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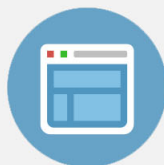
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Epitaxial growth of (111)-oriented $\text{LaAlO}_3/\text{LaNiO}_3$ ultra-thin superlattices

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The epitaxial stabilization of a single layer or superlattice structures composed of complex oxide materials on polar (111) surfaces is severely burdened by the reconstructions at the interface that commonly arise to neutralize the polarity. We report on the synthesis of high quality $\text{LaNiO}_3/m\text{LaAlO}_3$ pseudo cubic (111) superlattices on polar (111)-oriented LaAlO_3 , the proposed complex oxide candidate for a topological insulating behavior. Comprehensive X-Ray diffraction measurements, reflection high energy electron diffraction, and element specific resonant X-ray absorption spectroscopy affirm their high structural and chemical quality. The study offers an opportunity to fabricate interesting interface and topology controlled (111)-oriented superlattices based on ortho-nickelates. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773375>]

Over the past few years, complex oxide superlattices (SL) with correlated carriers have been widely studied owing to the range of exciting phenomena emerging at the interface which are unattainable in the bulk constituents.^{1,2} Recently, active experimental investigations^{3–7} on the class of SLs consisting of paramagnetic metal LaNiO_3 (LNO) and LaAlO_3 (LAO) were initiated after the prediction of a possible high T_c superconductivity in the $\text{LaNiO}_3/\text{LaMO}_3$ heterostructures (where LaMO_3 is a wide band-gap insulator).^{8,9} The experimental realization of LNO/LAO SLs grown on a (001) (Ref. 10) surface of SrTiO_3 (STO), however, revealed the presence of an unexpected transition to Mott insulating ground state with antiferromagnetic order due to quantum confinement and the effect of d -orbital polarization by the interface.^{4,6} Inspired by this approach, several recent theoretical proposals have been put forward regarding the physics which may emerge in a bilayer of LaNiO_3 sandwiched between LaAlO_3 layers grown along the [111] crystallographic direction. Specifically, the theory predicts the appearance of exotic topological phases (e.g., Dirac half-semimetal phase, quantum anomalous Hall insulator phase, or ferromagnetic nematic phase) modulated by the strength of electron-electron correlations.^{11–14} To date, very little experimental work has been done to develop such heterojunctions along the [111] direction to verify the theoretical predictions about this class of artificial materials with interesting electronic and magnetic ground states.

One of the main challenges in developing growth along [111] is that commonly used substrates such as LaAlO_3 (or SrTiO_3) consist of alternating $\text{LaO}_3^{3-}/\text{Al}^{3+}$ (or $\text{SrO}_4^{4-}/\text{Ti}^{4+}$) charged planes stacked along the [111] direction. The epitaxial thin film growth along this highly polar direction^{15–17} is far less understood due to the possible occurrence of complex surface reconstructions that act to compensate for the polar mismatch. For example, recently, it has been demonstrated that for the systems with strong polarity mismatch,

e.g., BiFeO_3 on STO or CaTiO_3 on LAO, the epitaxial stabilization is possible only if a “screening” buffer layer is grown first on the polar surface.¹⁸ On the other hand, the polarity matching at the interface can have strong influence on the epitaxial growth, defects formation, and overall stoichiometry of the layers as observed by the marked interfacial electronic reconstruction for polar LNO film grown on the top of charge neutral STO vs. polar LAO (001) surface.¹⁹

In this letter, we present the results of artificial layer-by-layer growth of a unique class of (111)-oriented $2\text{LNO}/m\text{LAO}$ heterostructures (with $m=2, 3$, and 4 unit cells) on LAO (111) single crystal (see Fig. 1(a)). The LAO substrate was selected to eliminate the effects of lattice mismatch (i.e.,

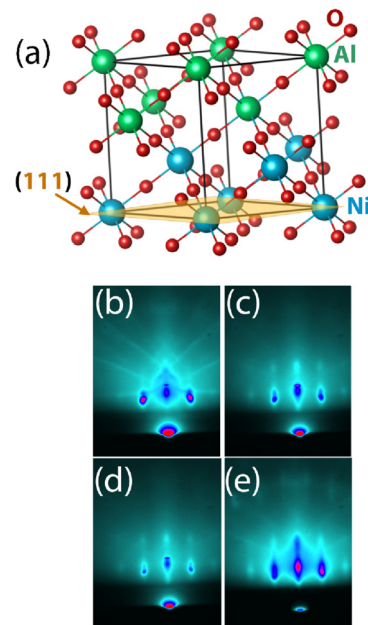


FIG. 1. (a) Structural arrangement of atoms in a bilayer of $\text{LaNiO}_3/\text{LaAlO}_3$ viewed along (111). La atoms are omitted for clarity. Note, the RHEED images are taken along [1-1 0] on (b) LAO substrate; (c) and (d) during the growths; (e) on $2\text{LNO}/2\text{LAO}$ film after cooling to room temperature.

