Strain control of electronic structure in epitaxial LaNiO₃

J. R. Petrie¹, V. R. Cooper¹, S. Okamoto¹, J. W. Freeland², and H. N. Lee¹.

¹Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA ²Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA

Perovskites that are conducting at room temperature have found a significant niche as electrodes for functional oxide devices. One such oxide is LaNiO₃, which exhibits a unique paramagnetic metallic behavior. While other strongly correlated oxides in the $d^7 ReNiO_3$ (Re = trivalent rare earth ion) system display a metal-to-insulator (MIT) transition due to the more compressed Ni-O bond associated with smaller Re ions, bulk LaNiO₃ shows no such transition¹. The larger La³⁺ ion results in a rhombohedral structure that remains metallic down to low temperatures as a more linear Ni-O-Ni bond angle closest to 180° substantiates increased Ni hybridization with the O (2p) states. However, structural modifications due to a lattice-mismatch across an interface can result in significant changes in NiO₆ octahedral bond lengths and rotations, resulting in novel electronic properties as the band structure of this e_g^1 system is altered. Recent theoretical work has postulated that by confining the e_g electron to the in-plane d_{x2-y2} orbitals, one could approach the high-Tc superconductivity seen in cuprates². Other work has emphasized the importance of the d_{r2} orbitals in surface catalysis³.

To systematically explore how we could use structural modifications to control the electrical transport and orbital polarization, we have taken advantage of the unique stoichiometric and thickness control offered by pulsed laser epitaxy to deposit LaNiO₃ thin films on different substrates. The resulting high quality (001)-oriented films were coherently grown, as confirmed by x-ray diffraction, and, at 10 nm, were thick enough to minimize the effects of dimensionality due to weak localization and polar disruption associated with films under 2 nm⁴. As the biaxial strain was swept from 2.7% to -1.3%, the tetragonality, as measured by the c/a ratio, increased from 0.96 to 1.04 with increasing levels of compressive strain. Likewise, the in-plane conductivity, as measured via the van der Pauw technique, was enhanced by

compressive strain. Average polarized X-ray absorbance spectroscopy (XAS) measurements verified in all cases the 3+ oxidation state of the Ni ion and its d⁷ occupancy. As seen in Figure 1, X-ray linear dichroism (XLD) studies showed that all strain resulted in orbital splitting while compressive (tensile) strain tended to orbitally polarize the e_g^1 electron towards the d_{z2} (d_{x2-y2}) orbital, an effect correspondingly observed in other thin films⁵.

Density functional theory calculations were able to correlate the increased tetragonality with compressive strain. We found such strain resulted in a larger Ni-O-Ni bond angle as a result of decreased octahedral rotation around the [110] direction, which led to increases in conductivity. In addition, calculated changes in the Ni-O bond length provided a structural basis for the observed orbital splitting and polarization. As determined in this study, compressive strain



Figure 1 Orbital polarization and splitting as a function of strain, as captured by the $d_{x2} - d_{x2-y2}$ differences in either XLD area or peak position of polarized X-rays, respectively.

leads to greater hybridization between Ni and O(2p), yielding a greater out-of-plane orbital polarization, whereas the tensile strain follows the opposite trend. Strain control of these properties thus provides a possible mechanism towards tuning electrical and catalytic properties.

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