Modulation of Electrical Transport and Structural Properties of $CaMnO_3$ Epitaxial Thin Films

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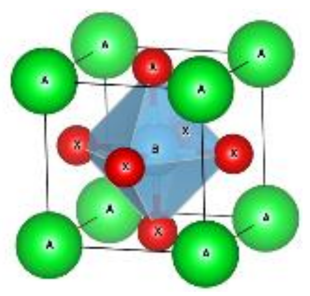
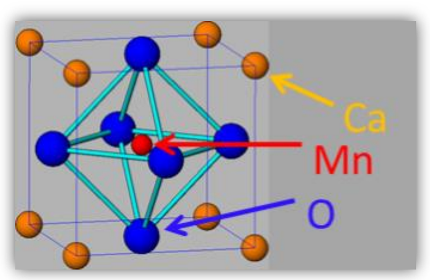
INTRODUCTION

Calcium manganese oxide ($CaMnO_3$ abbreviated as CMO) is a material belonging to the family of perovskite manganites, which have the general formula of ABO_3. Like many other perovskite oxides, CMO can exist in oxygen deficient phases $CaMnO_{3-y}$ over a wide range of oxygen deficiency.



$A = Ca$
$B = Mn$
$X = O_3$



The ideal perovskite unit cell is cubic with the A cations at the corners of the cube, the B cation at the cubic center, and the oxygen anions forming an octahedral space around the B cation.

Oxygen deficiency introduces mixed valent state of Mn.

$CaMnO_3$ (Fully Oxygenated)	$CaMnO_{3-y}$ (Oxygen Deficient)
$Ca^{+2}Mn^{+4}O_3^{-6}$	$Ca^{+2}Mn^{+4}_{(1-2y)}Mn^{+3}_{2y}O^{-(6-2y)}_{(3-y)}$

The electrical resistivity of manganese-based perovskite materials such as CMO depend on the chemical composition and the oxygen content of the compound. Fully oxygenated $CaMnO_3$ is an insulator with very high resistivity. Oxygen deficiency causes a decrease in resistivity.
The electrical conduction occurs by electron transfer between the Mn^{+3} and Mn^{+4} ions mediated by a connecting oxygen atom.

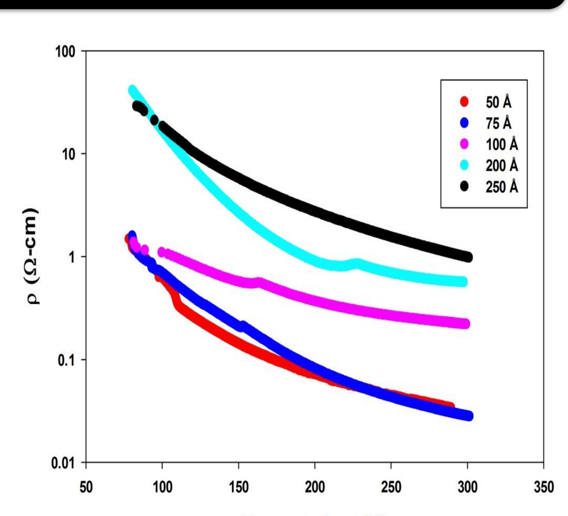
Technological Applications of CMO

- **Catalyst for biofuel to diesel conversion**
- **Photocatalyst for water splitting**
- **Fuel cell electrode**
- **Thermoelectric material**

Oxygen vacancies and resulting conductivity modulations are of interest for all these applications.

BACKGROUND & MOTIVATION

Previous research in our laboratory has revealed that electrical resistivity of 80 mTorr CMO films grown on $LaAlO_3$ substrates decreases significantly with decreasing thickness. This is understood as the result of tensile lattice mismatch strain promoting oxygen vacancies.



The goal of the current project is to study how the resistivity of CMO depends on the oxygen pressure, film thickness, and choice of substrate.

EXPERIMENTAL METHODS

PULSED LASER DEPOSITION

In the pulsed laser deposition (PLD) process, a laser is shot at a bulk target of material, which is ablated to form a plasma plume. The plume is deposited onto a single crystal substrate held at a high temperature. We can vary several parameters, such as oxygen pressure, pulse energy, and number of pulses.

