Compositional Analysis of Off-Stoichiometric Multiferroic $LuMnO_3$ and Electrode Nanopatterning of $(SrTiO_3)_n(BaTiO_3)_1SrO$ Thin Films

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Primary CNF Tools Used: Glen 1000 resist strip, Anatech resist strip, Manual resist spinners, ABM contact aligner, SC4500 odd-hour evaporator, Zeiss Supra SEM, Bruker energy-dispersive x-ray spectrometer (EDS)

Primary Cornell Center for Materials Research (CCMR) Tools Used: Asylum MFP-3D AFM

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Abstract:

Multiferroics are a class of materials that exhibit a combination of ferroelectricity, ferromagnetism, and ferroelasticity. $LuMnO_3$ is one such material with ferroelectric transition temperature of roughly 700 K and antiferromagnetic transition temperature of 90 K. Thin films of $LuMnO_3$ can be grown by molecular-beam epitaxy (MBE) to produce single crystal films with precise control over stoichiometry, $Lu_{1-x}MnO_3$, with up to 25% lutetium deficiency. Here, two $Lu_{1-x}MnO_3$ films with a composition gradient were explored. The films were characterized by atomic force microscopy (AFM) to identify the effects of lutetium deficiency on the surface morphologies, and by energy-dispersive x-ray spectroscopy (EDS) to quantify the surface composition gradient with a superimposed grid across the film. These measurements can be used to correlate ferroelectric and ferromagnetic properties with the observed composition gradient across each film. Additionally, nanoelectrodes were patterned on ferroelectric $(SrTiO_3)_n(BaTiO_3)_1SrO$ thin films.

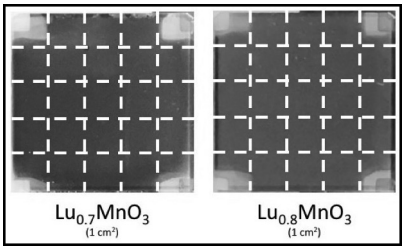


Figure 1: $Lu_{0.7}MnO_3$ on the left, $Lu_{0.8}MnO_3$ on the right, superimposed 5 × 5 grids dictating measurements.

Summary of Research:

Two projects were completed over the summer; characterization of off-stoichiometric lutetium-manganate ($Lu_{1-x}MnO_3$) thin films and patterning nanoelectrodes on strontium-barium titanate superlattice ($(SrTiO_3)_n(BaTiO_3)_1SrO$) thin films. Both materials were first grown using molecular-beam epitaxy (MBE) at Cornell by the REU intern's mentors.

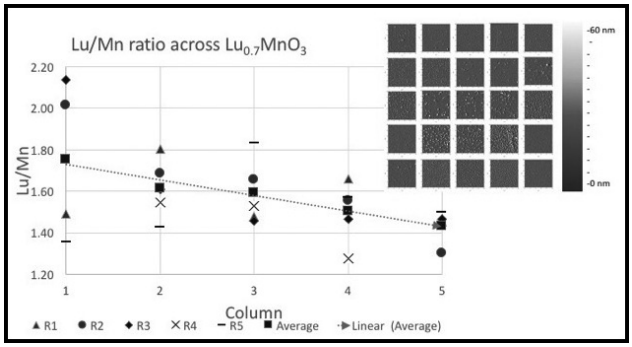
Two $Lu_{1-x}MnO_3$ films were grown by mentor Steinhardt with a composition gradient across the plane of the film by providing Lu and Mn fluxes from opposing directions during growth. The intern characterized the surfaces of these films with energy-dispersive x-ray spectroscopy (EDS) on the Bruker EDS/Zeiss Supra SEM in the CNF and atomic force microscopy (AFM) using the Asylum MFP-3D in the CCMR. In Figure 1, the films are divided into 5 × 5 grids; measurements were performed within the regions dictated by these grids to map the gradient.

Six $(SrTiO_3)_n(BaTiO_3)_1SrO$ films were patterned with nanoelectrodes for capacitance measurements. First, a photolithography mask was created to measure in-plane and out-of-plane dielectric and ferroelectric properties by modifying an L-Edit file already made by mentor Dawley. The final design for this mask is shown in Figure 4a.

The process flow for the second project is outlined below.

- Sonicate samples in acetone, followed by IPA, for five minutes each.
- Rinse in DI water and blow dry.
- Run in Anatech asher on the "descum" program for one minute.
- Pipette one drop of AZ-nLOF 2020 resist to each corner of the sample for an even coating, and spin using 4000 RPM, 100 RPM/s ramp, 45 seconds.
- Bake at 115°C for one minute.
- Expose for 7.5 seconds using the mask in Figure 4a on the ABM contact aligner.
- Rinse the mask with acetone and IPA between exposures.
- Bake for one minute at 115°C.
- Develop in AZ-MIF 726 developer for one minute, gently agitating.

