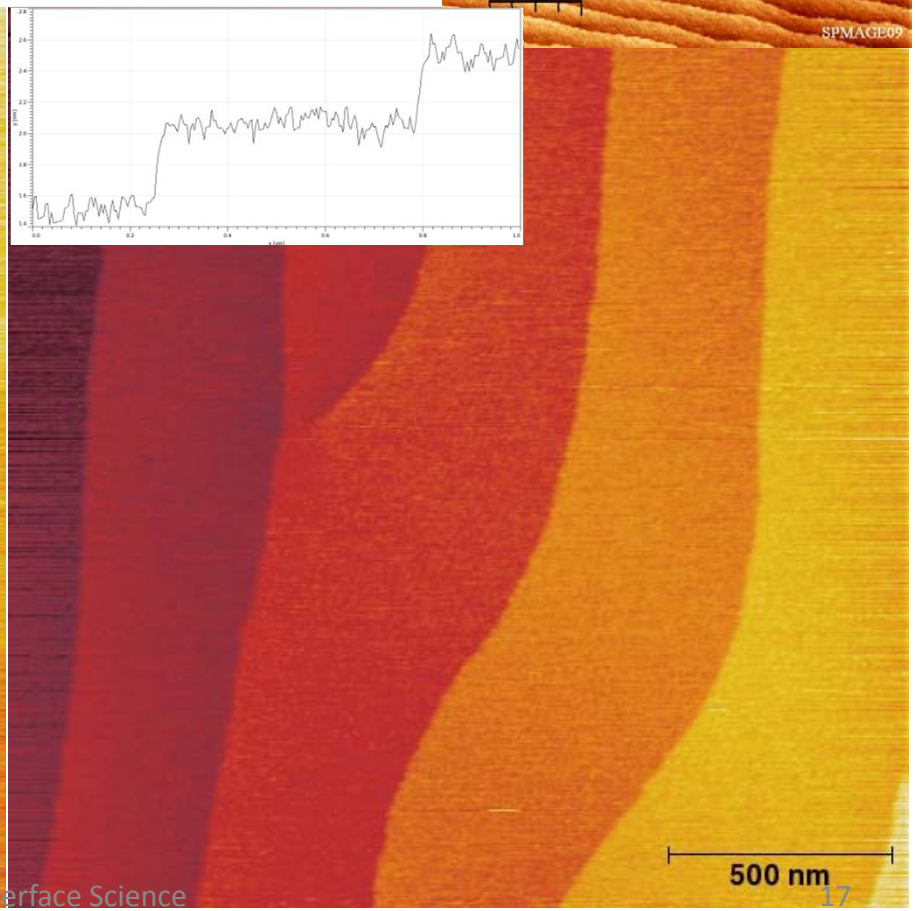



LAO on Nb-STO
3 shots at 809 C

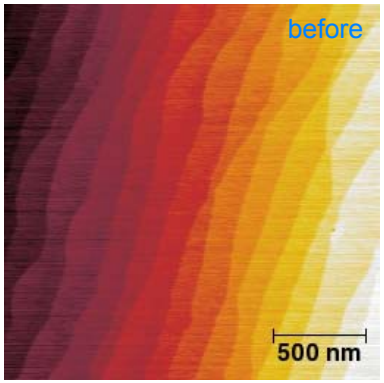
LAO on STO
several ML at 901 C
& anneal at 600 C



