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Electric-field tuning of the metal-insulator transition in ultrathin films of $LaNiO_3$

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Epitaxial ultrathin films of the metallic perovskite $LaNiO_3$ were grown on (001) $SrTiO_3$ substrates using off-axis rf magnetron sputtering. The film structure was characterized and their electrical properties investigated. Films thinner than 8 unit cells display a metal-insulator transition at a thickness dependent characteristic temperature. Hall measurements revealed p-type conduction, which was confirmed by electric field-effect experiments. Large changes in the transport properties and the metal-insulator transition temperature were observed for the thinnest $LaNiO_3$ films as the carrier density was electrostatically tuned. © *2009 American Institute of Physics*.
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The perovskite nickelates ($RNiO_3$, where R is a rare earth) are a fascinating family of compounds that display sharp temperature-driven metal-insulator (M-I) transitions with resistance changes of up to four orders of magnitude.[1,2] The conduction band is believed to be formed by the overlap of the Ni d orbitals and the O p orbitals. This overlap is structurally correlated with the ionic radii of the rare earths and influenced by the temperature. With decreasing temperatures, the NiO_6 octahedra buckle and the reduced overlap is thought to induce the M-I transition.[3,4] The precise mechanism for the gap opening, however, is still under debate, with the most recent data showing that charge disproportionation ($2Ni^{3+} \rightarrow Ni^{3+\delta}+Ni^{3-\delta}$) with an accompanying symmetry change from orthorhombic to monoclinic may be at the origin of the localization for the entire $RNiO_3$ series.[5,6] To date, the most technologically relevant of the nickelates is $LaNiO_3$. It is the only member of the family that does not display a M-I transition in its bulk form, remaining metallic down to the lowest temperatures. Bulk and thin films of this metallic oxide have been studied extensively in the past[7–9] and $LaNiO_3$ is a popular choice as an electrode material in oxide electronics. For instance, in the area of ferroelectric memories and devices, the use of conducting perovskite oxides such as $LaNiO_3$ and $SrRuO_3$ allows coherent growth of fully strained epitaxial perovskite thin films and is believed to improve device properties. One should also note that very thin oxide metallic films are of importance in devices with a low strain budget that require the thinnest possible electrodes. The metallicity of thin films can however be affected by several parameters. It was reported that a M-I transition can take place in $LaNiO_3$ if the amount of disorder is sufficiently increased, e.g., by introducing oxygen vacancies.[10] In this letter, we show that epitaxial $LaNiO_3$ thin films grown coherently on (001) $SrTiO_3$ exhibit a M-I transition as the film thickness is reduced below 8 unit cells (u.c.). The transition temperature T_{MI} was found to be tunable by up to 24 K using the electric field effect and resistivity changes of up to 10% were observed. The successful field tuning of the T_{MI} in $LaNiO_3$ paves the way to orders of magnitude larger field-induced resistivity changes that should be achievable by exploiting the intrinsic M-I transition of the other $RNiO_3$ compounds, and hence to the possibility of electronic devices based on nickelate thin films.[11] In addition, the field effect measurements, as well as Hall effect studies, reveal p-type conduction in our $LaNiO_3$ thin films, in contrast to previously published reports.

The primitive cell of bulk $LaNiO_3$ is rhombohedral, with lattice parameter $a=5.46$ Å, and rhombohedral angle $\alpha=60.49°$. It is well approximated by a pseudocubic cell with $a=3.84$ Å.[12] The $LaNiO_3$ films thus experience tensile strain when grown on $SrTiO_3$ ($a=b=3.905$ Å) due the 1.7% lattice mismatch between the two materials. The growth of $LaNiO_3$ thin films onto (001) insulating $SrTiO_3$ substrates was carried out by off-axis rf magnetron sputtering in 0.180 mbar of an oxygen/argon mixture of ratio 1:3 at a substrate temperature of 510 °C. Epitaxial c-axis oriented $LaNiO_3$ films with thicknesses ranging from 4 u.c. to more than 75 u.c. were successfully grown using these conditions. It was found that the $LaNiO_3$ lattice parameters, as well as the presence of parasitic phases, depend strongly on the oxygen stoichiometry which could be controlled either by changing the partial oxygen pressure during growth or by postannealing the samples in oxygen.

