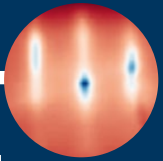

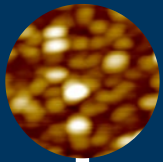

Understanding the Growth of Thin Oxide Films

Kimberly Gliebe
Alp Sehirlioglu

Case Western Reserve University
Dept. Materials Science and Engineering
Cleveland, OH 44106
AFRL 2021
12/10/2021

National Defense Science and Engineering Graduate Fellowship (NDSEG)

CASE SCHOOL OF ENGINEERING
CASE WESTERN RESERVE UNIVERSITY

Background

Bachelor's Chemical Engineering from University of Dayton 2018

- National Renewable Energy Laboratory (polymers)
- University of Dayton Research Institute (composites)
- Air Force Research Laboratory (transition metal dichalcogenides)

PhD Case Western Reserve University, 4th year Materials Science and Engineering (thin film oxides)

- Member of ACerS and ASM
- Expected graduation: August 2022

National Defense Science and Engineering Graduate Fellow

Motivation

Understanding the growth of multilayer heterostructure oxides

- These structures can be built into devices
- Specifically, I aim to achieve single crystal films to understand ionic and electronic conductivity of $LiCoO_2$
- Utilize data science to better understand growth characteristics of oxides in pulsed laser deposition

Overview

- Brief background of techniques
- Thin film growth and structural characterization
  - $SrRuO_3$ (SRO)
  - $LiCoO_2$ (LCO)
- Applied data science work

Journal of Applied Physics METHOD scitation.org/journal/jap

Distinct thin film growth characteristics determined through comparative dimension reduction techniques

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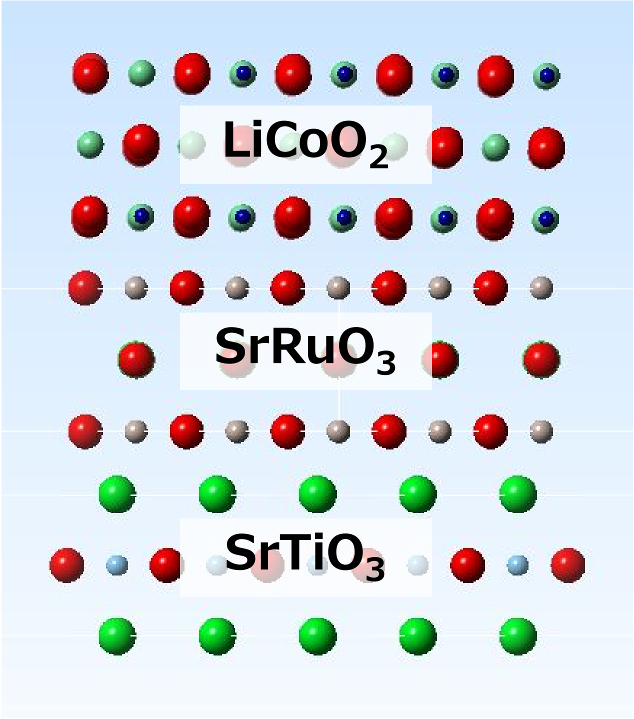
Kimberly Gliebe[a] and Alp Sehirlioglu

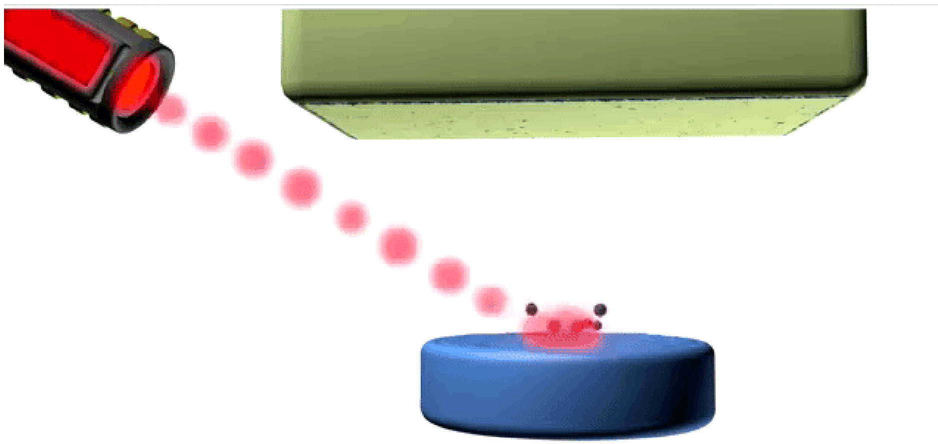
AFFILIATIONS

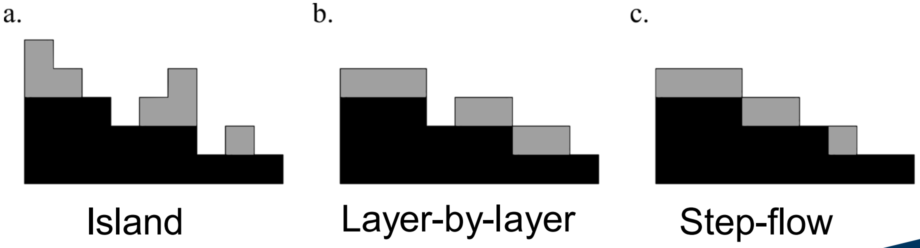
Department of Materials Science and Engineering, Case Western Reserve University, 10900 Euclid Avenue, White Building, Cleveland, Ohio 44106, USA

Pulsed Laser Deposition

- Pulsed laser deposition (PLD) can make heterostructures of thin films
- PLD uses a laser to deposit a film from a target of the material of interest in a controlled environment
- Parameters: temperature of substrate, background oxygen pressure, laser energy, laser spot size, laser frequency, target composition
- There are three growth modes a. island b. layer-by-layer c. step flow

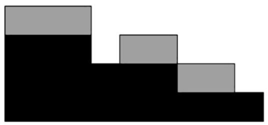


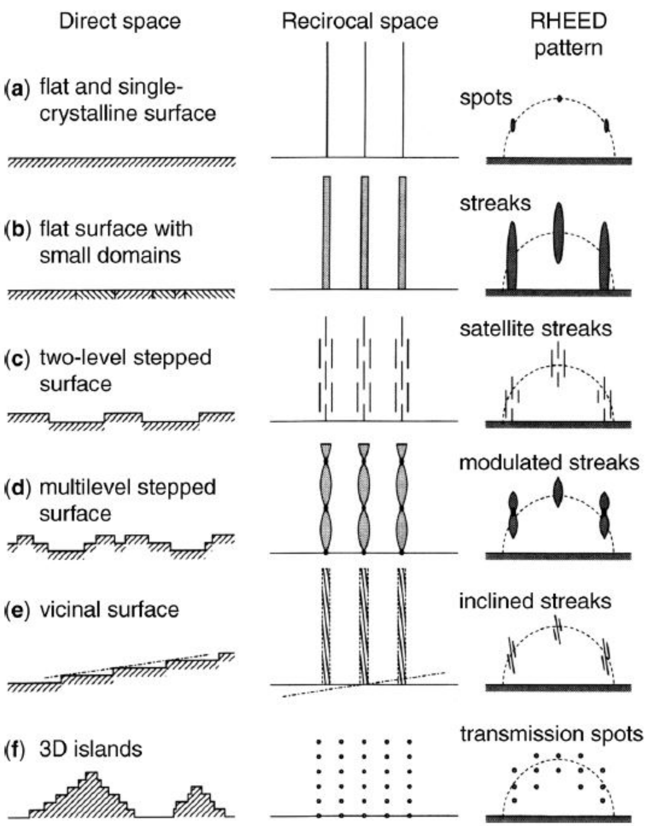


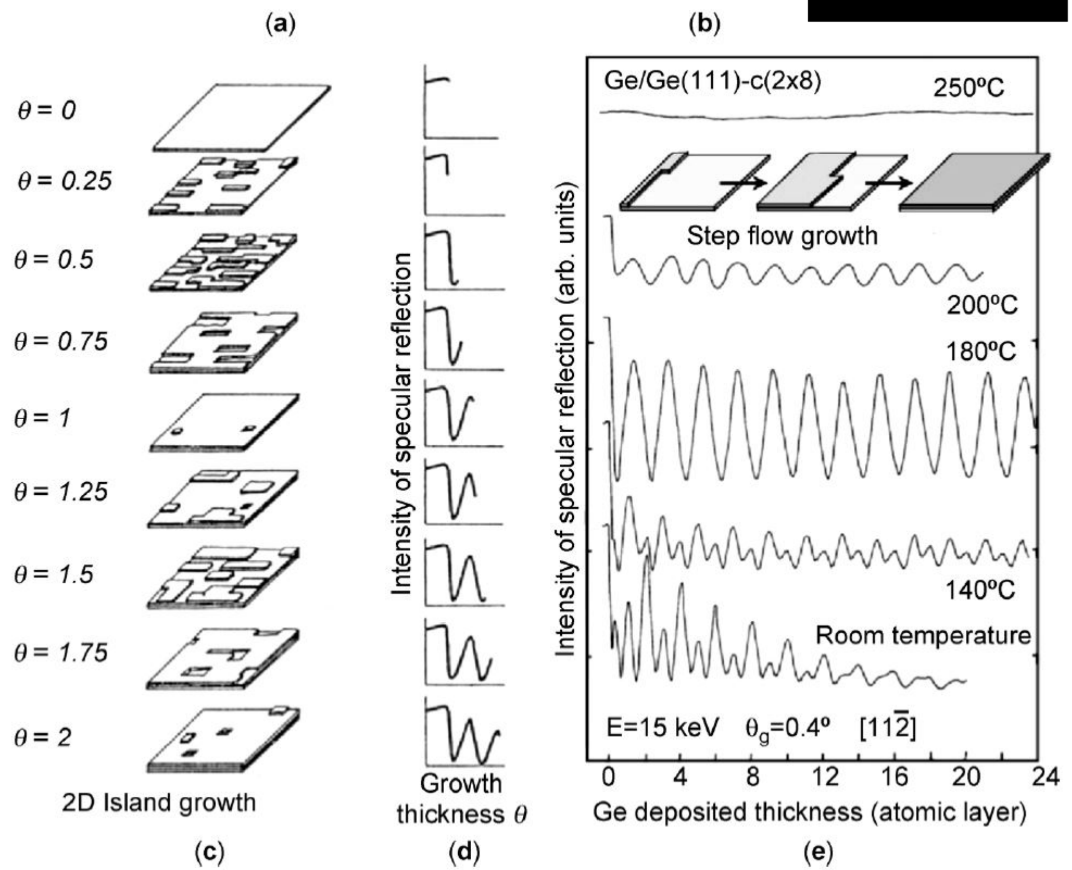


Corrosion, C. *Pulsed Laser Deposition PLD Explained With Animations*. (2019).