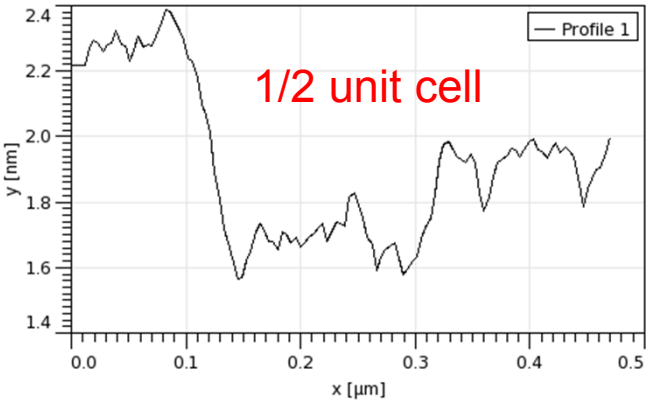



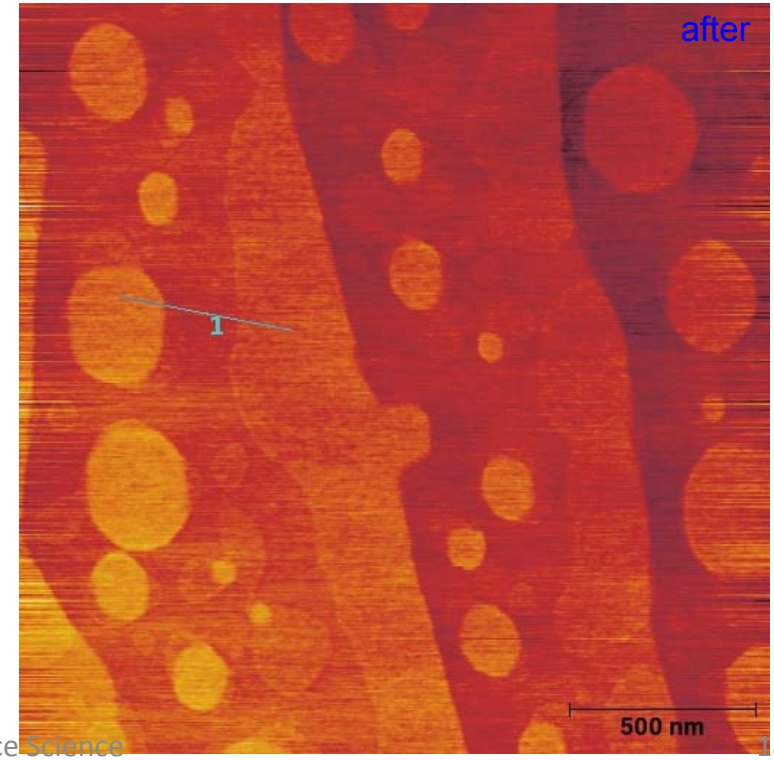



# LAO/LAO AFM images



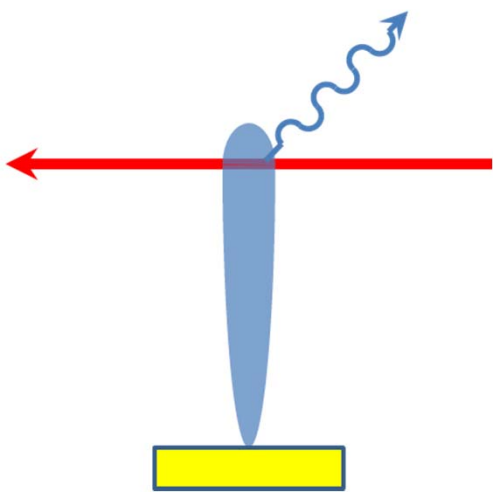

sample : yk20_37
growth temp. : 950 C
thickness : ~6ML

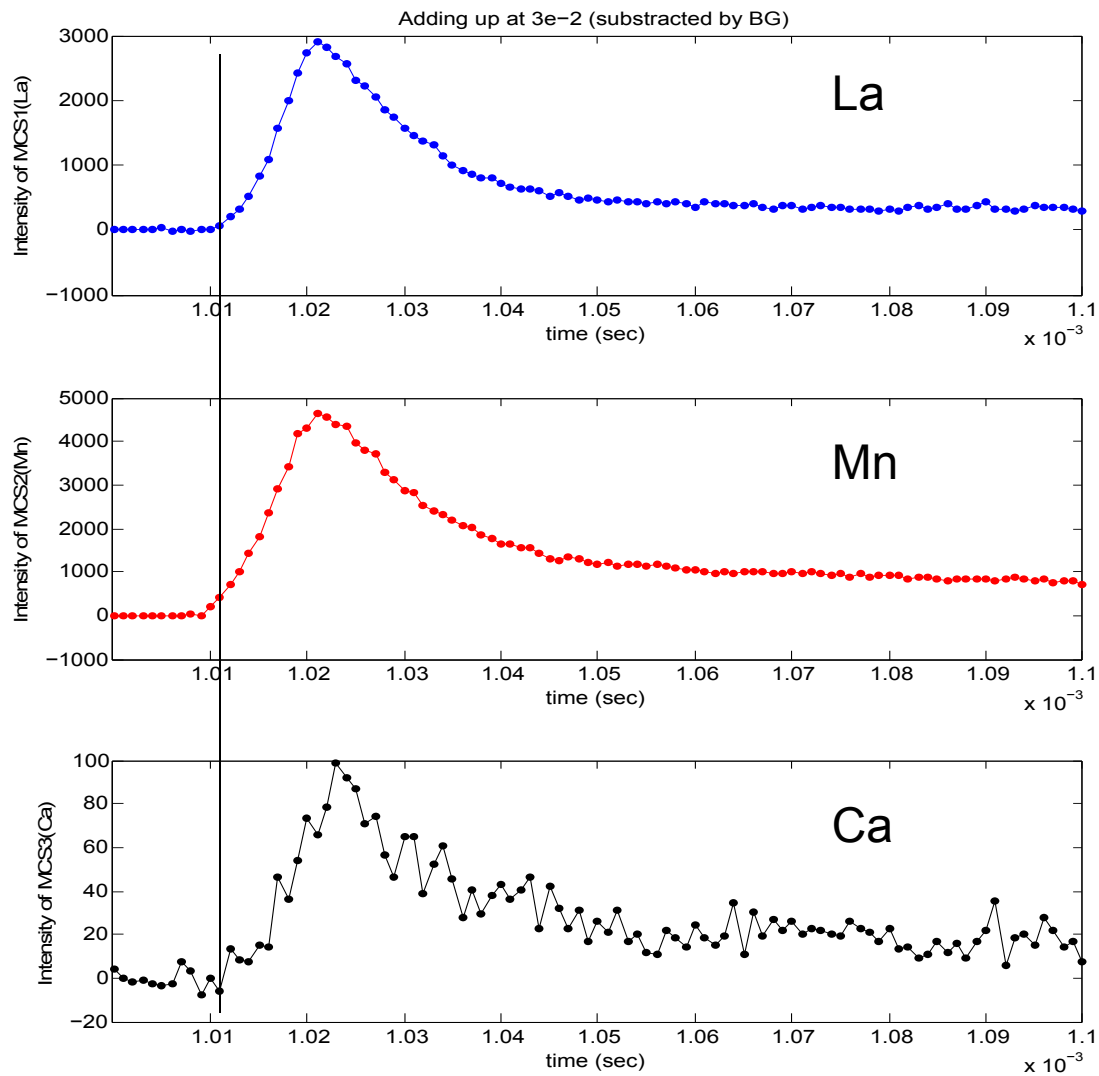




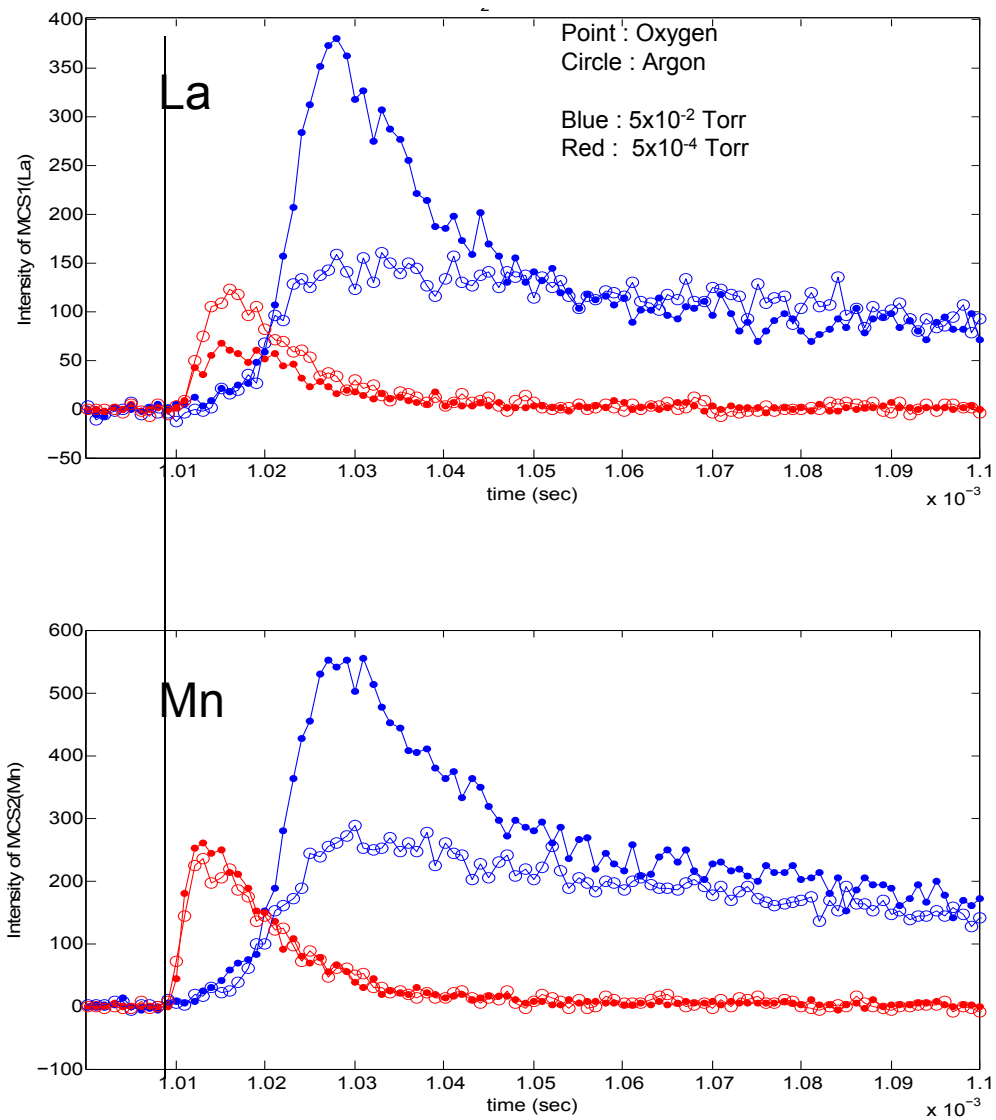
# Tr-XRF

**$(La,Ca)MnO_3$**



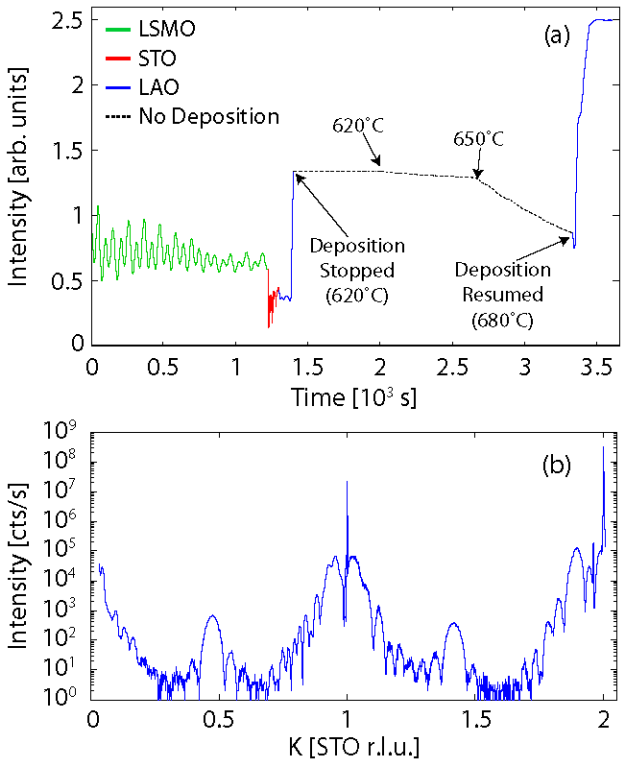


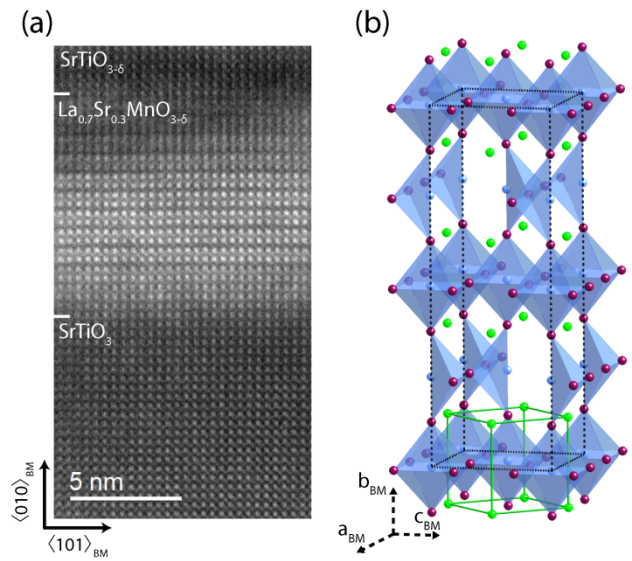
# $O_2$ vs Ar




Mass and size dependence is consistent with generic behavior associated with elastic scattering of hard spheres.

# A surprise in LSMO heterostructures: the formation of epitaxial brownmillerite phases




J. D. Ferguson, Y. Kim, L. Fitting Kourkoutis, A. Vodnick, A. R. Woll, D. A. Muller, and J. D. Brock, "Epitaxial Oxygen Getter for a Brownmillerite Phase Transformation in Manganite Films," Advanced Materials **23** (10), 1226-1230 (2011).

# What are we going to need?

- Excimer laser system?
- Fs laser system?
- Hazardous gas handling (e.g., Fluorine for laser)
- Detectors (high-speed area detectors for diffuse/specular, large area energy resolving for tr-XRF)
- Simultaneous RHEED and X-ray
- AFM
- Chemical surface prep
- Background (e.g., oxygen) gas control
- Substrate heating and temperature control
- Multiple targets