Synthesis and Science of Correlated Complex Oxides at the Nanoscale

Tiffany Santos[1], Anand Bhattacharya[1,2]

[1] *Center for Nanoscale Materials, Argonne National Laboratory.*
[2] *Materials Science Division, Argonne National Laboratory.*

Scientific Thrust Area:

Complex oxide materials can host to a vast array of ordered collective states, including high temperature superconductivity, room temperature multiferroicity, half-metallic ferromagnetism, charge/orbital ordering, and stripe phases. These states arise out of the correlations between the spin, charge and lattice degrees of freedom unique to these materials. Our research program seeks to break new ground by exploring how these states behave on the nanoscale. We will create high quality epitaxial thin films and heterostructures of complex oxides that are known to have collective states of interest. Using the unique capabilities at the CNM to create and probe structures at the nanoscale, we will measure and understand fundamental electronic and optical properties of these materials at this length scale. The program will explore electronic phase-separation and competing ordered states that occur either intrinsically at the nanoscale or are promoted by confinement in nanoscale wires and constrictions. It includes studies of spin and charge dynamics, including correlation lengths and times to learn if these materials may be useful for information science and energy related applications.

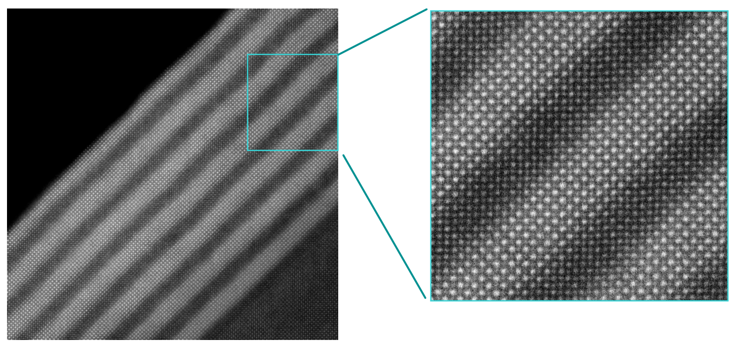

Fig. 1 Superlattice of $(LaMnO_3)_6/(SrMnO_3)_6$ synthesized by oxide MBE at the CNM, Argonne. Image: Amish Shah, Jian-Min Zuo,

Research Achievement:

The first step towards achieving our goals is to demonstrate the capability of creating complex oxide thin films and heterostructures (see Fig. 1) with fine control of stoichiometry, morphology (see Fig. 2) and thickness. To this end, we have commissioned a state-of-the-art oxide-MBE (Molecular Beam Epitaxy) synthesis tool. We have carried out careful calibration of the relative deposition rates of the various constituent elements to attain the correct sto ichiomery, and also an accurate measure of the total flux of atoms being deposited to attain the correct thickness. Annealing steps have been optimized to obtain atomically smooth films. Furthermore, the use of ozone at the appropriate pressure ensures that the materials are oxidized to their full extent to attain the desired properties. To demonstrate our capability, we have synthesized digital superlattices of $LaMnO_3/SrMnO_3$ where using x-ray scattering and reflectivity, we demonstrate that we have control at the level of a single atomic layer. We have also

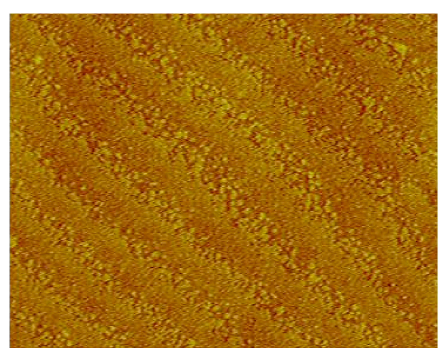

Fig. 2 AFM image of a surface of a superlattice of $(LaMnO_3)_1/(SrMnO_3)_1$ synthesized by oxide MBE at the CNM, Argonne. Image: Tiffany Santos

synthesized films and heterostructures of titanates, nickelates and cobaltates. Using these materials, we have begun a number of projects to explore nanoscale phenomena.

Nickelate/Manganite superlattices: Strained superlattices of $LaNiO_3$ sandwiched between insulating layers may be superconducting according to some theoretical predictions. This is because the under tensile strain, Ni^{3+} would mimic the Cuprate materials, having only one orbital participating at the Fermi level, and being quasi two-dimensional[1]. With Steve May (user, Materials Science Division, Argonne) we synthesized superlattices of $(SrMnO_3)_2/(LaNiO_3)_n$ (n = 1, 2, 4) using oxide MBE at the CNM. A metal-insulator transition was observed as n is decreased from 4 to 1. Analysis of the transport data suggests an evolution from gapped insulator (n = 1) to hopping conductor (n=2) to metal (n=4) with increasing LaNiO3 concentration.

Edge states in Manganite Nanowires: Any finite sized system with an energy gap, when pattened into a finite structure, is expected to have elementary excitations that are characteristic of the boundary. With Peter Abbamonte (user, UIUC) we seek to detect these edge states in patterned thin films of transition metal oxides such as the cuprates and manganites using transport and resonant (soft) x-ray scattering. Manganite films synthesized using oxide MBE at the CNM have been patterned into nanowire arrays in UIUC. Results of studies using resonant x-ray scattering and transport will be presented.

Future Work:

a. We have synthesized thin films of $(Sr,Ba)MnO_3$ which are predicted to allow off center distortions of the nominally Mn^{4+} ($3d^3$) cations. This prediction is remarkable in that typical of-center disortions in ferroelectrics involve d^0 cations (e.g. Ti^{4+}, Ta^{5+} and W^{6+}).[2]

b. Spin-polarized STM investigations of the Neel transition in A-type antiferromagnetic manganite films. This will seek analogs of the Griffiths phase, and antiferomagnetic domain formation in real space in an antiferromagnet.[3]

c. Systematic studies of nanoscale wires and dots, explore the effects of quantum confinement on phase separation with real space probes and transport/magnetic measurements.

d. Tool development: Development of *in-situ* real time rate measurement capabilities using atomic absorption spectroscopy.

References:

1. J. Chaloupka and G. Khaliullin, *Phys. Rev. Lett.* **100** 016404 (2008).

2. S. Bhattacharjee, E. Bousquet, P. Ghosez, "Engineering Multiferroism in $CaMnO_3$," *Phys. Rev. Lett.* **102** 117602 (2009).

3. M. Kleiber, M. Boder, R. Ravlić, R. Wiesendanger, "Topology-Induced Spin Frustrations at the Cr(001) Surface Studied by Spin-Polarized Scanning Tunneling Spectroscopy," *Phys. Rev. Lett.* **85** 4606 (2000).

Publications:

1. "Onset of metallic behavior in strained $(LaNiO_3)_n/(SrMnO_3)_2$ superlattices", S. J. May, T. S. Santos and A. Bhattacharya, *Phys. Rev.* B **79**, 115127 (2009).