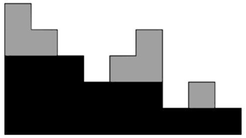
Reflection High Energy Electron Diffraction







Diffraction pattern shapes give information about the surface

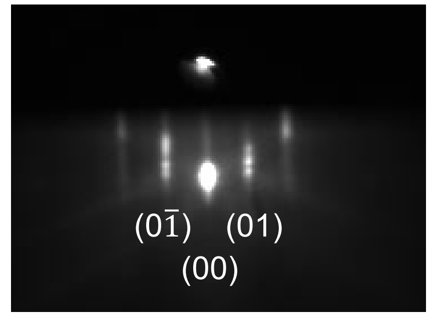


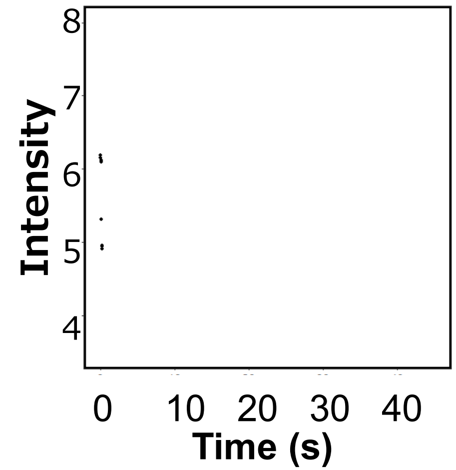
Intensity with time oscillates for layer-by-layer growth

Hasegawa, S. Reflection High-Energy Electron Diffraction. in *Characterization of Materials* (ed. Kaufmann, E.) 1935 (Wiley-Interscience, 2003).

Data Science

- Unsupervised learning techniques use unlabeled data
- Dimension Reduction reduces the overall amount of data, particularly from variables, without losing integrity
  - Principal component analysis (PCA)
  - Nonnegative matrix factorization (NMF)
  - Kmeans Clustering





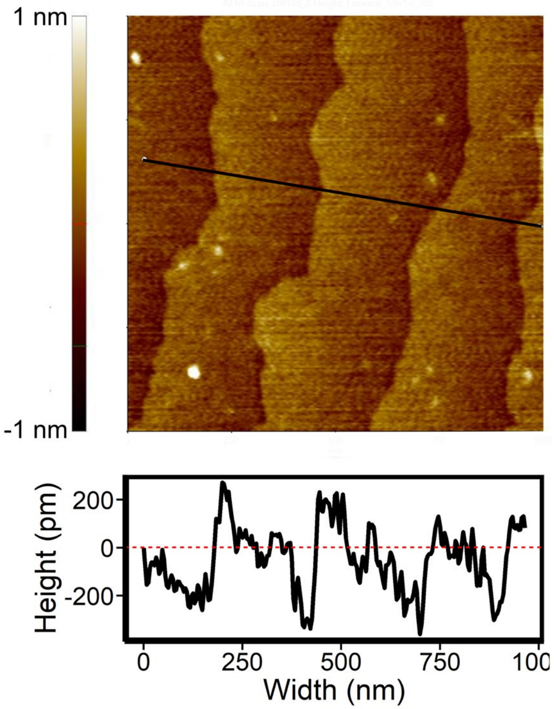
Time (s)	X1Y1	X2Y1	…	X1Y2
0.25	1.0	1.0	…	1.0
0.50	1.0	1.0	…	1.0
0.75	1.0	1.0	…	1.0

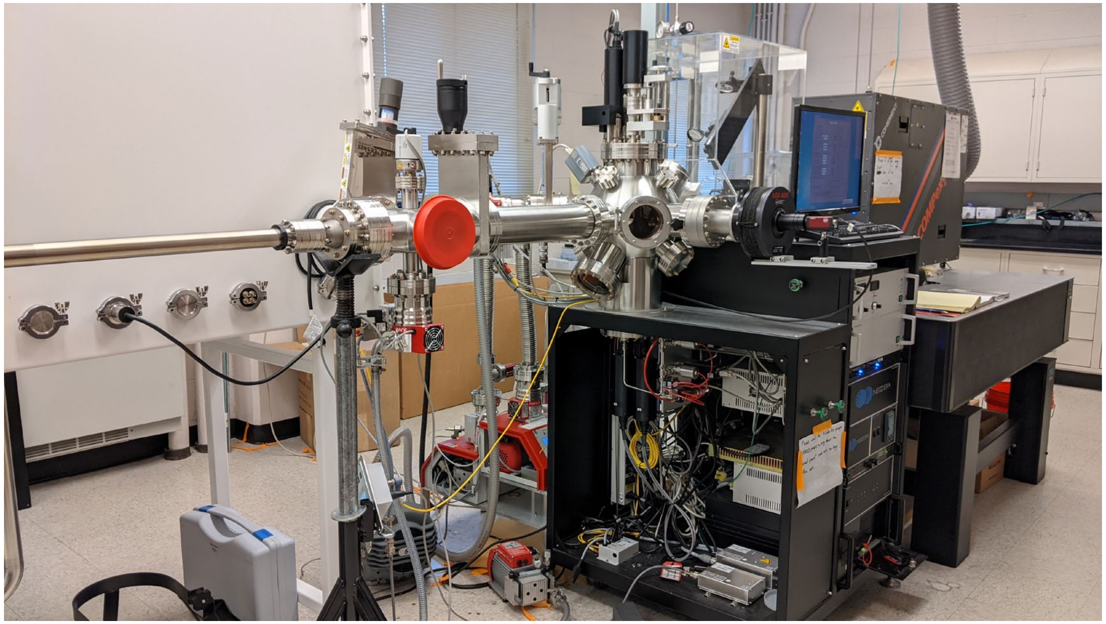
James, G., Witten, D., Hastie, T. & Tibshirani, R. *An Introduction to Statistical Learning: with applications in R*. (Springer, 2013). doi:10.1007/978-1-4614-7138-7

Processing

Thin Film Processing

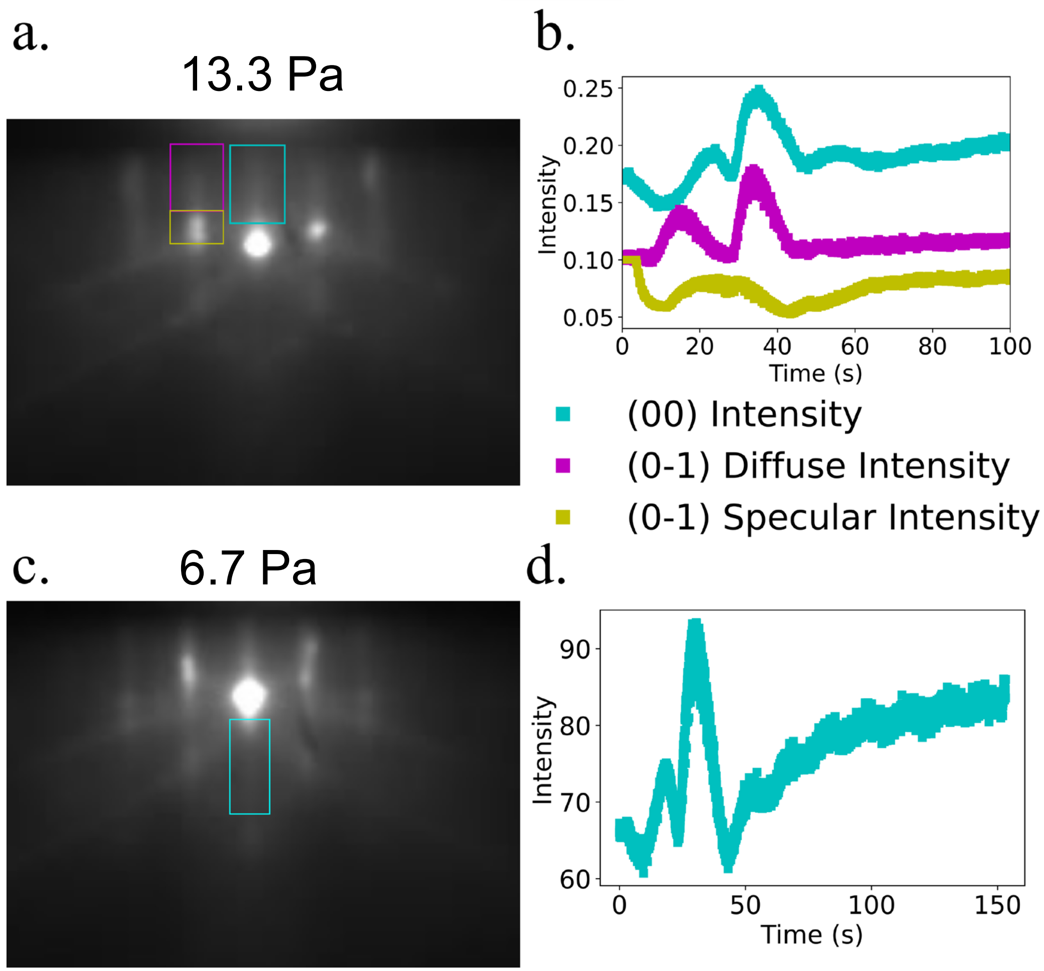
- $SrTiO_3$ (100) substrates
- Etch substrates for TiO_2 termination
- KrF Excimer laser (248 nm)
- Stoichiometric $SrRuO_3$ target
- Stoichiometric $LiCoO_2$ target