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strain) between the layers, which otherwise may hinder the quality of growth. The extensive characterization using reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), X-ray diffraction (XRD), and synchrotron based resonant X-ray absorption spectroscopy (XAS) confirm the high structural, chemical, and electronic quality of these superlattices designed to facilitate the realization of the geometry driven electronic and magnetic phases.

Fully epitaxial 2LNO/*m*LAO SLs were grown by laser MBE operating in interval deposition mode on commercially available high-quality mixed terminated LAO (111) substrates.²⁰ The *in-situ* growth was monitored by high-pressure RHEED. The growth was carried out under 50 mTorr of partial pressure of oxygen at a deposition rate of 20–30 Hz; the substrate temperature was set at 670 °C. To maintain correct oxygen stoichiometry, the grown samples were subsequently post annealed *in-situ* for 30 min in 1 atm of ultra pure oxygen. Electrical d.c. transport was performed in a commercial physical properties measurement system using the *van der Paw* geometry.

In order to elucidate how the formally polar (111) surfaces of LAO substrate neutralizes the charge, we have investigated the as-received LAO substrate by combination of AFM and X-ray photoelectron spectroscopy (XPS) obtained at the different core states at both the grazing and normal orientation between the detector and the sample surface. The detailed characterization has revealed that the substrate possesses mixed termination (i.e., Al³⁺ and (LaO₃)³⁻) and the charge polarity is largely compensated by the formation of hydroxides on the LAO surface;²¹ heating of the LAO substrate to the high growth temperature removes hydroxides.²² In addition, a sequence of RHEED images was recorded at different stages of the growth and is shown in Figs. 1(b)–1(e). As seen in Fig. 1(b), the streak pattern observed along the Laue circles and the strongly developed Kikuchi lines clearly exclude the possibility of faceted morphology of the bare LAO (111) substrate.²³ Furthermore, as seen in Figs. 1(c) and 1(d), the specular intensity oscillations (not shown) along with the retention of the original (111) diffraction pattern after the subsequent deposition of LNO and LAO layers

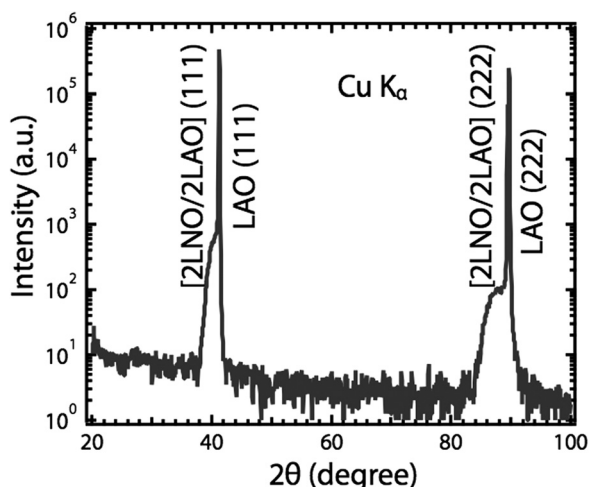


FIG. 2. 2θ - ω XRD scan for [2LNO/2LAO] superlattice using Cu K α radiation.

confirm the layer-by-layer growth along [111] direction; upon cooling down to ambient temperature, the high morphological quality of the [2LNO/2LAO] superlattices remained unaltered (see Fig. 1(e)). In order to gain further insight into the structural quality of growth along the [111] direction, we have recorded X-ray diffraction $2\theta - \omega$ pattern using Cu K α radiation. Fig. 2 displays the X-ray diffraction obtained in the vicinity of the LAO (111) and (222) reflections. The XRD data further support the proper [111] orientation of the heterostructures and negate the possibility of a detectable impurity phase formation. The analysis of the Bragg reflections yields the expected 1.5% tetragonal enhancement of the unit cell along the growth direction due to the in-plane compressive strain characteristic of full heteroepitaxy.