Detailed x-ray measurements were performed with a high-resolution PANalytical X'Pert PRO diffractometer using the Cu $K\alpha_1$ radiation. The θ-2θ scans around the (001) $SrTiO_3$ and $LaNiO_3$ diffraction peaks for samples with different thicknesses were obtained with a triple axis detector and are shown in Fig. 1(a). Finite size Fresnel oscillations were observed around the diffraction peak and simple fits to these curves allow the thickness and c-axis lattice parameter of the films to be obtained. The lattice parameter was found to be ~3.80–3.81 Å for all the samples measured. The thickness obtained was also confirmed by reflectometry measurements. Atomic force microscopy (AFM) investigations of the film surfaces revealed atomically smooth terraces separated by a step height of 1 u.c. [see inset of Fig. 1(a)]. The full width at half-maximum of the rocking curves matched the one of the substrates. Finally, reciprocal space maps were made with a pixel detector to investigate the coherence of the $LaNiO_3$ films grown onto the $SrTiO_3$. Measurements around the ($\bar{1}03$) diffraction peaks for the film and the substrate, Fig. 1(b), showed that the in-plane lattice pa-

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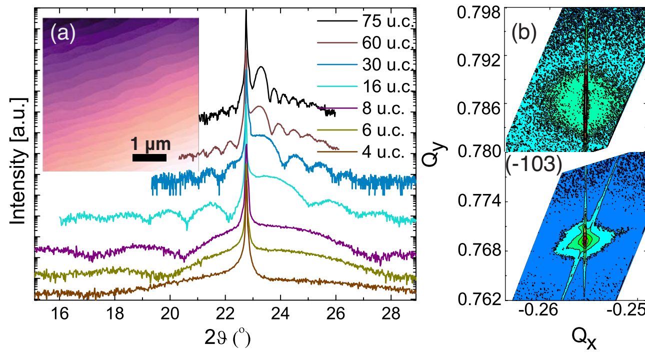

FIG. 1. (Color online) (a) θ-2θ diffractograms for a series of $LaNiO_3$ films grown on (001) $SrTiO_3$ with thicknesses ranging from 4 to 75 u.c. The inset shows a 5×5 μm^2 AFM scan of a typical film surface. (b) Reciprocal space map around the $(\bar{1}03)$ reflection with $Q_x = h/a$ and $Q_y = l/c$ obtained on a 30 u.c. thick sample.

rameter of the $LaNiO_3$ layer was equal to the one of the $SrTiO_3$ substrate for all films investigated.

Electrical resistivity measurements (30 mK$<T<$300 K), Hall measurements (1.5 K$<T<$260 K) and field-effect studies were performed on films of different thicknesses. For the resistivity measurements, each sample was patterned in a way suitable for four-point resistance and Hall measurements and every measurement was reproduced on different locations of the 5×5 mm^2 sample and on at least two other equivalent samples. The experimental geometry used is sketched in the inset of Fig. 2. Figure 2 shows the observed behavior from room temperature down to 4.2 K. For samples thicker than 7 u.c. the resistivity drops by nearly a factor of 3 from a room temperature value ranging from 280 to 400 $\mu\Omega$ cm, to a residual resistivity typically found to be between 100 and 140 $\mu\Omega$ cm, in agreement with previously published values.[7,8] A 75 u.c. film was mounted in a dilution refrigerator enabling measurements down to 30 mK. The resistivity was found to be essentially constant between 4.2 K and 30 mK. *I-V* curves up to 1 mA showed linear behavior at all temperatures.

As the thickness of the films decreases below 8 u.c. a M-I transition can be observed. For 7 and 6 u.c. an upturn in

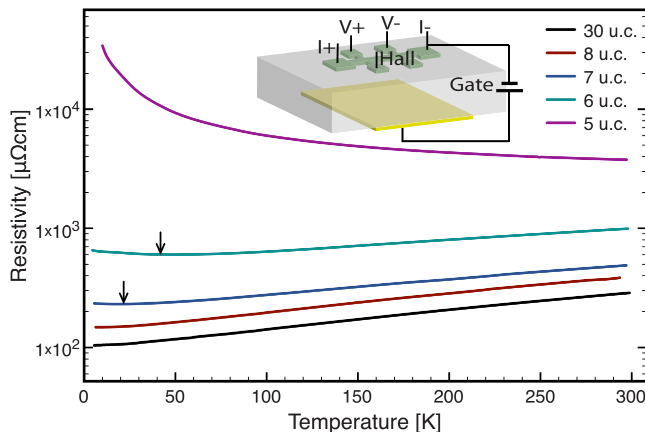

FIG. 2. (Color online) Temperature dependence of the resistivity for a series of $LaNiO_3$ films with thickness ranging from 5 to 30 u.c. A M-I transition is observed as the thickness is reduced. Arrows are indicating the onset of the M-I transition. The inset shows the geometry of the device, enabling four-point resistivity measurements, Hall measurements, and field effect experiments using a backgate configuration.

resistivity is observed, respectively, around 20 and 40 K, while for a thickness of 5 u.c. the behavior is insulating over the entire temperature range. Using the free electron model, the elastic scattering length in these thin films is found to be about ~20 Å, a value comparable to the thickness of the thinnest films.[25] An enhancement of the scattering at the film surface may contribute to the observed increase in resistivity. We note that rather similar M-I transitions have been observed in $SrRuO_3$ samples thinner than 4 u.c.[15,16]

The nature of the observed M-I transition as a function of thickness is not at present understood. The simple explanation that the concentration of oxygen vacancies is larger near the interface with the substrate, thus increasing the relative fraction of nonstoichiometric material as films get thinner, seems unlikely due to lack of qualitative changes in behavior upon annealing the samples in oxygen. The weak localization scenario proposed to explain the M-I transition in bulk $LaNiO_{3-\delta}$,[17,18] combined with a progressive change in dimensionality as the sample thickness is reduced could explain the observed behavior. Further studies are however necessary to be able to draw firm conclusions on this point.