K. Gliebe and A. Sehirlioglu, “Distinct thin film growth characteristics determined through comparative dimension reduction techniques.” J. Appl. Phys., vol. 130, pp. 125301, 2021, doi: 10.1063/5.0059655

$SrRuO_3$: Comparison

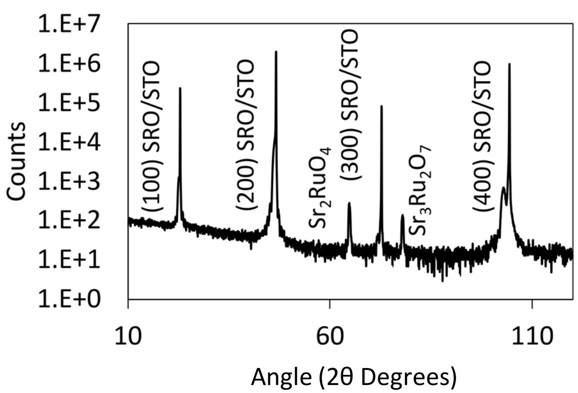


- Both SRO had temperature = 670° C, pulse frequency = 2 Hz, fluence = 1.5 J/cm^2
- The SRO grown at 13.3 Pa has intensity oscillations that fade away
  - This is caused by either step flow growth or island growth
- The SRO grown at 6.7 Pa has intensity oscillations that continue

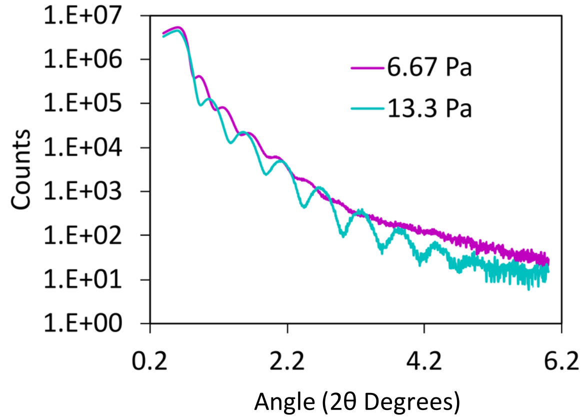
K. Gliebe and A. Sehirlioglu, "Distinct thin film growth characteristics determined through comparative dimension reduction techniques." J. Appl. Phys., vol. 130, pp. 125301, 2021, doi: 10.1063/5.0059655

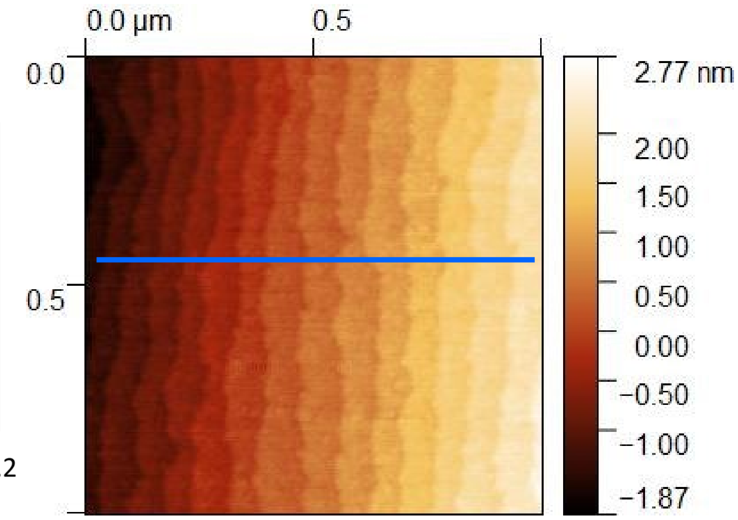
$SrRuO_3$: Comparison

X-ray Diffraction

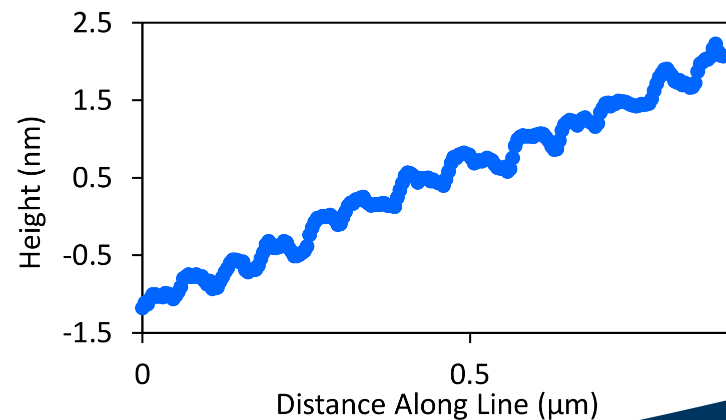


X-ray Reflectivity





- The SRO at pressure = 13.3 Pa had less impurity and a better interface
- 10 nm thick SRO has a conductivity of 50.3 S/m
- 30 nm thick SRO has a conductivity of 20,000 S/m



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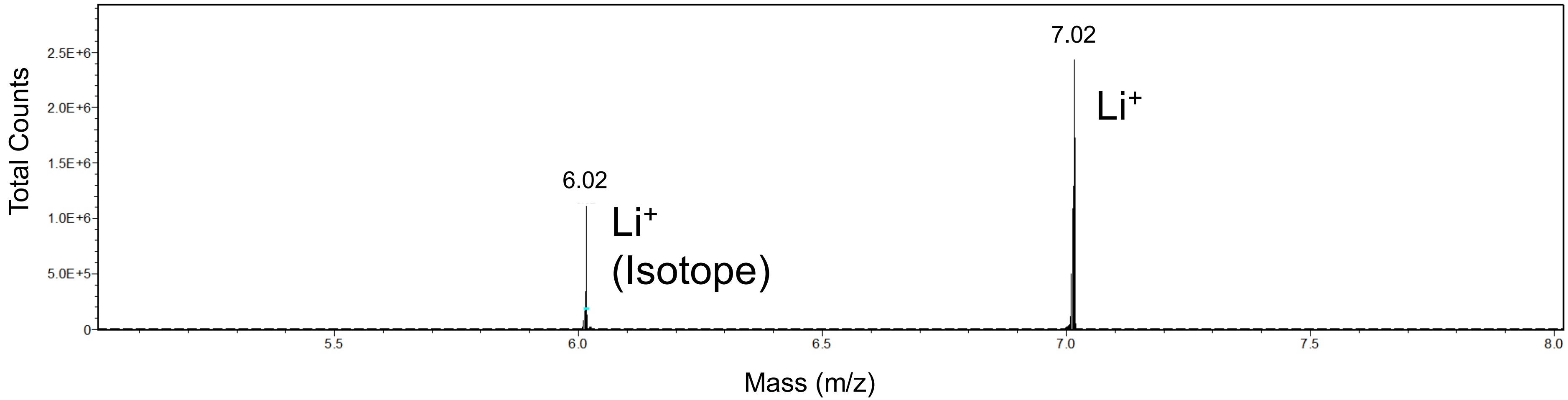
$LiCoO_2$