Since perovskite rare-earth nickelates are characterized by the unusually high valence state of Ni³⁺, the high structural quality of the ultra-thin SLs cannot guarantee their proper stoichiometry, especially against the formation of oxygen defects. In order to investigate the electronic and chemical structure of the SLs, measurements on the Ni L-edge, sensitive to the Ni charge state were performed in both total electron yield (TEY) and total fluorescence yield (TFY) modes at the soft X-ray branch of the 4-ID-C beam line at the Advanced Photon Source in Argonne National Laboratory. The absorption data are depicted in Fig. 3 along with the absorption on the bulk LaNi(3+)O₃ and Ni(2+)O reference samples taken in TFY mode to avoid the chemical issues associated with the surface. The absence of the characteristic of Ni²⁺ multiplet structure in line-shape on Ni L₂-edge and the peak position at 870.5 eV perfectly aligned to the bulk LaNi(+3)O₃ reference testify for the expected +3 charge state of Ni in these (111) SL's and further affirms the lack of any sizable charge transfer at the LNO/LAO interface. These results validate a proper superlattice stoichiometry critical for material quality which is in sharp contrast to

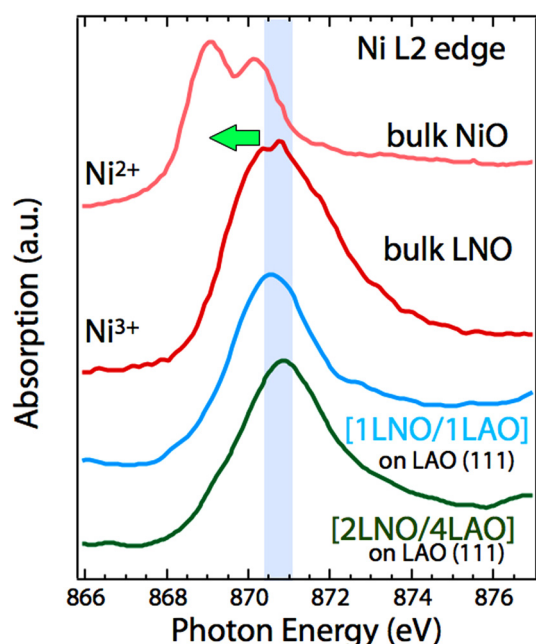


FIG. 3. Polarization averaged Ni L₂ XAS spectra obtained for 1LNO/1LAO and 2LNO/4LAO (111) superlattices and compared with bulk Ni(2+)O and bulk LaNi(3+)O₃ reference samples.

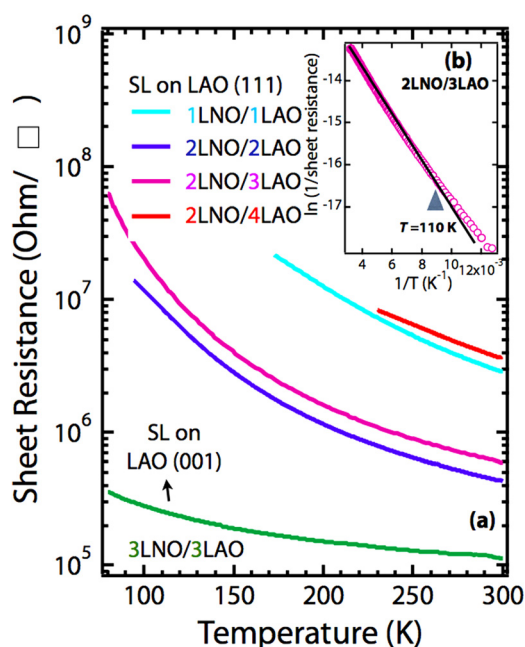


FIG. 4. (a) Sheet resistance for different superlattices are plotted as a function on temperature. (b) The conductance can be fitted by activated behavior above 110 K.

the case of polar LNO grown on non-polar STO (100) surface.¹⁹

After structural and local chemical quality had been verified, we proceed with the macroscopic d.c. transport measurements. Figure 4(a) shows the evolution of sheet resistance with temperature for a series of SL with varying LAO layer thickness. The data show a strong variance with the metallic state deduced from the earlier band structure calculations;¹³ all the heterostructures are highly insulating instead, hinting for a possible Mott behavior. However, further work are needed to confirm the nature of this insulating phase. The analysis of the transport temperature dependence under assumption of a single exponentially activated gap [$\sigma \propto \exp(-E_g/2k_B T)$] illustrated in Fig. 4(b) yields the value of gap E_g of ~ 95 meV. The importance of the geometrical stacking of atoms is further highlighted by the observation that the (111) SL's exhibit markedly higher resistivity compared to (001) SL (see Fig. 4(a)). Moreover, the transport for the 3LNO/3LAO SL grown on LAO (001) follows the variable-range hopping⁴ contrary to the single gap activated behavior observed in the (111) SLs.

In summary, we have synthesized the high-quality fully epitaxial 2LNO/ m LAO superlattices on formally polar LAO (111). A combination of RHEED, XRD, and XAS studies has confirmed the excellent structural, chemical, and electronic quality of these heterostructures. All the fabricated SL's are insulating in nature, contrary to the metallic ground

state, proposed from *ab-initio* calculations. The presented results also open the exciting prospects for fabrication of other ortho-nickelate based (111) superlattices (e.g., NdNiO₃/LAO and EuNiO₃/LAO) with interesting geometry-driven magnetic and electronic ground states.

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