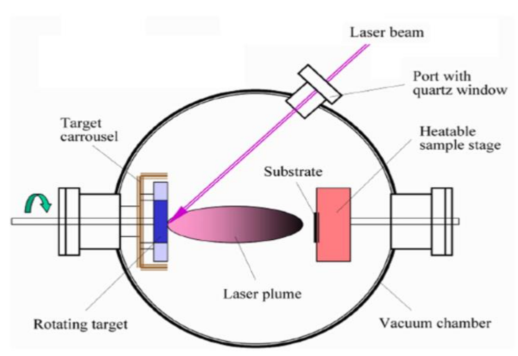


Figure 1. Diagram of PLD thin film growth

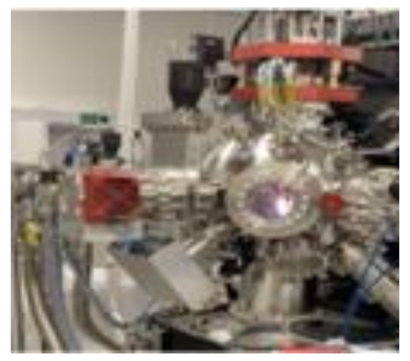
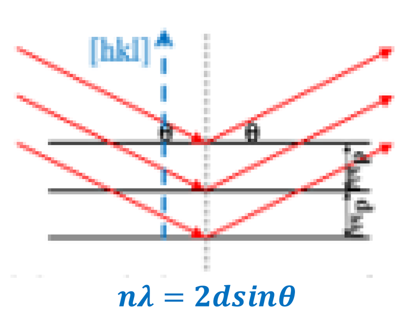


Figure 2. PLD chamber

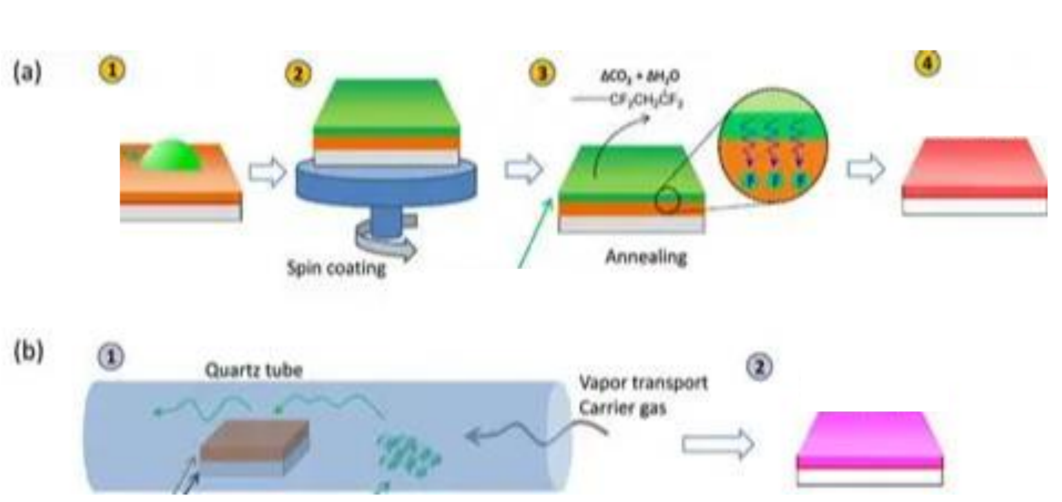
X-RAY DIFFRACTION

For parallel planes of atoms with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied. For a fixed wavelength, a family of planes produces a diffraction peak only at a specific angle θ, which depends on the spacing between the planes, according to Bragg's law.