Time of flight secondary ion mass spectroscopy

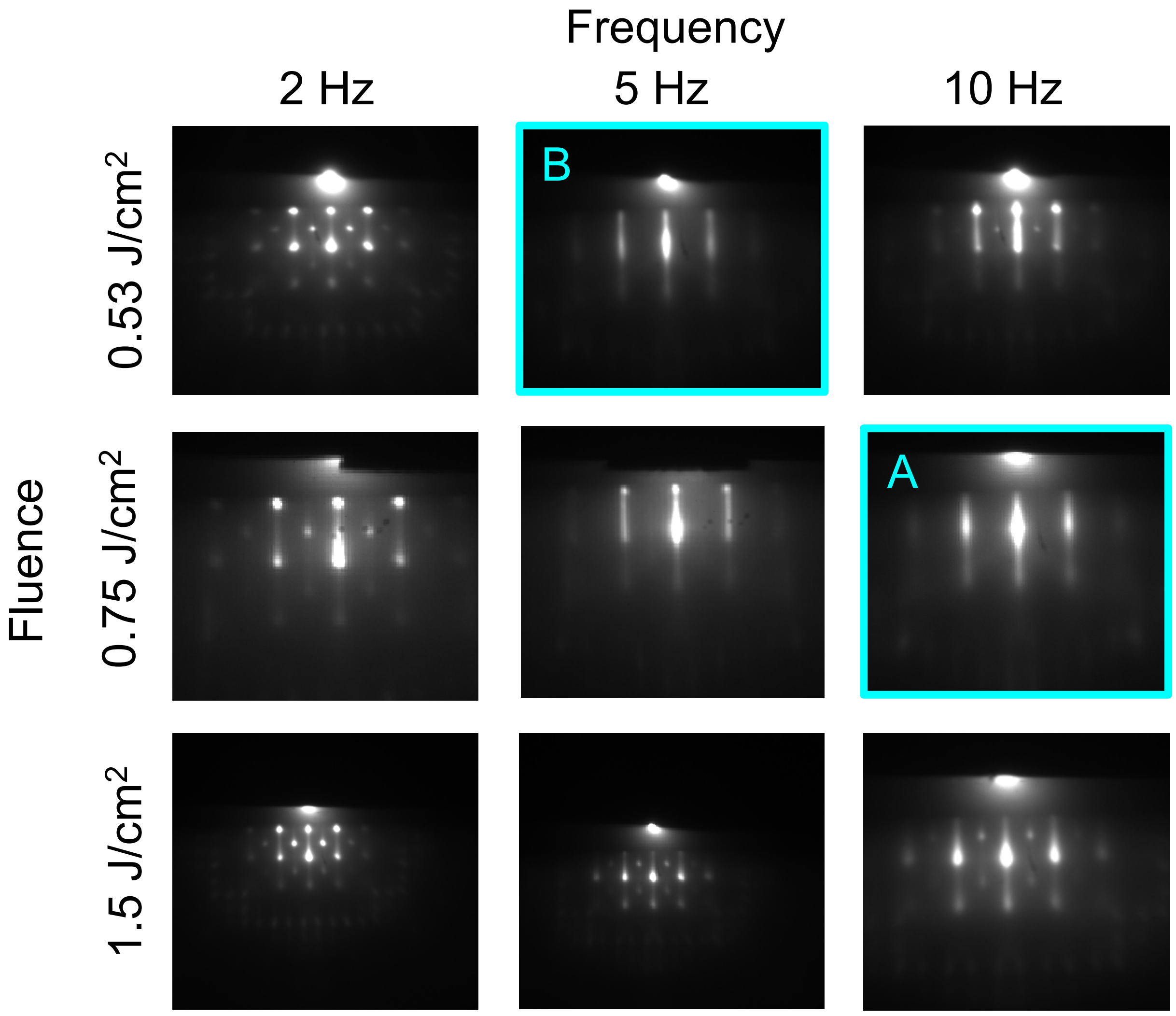
- Used to identify presence of elements within a sample
- LCO was grown at conditions in the range of literature values
  - Oxygen can scatter lithium in PLD
  - Lithium is more volatile and is more susceptible to loss at higher temperatures

LCO deposited at 670° C and 13.3 Pa



7,572,988 ^{7}Li : 3,036,473 ^{59}Co : 21,625,039 total ions

$LiCoO_2$: RHEED

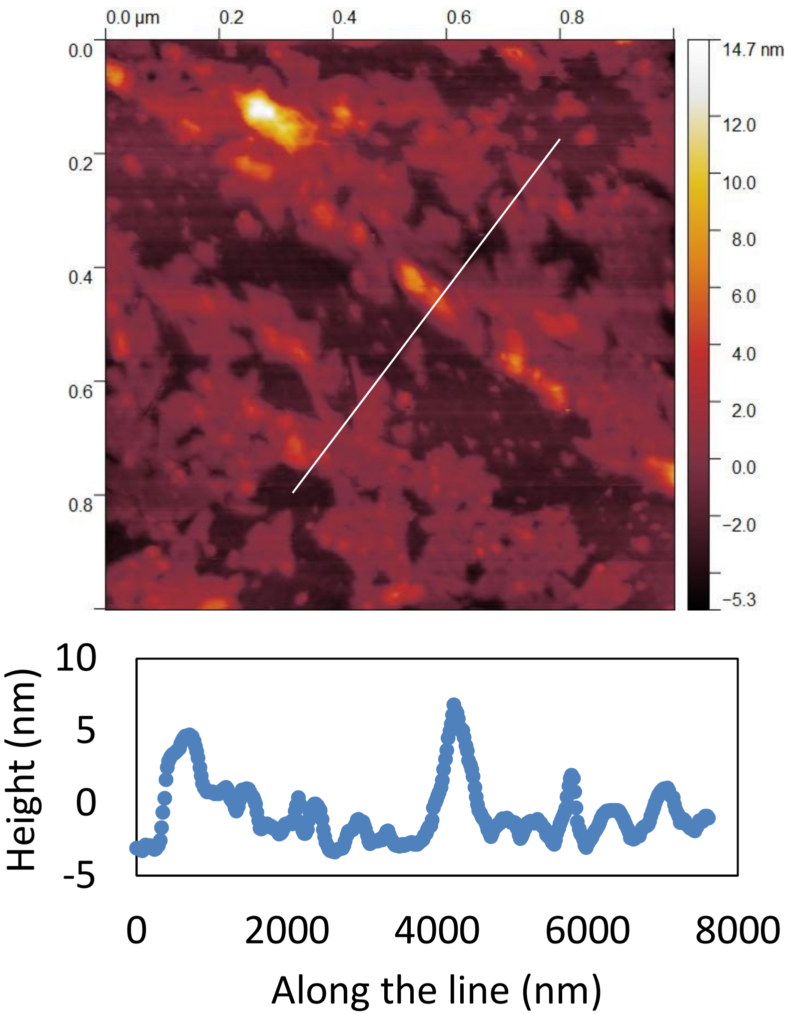


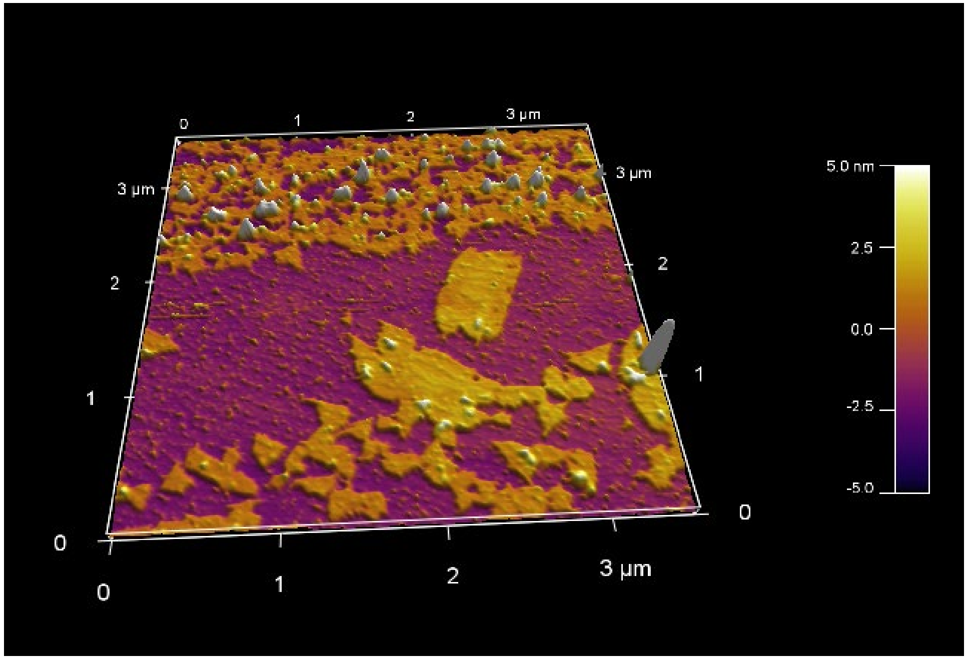
Temperature = 620° C, Pressure = 26.7 Pa, 1500 pulses

From this diagram, I chose two sets of conditions to examine further.

Atomic Force Microscopy

A





Substrate = STO
Temperature = 620˚ C
Pressure = 26.6 Pa
Fluence = 0.75 J/cm^2
Frequency = 10 Hz
Pulses = 1500

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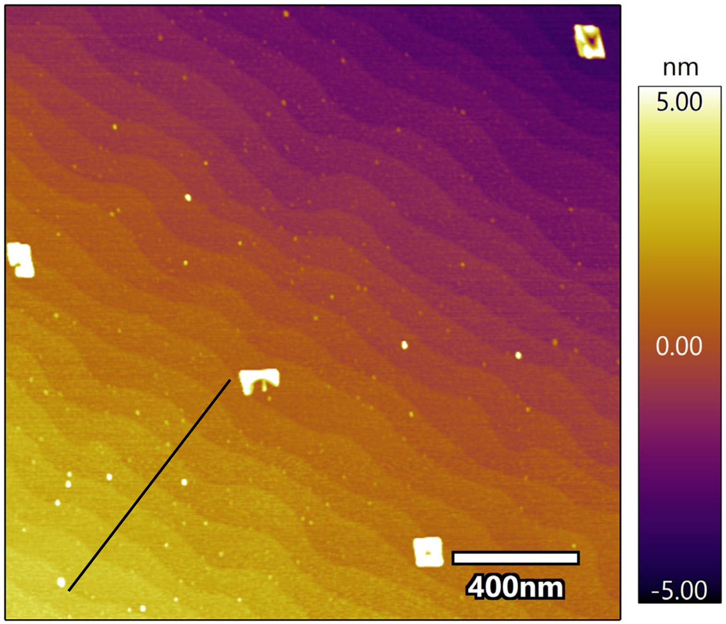
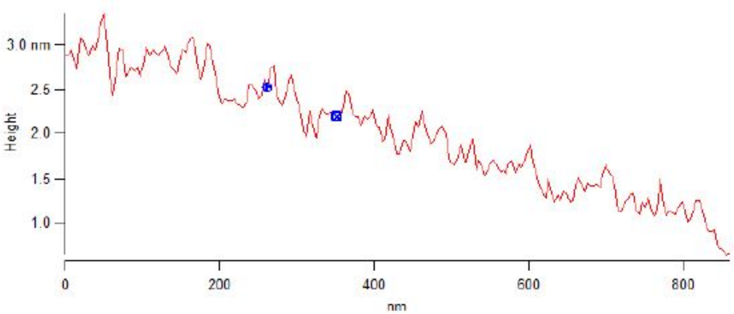
Atomic Force Microscopy

