MATERIALS ENGINEERING
SEMINAR

"Synthesis and Electrical Properties of Perovskite Nickelates"

By

Qi Wang
Purdue MSE PhD Dissertation

Advisor: Professor Shriram Ramanathan

ABSTRACT

Perovskite nickelates $ReNiO_3$, where Re stands for rare earth elements like La, Nd, Sm … etc, display metal-insulator transition (MIT) due to temperature variation and/or electron doping. In this work, perovskite nickelate thin films were deposited by physical vapor deposition (PVD) and chemical solution deposition (CSD) on LaAlO3 (LAO) substrate for epitaxial single-crystalline phase or on other substrates such as Si / SiO2 and fluorine doped tin oxide coated glass (FTO glass) for the polycrystalline phase. Detailed deposition parameters will be discussed and the thin film characteristics by the two deposition methods will be compared.

Redox reactions between pristine conducting phase (Ni^{3+}) and correlated insulating phase (Ni^{2+}), controlling the band gap as well as the optical transparency of nickelates, lead to the electrochromic activities of $NdNiO_3$ (NNO) thin films in smart window applications. Both CSD-NNO and PVD-NNO thin films on LAO substrates were systematically studied by electrochemical testing, including cyclic voltammetry scans and bleaching/coloration treatments in an electrolyte. A three-electrode set up was utilized with NNO thin film as the working electrode and pH 12 KOH aqueous solution as the electrolyte. It was confirmed that both CSD-NNO and PVD-NNO are electrochemically stable in the chosen solution and the optical transmittance of the NNO films is highly tunable. One significant advantage for CSD-NNO over PVD-NNO is the stronger electrochromic activity due to the porous nature of the films prepared by CSD method.

The electron-doping induced conductivity modulation of 10^8 orders of magnitude motivates the design of electronic devices with nickelates. During the process of platinum (Pt) or palladium (Pd) assisted hydrogenation of nickelate thin films, the nickel ions in the pristine state will be reduced due to the electron doping while the protons will remain in perovskite lattice as interstitial defects. The electron doping not only opens the energy band gap of the material, but also creates a Schottky barrier at the metal-semiconductor interface simultaneously. We will present an asymmetrical memory device with two terminals, one side Pd and the other side Au, fabricated on $SmNiO_3$ or $NdNiO_3$ thin films by e-beam lithography and photo lithography. The charge carrier transport mechanisms of the devices will be discussed with the current-voltage (I-V) characteristic analysis and resistance-temperature (R-T) dependence study. In addition, collaborative work based on such micro-nano devices including X-ray absorption (XAS) mapping affirming the proton drift under external electrical fields and more device performances with potential applications in neuromorphic computing and artificial intelligence, will be discussed.

$LaNiO_3$ (LNO), as the only member of rare earth nickelates which does not display thermally driven MIT, has been constructed in literature with structural modifications such as LNO/LAO superlattice or ultrathin LNO with only a few unit-cell thickness, to obtain MIT depending on temperature. Here we have successfully deposited epitaxial LNO thin films on LAO substrates by CSD method with two different solution concentrations (0.1M and 0.2M) resulting two sets of films, namely 0.1M-LNO and 0.2M-LNO, with different thicknesses. Like other nickelates such as SNO or NNO, the conductivity of LNO can also be suppressed by Pt assisted electron doping which turns the pristine metallic LNO into insulating H-LNO. LNO is so sensitive to hydrogen that its conductivity even shows response at room temperature in H_2 rich gas. A series of devices with "+" shaped LNO thin films were designed and fabricated by photo lithography, with Pd electrodes at the film center and Au electrodes at four corners. Devices fabricated on both 0.1M-LNO and 0.2M-LNO thin films showed resistive switching and synaptic behavior across Pd-LNO-Au connection, triggered by voltage pulses with a duration of hundreds of nanoseconds. The detailed resistive switching mechanisms is proposed based on the electrical testing results and thin film characterization.

Date: Wednesday, March 23, 2022
Time: 10:00am
Place: Via WebEx or ARMS 3115
https://purdue.webex.com/meet/shriram?_ga=2.13565431.1938329994.1642781946-250677051.1567446309

PURDUE UNIVERSITY

School of Materials Engineering