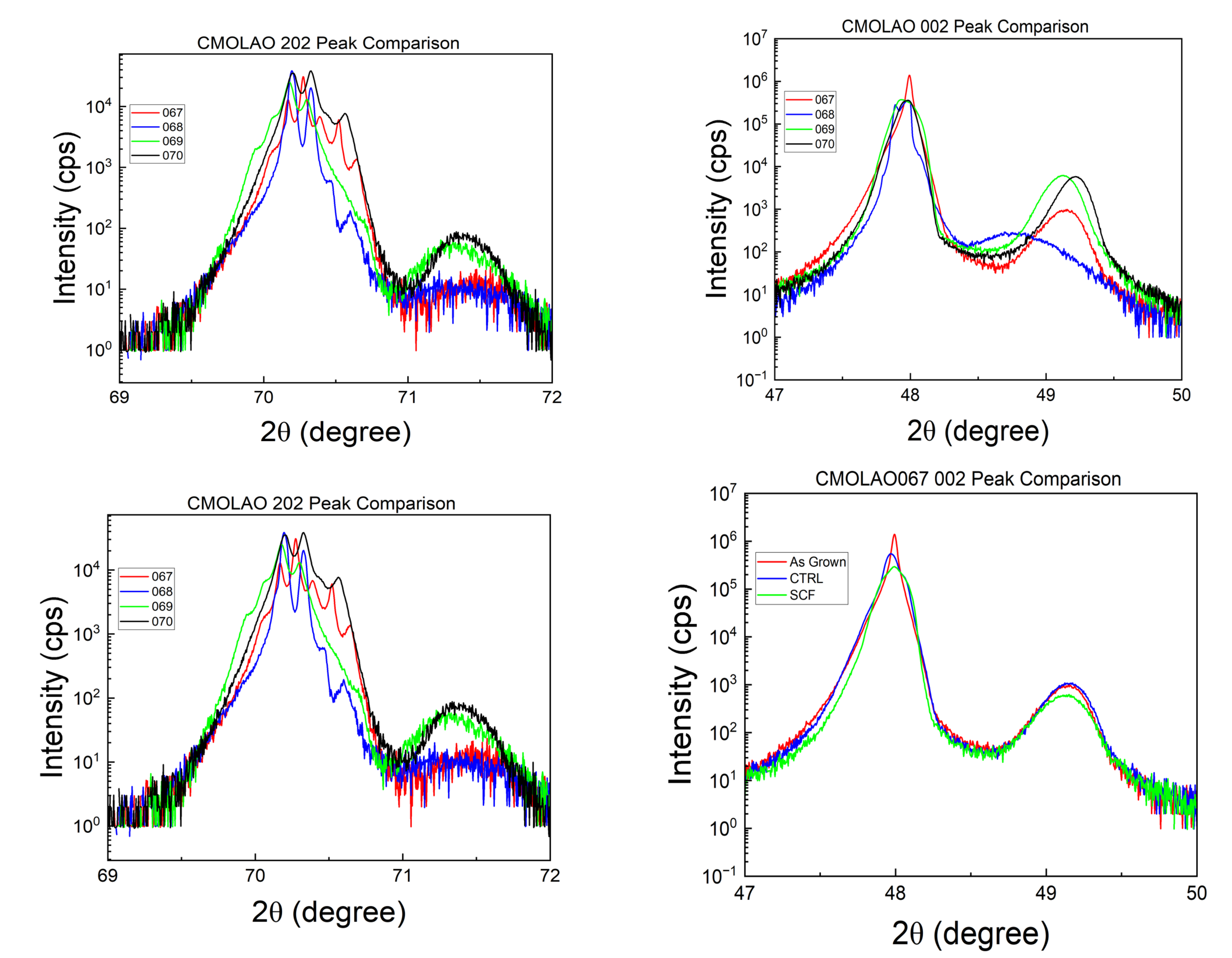


FLOURINATION

Using a Polyvinylidene fluoride (PVDF) and Dimethylformamide (DMF) mixture with 18.7% PVDF and 81.3% DMF. We then spin-coated the DMF-PVDF solution with one drop onto the CMOLAO67 sample to fluorinate it and left it in the furnace overnight.



RESULTS



Sample Names	PLD Chamber Pressure	2 Probe Resistance Measurement	A Lattice Constant	C Lattice Constant
CMOLAO 067	80 mTorr	OL	3.7570 Å	3.7040 Å
CMOLAO 068	Vacuum	10-12 MΩ	3.7318 Å	3.7293 Å
CMOLAO 069	1 mTorr	OL	3.7704 Å	3.7057 Å
CMOLAO 070	10 mTorr	OL	3.7744 Å	3.6997 Å

CMOLAO 067 Sample	2 Probe Resistance Measurement
As Grown	OL
CTRL	OL
SCF	0.3-0.4 MΩ

ACKNOWLEDGEMENTS

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SUMMARY & CONCLUSIONS

- The fluorinated CMOLAO 067 peaks (CMOLAO 067 SCF) are slightly lower than the as grown and control samples in the 002 XRD comparison.
- Future work could be fluorinating the CMOLAO 068, 069, and 070 samples and testing the XRD results.
- Samples 067 and 068 had much more outlier results than 069 and 070, which were similar to each other. This makes sense since 067 was created in a much higher 80 mTorr environment while 068 was created in a vacuum.
- The C-lattice constant of CMOLAO 068 sample, which was created in a vacuum, was higher than the consistent constant of around 3.700 Å that samples CMOLAO 067, 069, and 070 had.
- All 2-Probe Measurements taken from all samples came out in OL except for CMOLAO 068 which was put in a vacuum during the PLD Process.
- 2 Probe Resistance Measurements for the CMOLAO 067 CTRL and As Grown Samples were OL. The fluorination of the CMOLAO 067 sample decreased the 2 Probe Resistance of the 067 sample.
- Future work could be taking 4-Probe resistance measurements in recreating the work or on the samples.
- In the 002 XRD Peak Analysis, the substrate peak of sample CMOLAO 068 did not show much of a peak at all, which it also was created in a vacuum environment.
- In the 202 XRD Peak Analysis, the substrate peaks of both samples CMOLAO 067 and 068 were close to each other and much lower than were the peaks of samples CMOLAO 069 and 070.