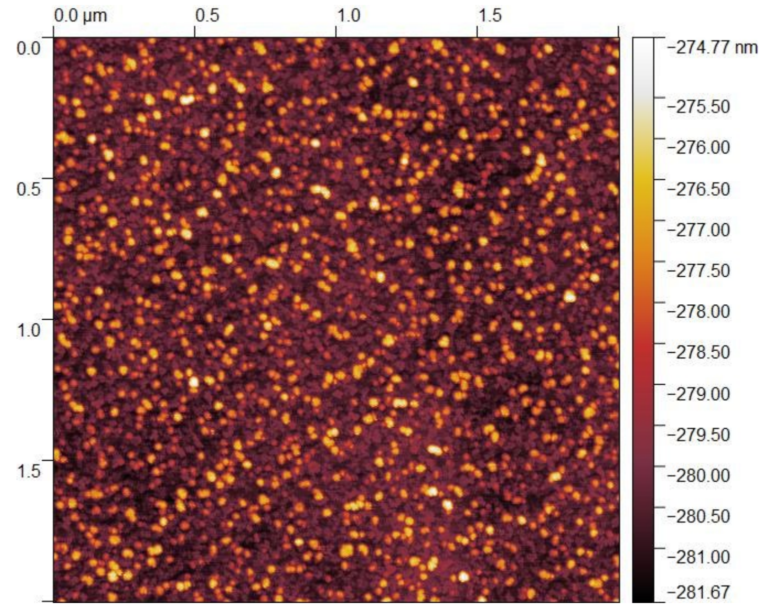
B

Thin sample (300 pulses)



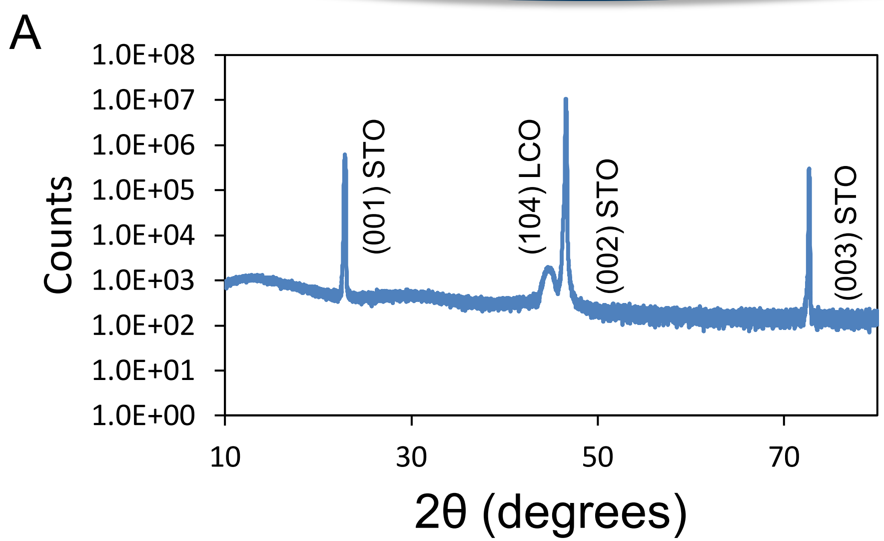


Thick sample (1000 pulses)

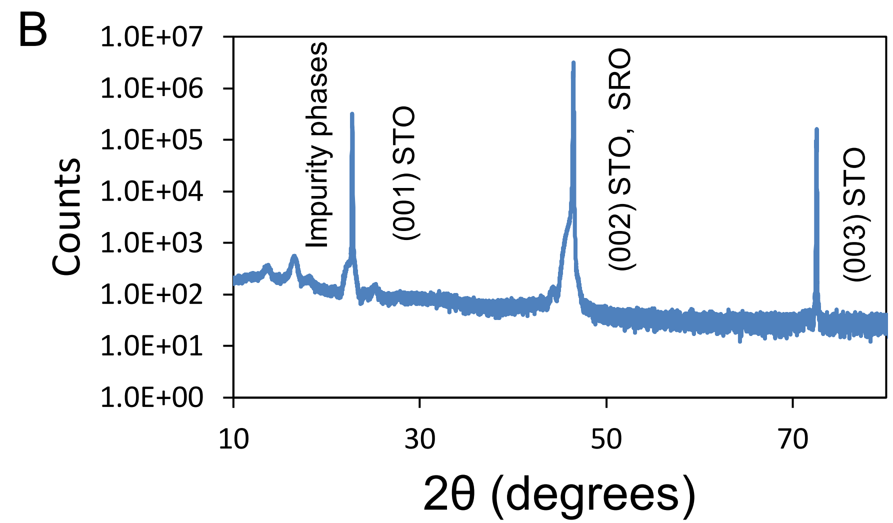


Substrate = SRO/STO
Temperature = 620˚ C
Pressure = 26.6 Pa
Fluence = 0.53 J/cm^2
Frequency = 5 Hz

X – Ray Diffraction



Substrate = STO, Temperature = 620˚ C, Pressure = 26.6 Pa, Fluence = 0.75 J/cm^2 , Frequency = 10 Hz Pulses = 1500



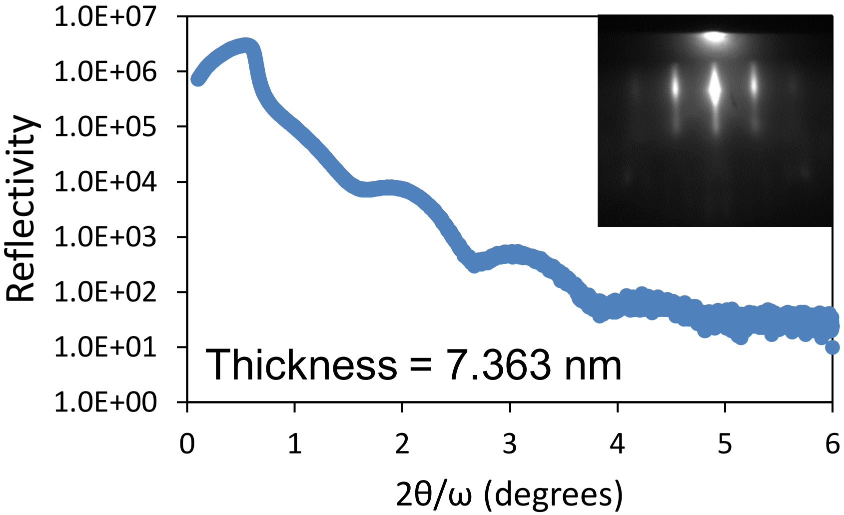
Substrate = SRO/STO, Temperature = 620˚ C, Pressure = 26.6 Pa, Fluence = 0.53 J/cm^2 , Frequency = 5 Hz, Pulses = 1000

- The right XRD pattern has more impurity phases in the lower angles
- This same pattern has shoulders for the (001) and (002) peaks
- The left XRD pattern has another peak right next to the (002) STO peak. This extra peak signifies LCO

