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Epitaxial growth of (111)-oriented LaAlO$_3$ / LaNiO$_3$ ultra-thin superlattices
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Epitaxial growth of (111)-oriented LaAlO₃/LaNiO₃ 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 LaNiO₃/ LaAlO₃ pseudo cubic (111) superlattices on polar (111)-oriented LaAlO₃, 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]
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/mLAO SLs were grown by laser MBE operating in interval deposition mode on commercially available high-quality mixed terminated LAO (111) substrates. 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., Al\(_{3+}\)) and the charge polarity is largely compensated by the formation of hydroxides of the LAO surface; heating of the LAO substrate to the high growth temperature removes hydroxides.

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. 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 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 in to the structural quality of growth along the [111] direction, we have recorded X-ray diffraction 2\(\theta\) – \(\phi\) pattern using Cu K\(_\alpha\) 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 heteropitaxy.

Since perovskite rare-earth nickelates are characterized by the unusually high valence state of Ni\(^{3+}\), 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+)O\(_3\) and Ni(2+)O references taken in TFY mode to avoid the chemical issues associated with the surface. The absence of the characteristic of Ni\(^{2+}\) multiplet structure in line-shape on Ni L\(_2\)-edge and the peak position at 870.5 eV perfectly aligned to the bulk LaNi\((+3)O_3\) 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
the case of polar LNO grown on non-polar STO (100) surface.

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, 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 $\sim$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 hopping contrary to the single gap activated behavior observed in the (111) SLs.

In summary, we have synthesized the high-quality fully epitaxial 2LNO/mLAO 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., NdNiO$_3$/LAO and EuNiO$_3$/LAO) with interesting geometry-driven magnetic and electronic ground states.

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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.