- Rinse in DI water and blow dry.
- Run in the Anatech asher on the "descum" program for one minute.
- Deposit 10 nm of Cr, followed by 100 nm Au by e-beam evaporation.
- The samples may be taped to the evaporation plate if none of the devices are covered up by tape.
- Place the samples in acetone for approximately two hours for liftoff. The excess resist and metal may not fully lift off during this time; if not, sonicate very briefly (15 seconds max) and quickly remove the samples from the acetone solution.
- Place in IPA for two minutes, rinse with DI water, and blow dry.



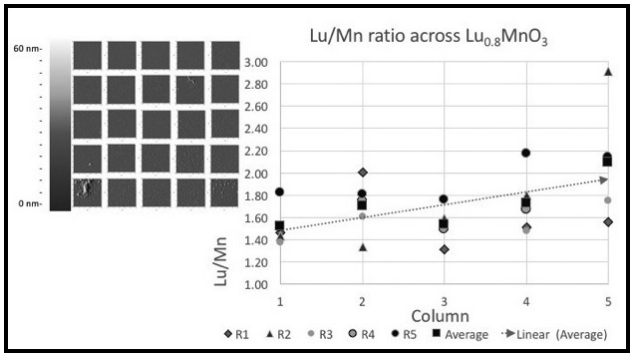


Figure 2, top: Ratio of Lu/Mn across $Lu_{0.7}MnO_3$ film across the surface of the film. Inset: 10 µm × 10 µm AFM images across the surface of the film. Figure 3, bottom: Ratio of Lu/Mn across $Lu_{0.8}MnO_3$ film across the surface of the film. Inset: 10 µm × 10 µm AFM images across the surface of the film.

Results:

Figures 2 and 3 show Lu/Mn ratios progressing across both films from left to right, in five rows, with insets showing the AFM images for each sample. Together, these two techniques show a trend of increasing surface roughness and "islands" with decreasing lutetium content. EDS does not register a chemical difference between these islands and the general surface.

Additionally, there is considerably more Lu on the surface than expected; roughly double the amount of Mn across the entire sample. Our hypothesis is excess Lu segregates to the growth surface during deposition.

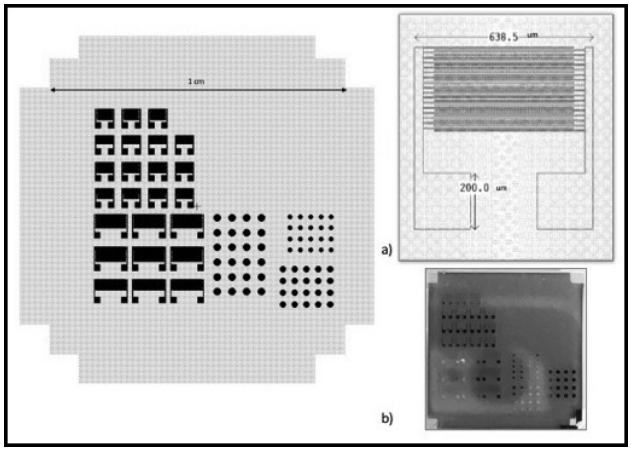


Figure 4: Patterned $(SrTiO_3)_n(BaTiO_3)_1SrO$ capacitive devices. Inset (a): L-Edit mask file. Inset (b): close-up of interdigitated electrode.

The results for the second project are the devices themselves, shown patterned on a sample in Figure 4.

Future Work:

The $LuMnO_3$ samples will undergo further elemental analysis via Rutherford backscattering spectroscopy. This will inspect the bulk composition while EDS is only surface sensitive. Once the composition of each sample is known, ferroelectric and ferromagnetic measurements may be taken which will be correlated to the compositions.

The electrodes on the $(SrTiO_3)_n(BaTiO_3)_1SrO$ samples will be used for capacitance measurements. The interdigitated electrodes (Figure 4b) will be used to measure in-plane capacitance by placing probes on the two terminating pads and applying a voltage across the electrode. The dots will be used to measure out-of-plane capacitance. The $(SrTiO_3)_n(BaTiO_3)_1SrO$ film will be partially removed to access the conductive $SrRuO_3$ layer beneath it. One probe will be placed on the bottom layer, and another probe on a dot, creating a capacitor with $(SrTiO_3)_n(BaTiO_3)_1SrO$ as the dielectric. A voltage will be applied across the two probes to measure capacitance through the film.

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References:

[1] L.W. Martin, R. Ramesh, "Multiferroic and magnetoelectric heterostructures," Acta Materialia, 60. 6-7, April 2012.

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