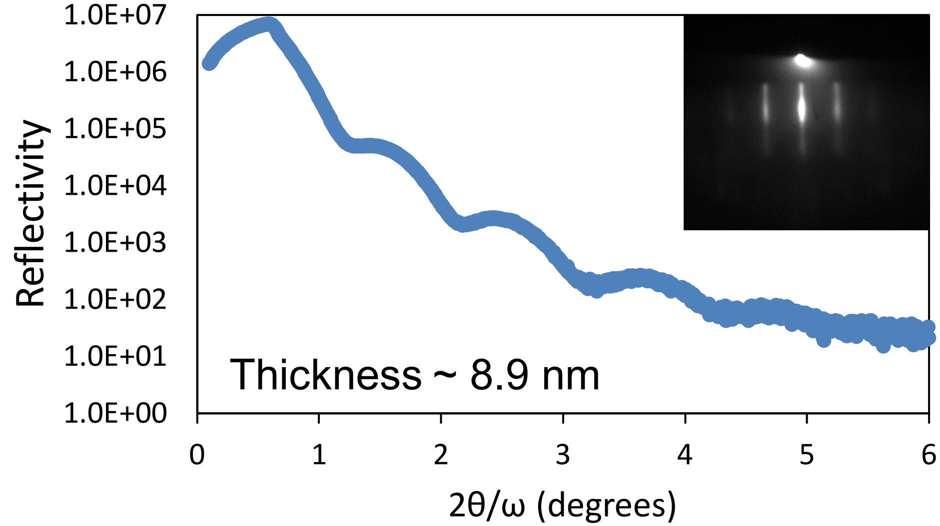
Processing

X – Ray Reflectivity

A



B



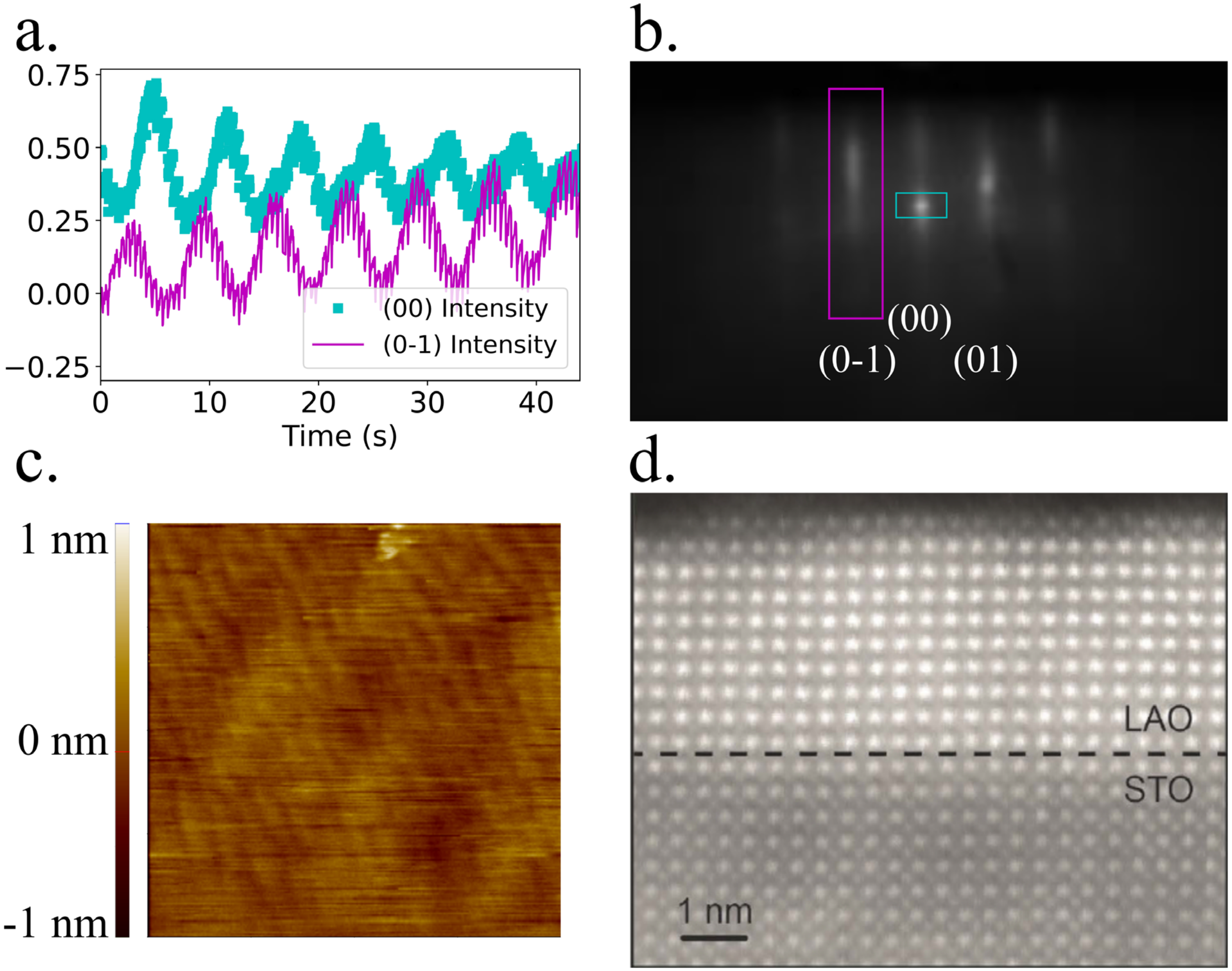
Substrate = STO, Temperature = 620˚ C, Pressure = 26.6 Pa, Fluence = 0.75 J/cm^2 , Frequency = 10 Hz Pulses = 1500

Substrate = SRO/STO, Temperature = 620˚ C, Pressure = 26.6 Pa, Fluence = 0.53 J/cm^2 , Frequency = 5 Hz, Pulses = 1000

- The interface looks sharper on the right image
  - This may only be accounting for the sharp interface of SRO/STO
- The thickness of LCO on the left sample is much greater than that of the right sample
  - This could be just picking up SRO in B, whereas thickness only accounts for LCO in A.

Data Science

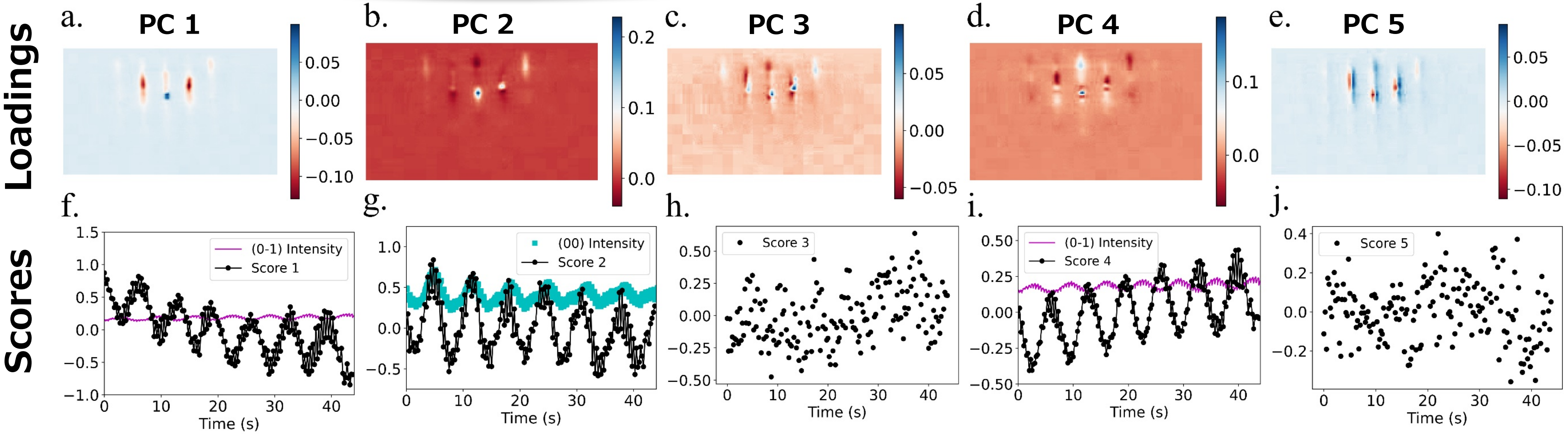
$LaAlO_3$



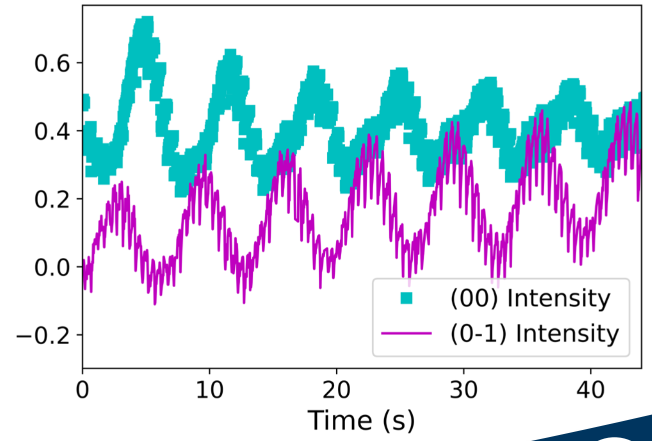
- Grows layer-by-layer over a range of conditions
- This sample was grown:
  - Temperature = 770˚C
  - Fluence = 1.5 J/cm^2
  - Pulse frequency = 2 Hz
  - Background oxygen pressure = 0.1 mTorr
- All samples grown on TiO_2 terminated $SrTiO_3$

K. Gliebe and A. Sehirlioglu, “Distinct thin film growth characteristics determined through comparative dimension reduction techniques.” J. Appl. Phys., vol. 130, pp. 125301, 2021, doi: 10.1063/5.0059655

Principal Component Analysis



- PC1: positive scores dominate in the beginning and correspond to the (00) spot in loadings. Negative scores dominate later and correspond to (01), (0-1). Minimum in scores corresponds to maximum of (0-1)
- PC2: relates to (00) spot; scores decrease with increasing thickness. (00) contains information from the substrate.
- PC4 Effects from incoherent scattering, correction to intensity from PC1
- Intensity oscillation phase shift



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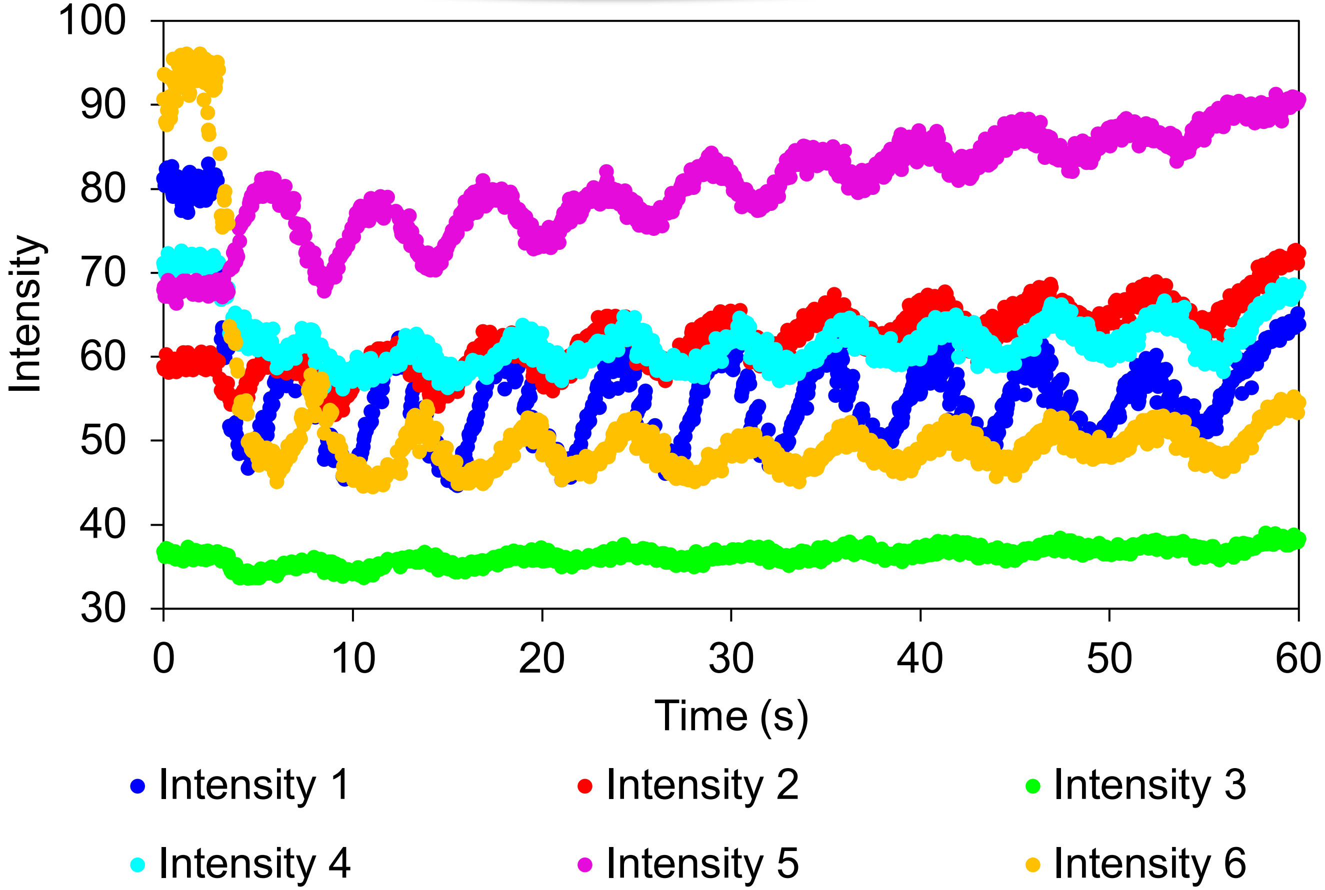
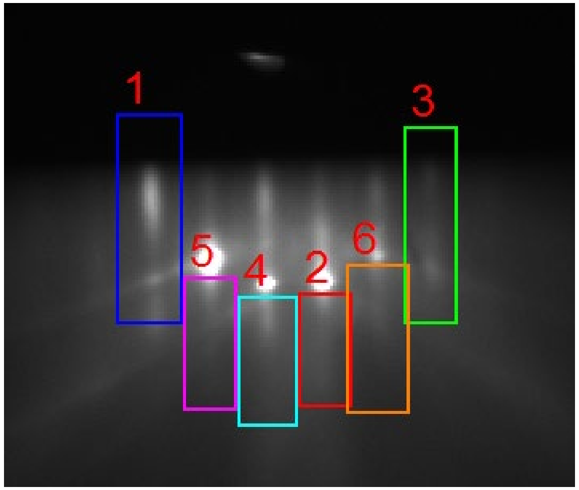
Same phase shift in other materials



$SrTiO_3/SrTiO_3$



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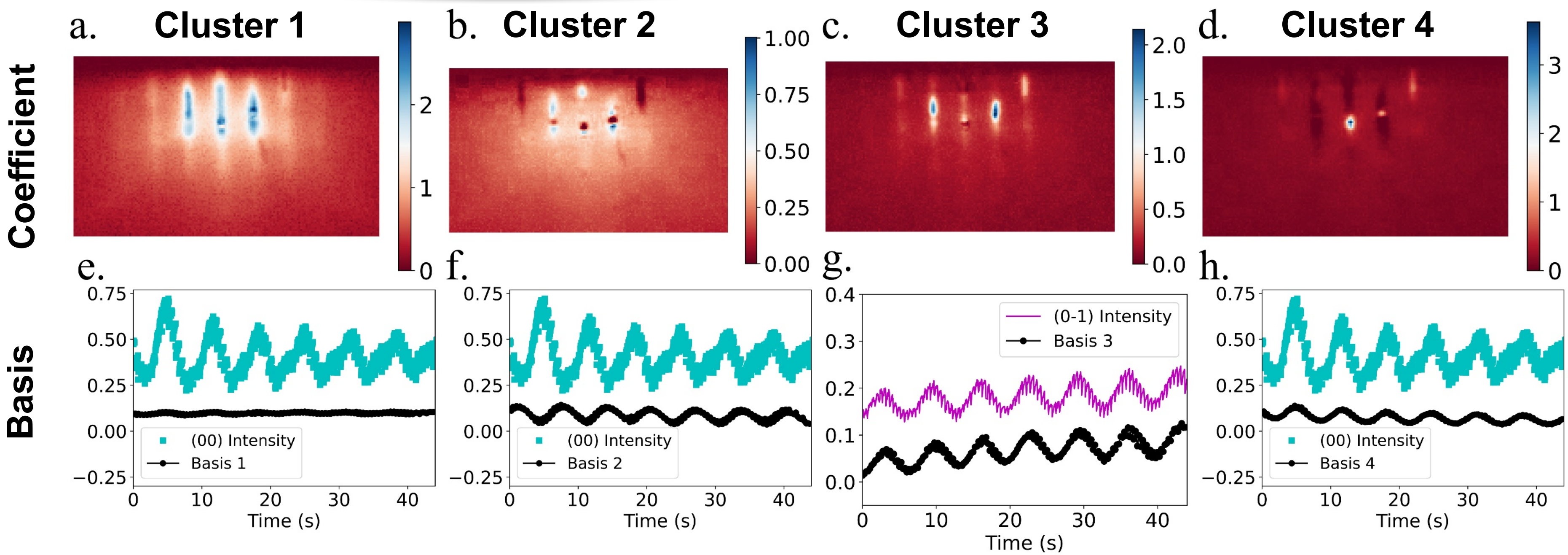
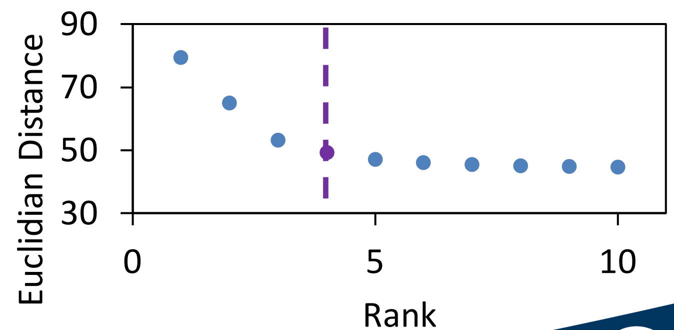
Nonnegative Matrix Factorization



- NMF has more easily interpretable data than PCA
- Cluster 1 represents the overall intensity change
- Cluster 2 demonstrates incoherent scattering
- Cluster 3 the (0-1) RHEED spot intensity oscillation
- Clusters 4 aligns to the (00) intensity oscillation
- Clusters 3 and 4 separate the data shown in PC1



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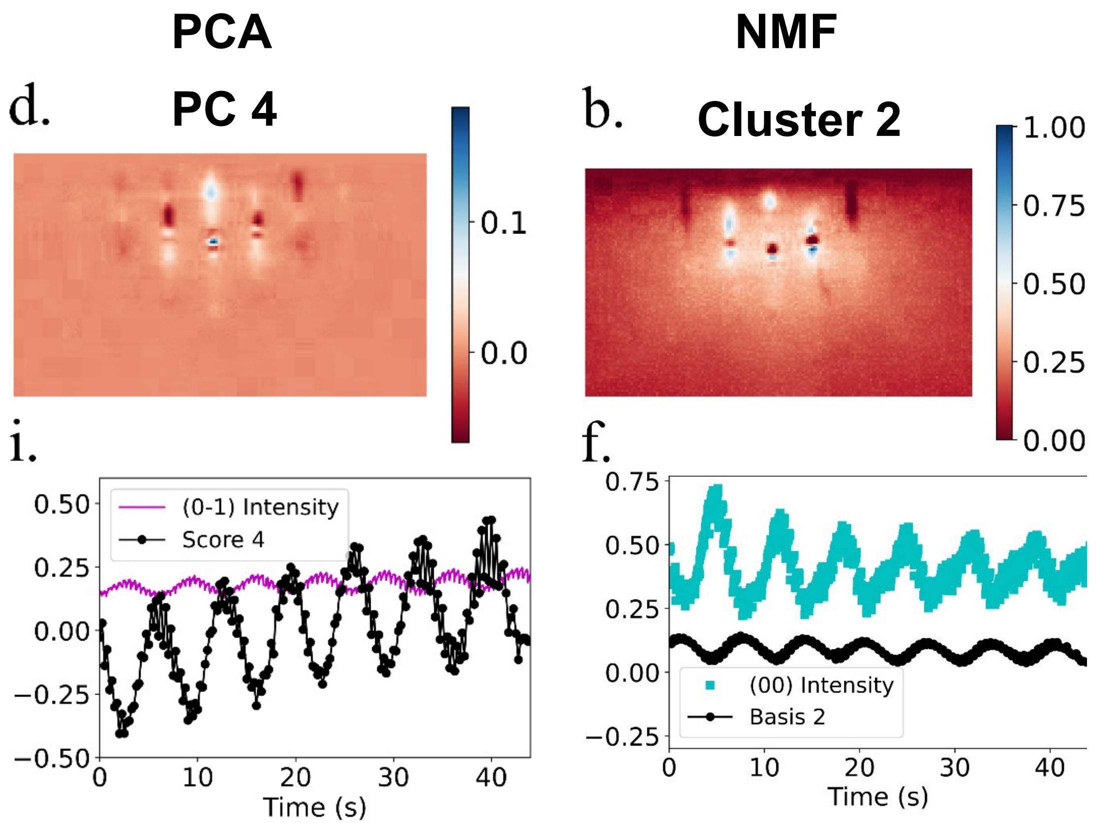
Nonnegative Matrix Factorization



Incoherent scattering is present in both cluster 2 in NMF and PC 4

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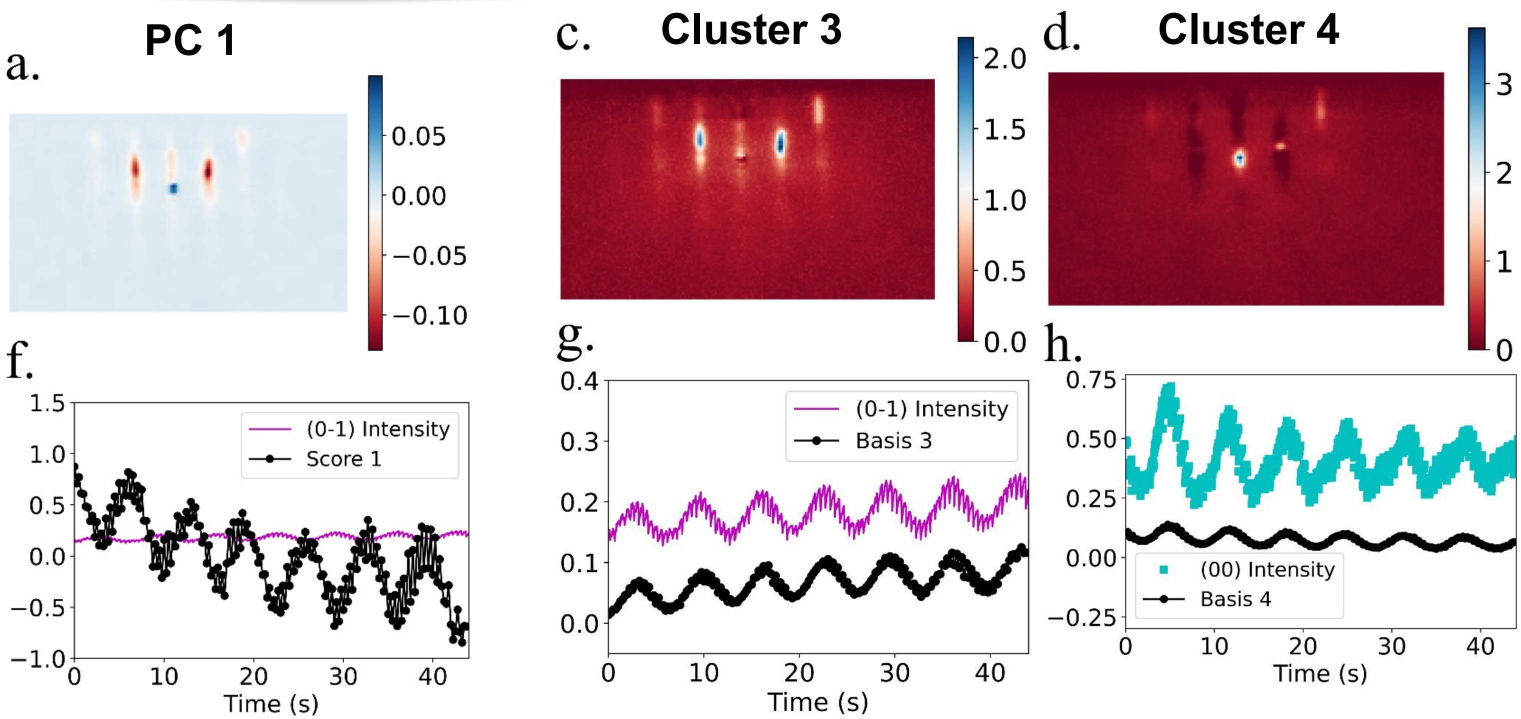
Data Science

Nonnegative Matrix Factorization



- NMF automatically separated the (00) and (0-1) diffraction spot information
- In PC1 the information from the different diffraction spots is mixed

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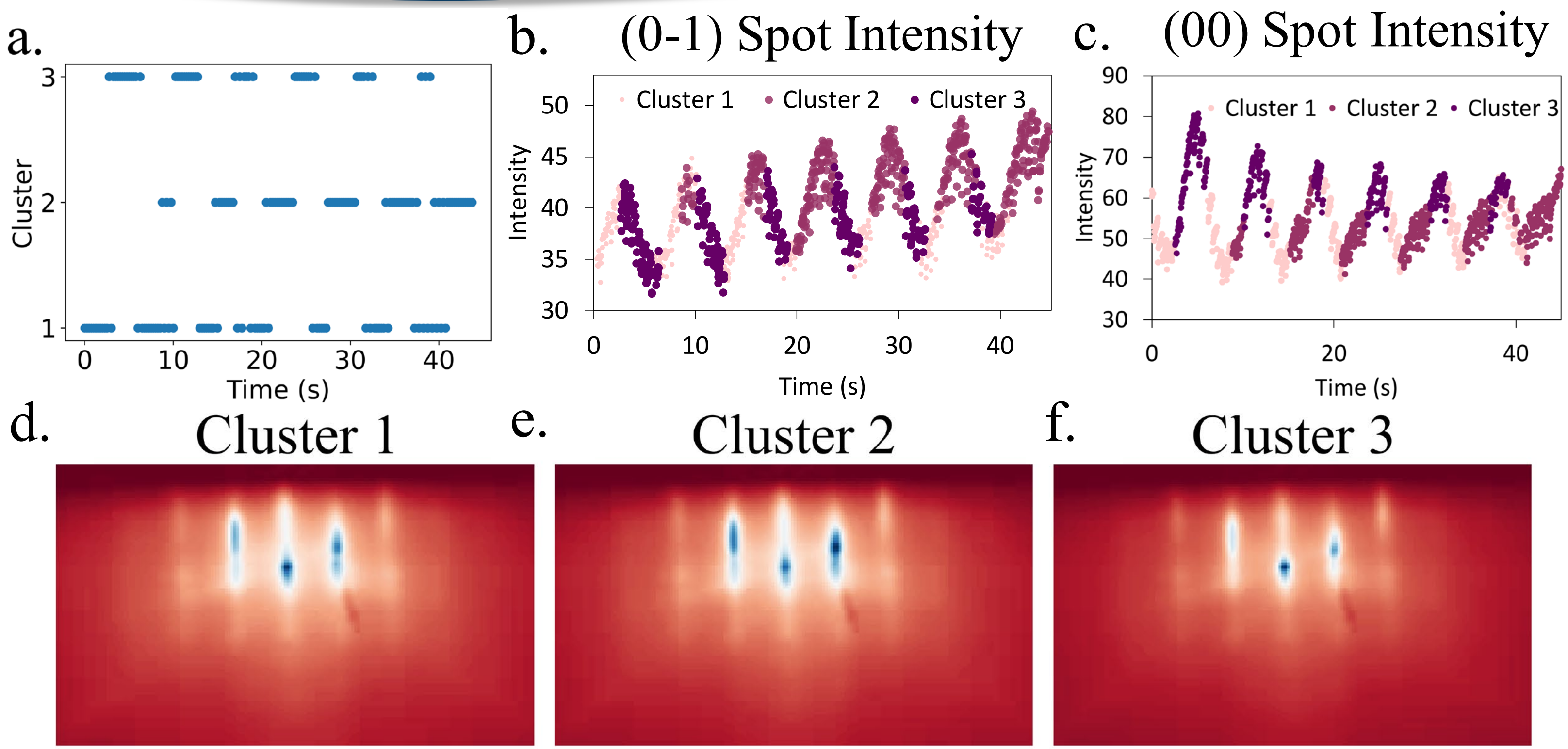
Kmeans



- Clusters 1 and 3 emphasize the (00) spot
- The (01) and (0-1) spots are more prominent in cluster 2
- Cluster 2 is increasing with time, whereas 1 and 3 decrease, indicating (00) relates to substrate
- Changing the spot the intensity is from changes the cluster at maximum

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Conclusions

- Processing
  - The best growth conditions I have found so far are: temperature = 620° C, pressure = 26.6 Pa, fluence = 0.75 J/cm^2 , frequency = 10 Hz
  - This sample demonstrated a larger amount of LCO, and regions where the films were evenly spread across the surface
- Data Science
  - A shift in the intensity oscillations of different diffraction spots was noticed
  - Noise, as well as enhanced incoherent scattering were distinguished
  - NMF is the most easily interpreted method of the three unsupervised learning techniques

What's Next?

- More structural characterization for understanding of epitaxial LCO/SRO/STO
- Electrical and electrochemical characterization
  - LCO/SRO/STO half cell
  - LLTO solid electrolyte

Acknowledgements

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Electro-ceramics Group, the National Defense Science and Engineering Graduate Fellowship, the SDLE Group, and CWRU High Performance Computing Clusters.

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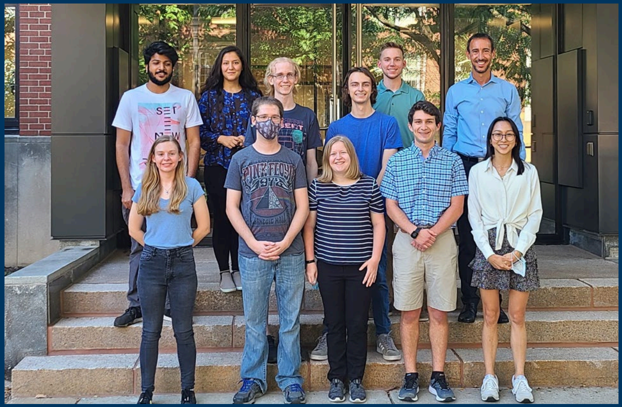

Questions?

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Kimberly Gliebe[a] and Alp Sehirlioglu

AFFILIATIONS

Department of Materials Science and Engineering, Case Western Reserve University, 10900 Euclid Avenue, White Building, Cleveland, Ohio 44106, USA