In order to elucidate the nature of charge carriers in $LaNiO_3$ films, Hall measurements were carried out from 1.5 to 260 K in a pumped He cryostat equipped with a superconducting magnet enabling magnetic fields up to 8 T. This setup also allows one to perform detailed magnetoresistance studies, which are currently underway and should help clarify the nature of the M-I transition. For samples thicker than 8 u.c. we obtain room temperature carrier densities of $\sim2\times10^{22}$ cm^{-3}, a value close to the 1.7×10^{22} cm^{-3} expected if each Ni atom contributes one carrier. For thinner films, the charge density is gradually reduced to 1.5 and 1.0×10^{22} cm^{-3} for 7 and 6 u.c. samples, respectively. The carriers are found to be positive, i.e., holes rather than electrons, a result in contradiction with other studies.[8,9,20] Indeed, previous work on bulk ceramics reports negative thermopower coefficients, concluding that electrons are the dominant charge carriers.[8,9,19] Hall measurement data are scarce and less consistent. Noun *et al.*[20] report electronic transport with $n\approx4\times10^{22}$ cm^{-3} in their epitaxial films grown on $SrTiO_3$, whereas Gayathri and co-workers[17] measure a positive Hall coefficient, attributed to holelike pockets arising from charge transfer from the oxygen *p* to the metal *d* band. At the same time, Gayarthi *et al.* also observe a negative Seebeck coefficient *S*. It is interesting to note that most of the previous measurements have been performed on either bulk ceramics or relaxed films with lattice parameters close to the bulk $LaNiO_3$ values. Our single crystalline films are lattice matched and fully strained to the substrate. First-principles calculations[21] have shown that hypothetical cubic $LaNiO_3$ has a large hole Fermi surface, confirmed by recent photoemission measurements on tetragonal $LaNiO_3$ films.[22] A setup for thermopower measurements is currently being developed in order to clarify this issue.

Another way to probe the nature of the carriers is to perform electric field-effect experiments, where the carrier density is modulated by applying an electric field between a gate and the conducting channel across a dielectric. Due to the large carrier density in $LaNiO_3$, ultrathin films with thicknesses below 30 Å are necessary to obtain substantial charge modulation.[23] In our field effect experiments, a backgate geometry was used, the dielectric being the $SrTiO_3$ substrate itself. The gate is a gold electrode deposited on

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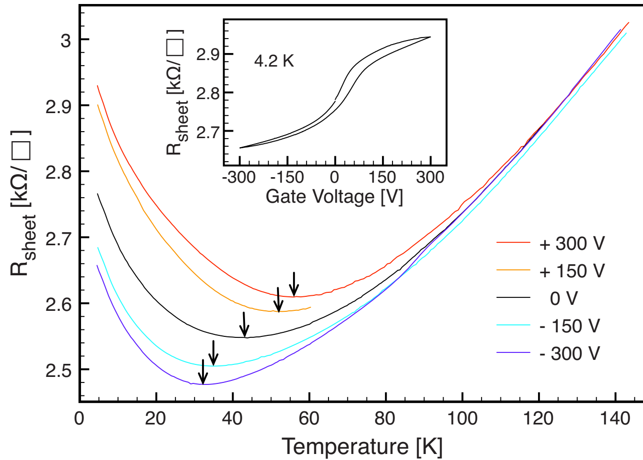

FIG. 3. (Color online) Sheet resistance R_{sheet} vs temperature for a 6 u.c. thick film and for different applied gate voltages. The inset shows the sheet resistance vs applied voltage at 4.2 K vs applied voltage at 4.2 K.

the backside of the substrate, opposite to the channel area. This configuration benefits from the high dielectric constant of $SrTiO_3$, which increases substantially at low temperatures.[13,14] The large thickness of the dielectric (0.5 mm) compared to the small width of the conducting channel (typically 10 to 100 μm) allows a further enhancement of the charge modulation due to the fringing field effect. Dynamic capacitance measurements as a function of gate voltage revealed that the average charge density modulation in the $LaNiO_3$ electrode was ~ 8 μC cm^{-2} at 200 V and 4.2 K.

Figure 3 shows sheet resistance measurements for a 6 u.c. thick film and for gate voltages varying between -300 and 300 V. The inset shows the sheet resistance R_{sheet} versus applied gate voltage at 4.2 K. A change in R_{sheet} of $\sim 10\%$ from -300 to 300 V is observed, a large effect given the metallic nature of $LaNiO_3$. We note that a similar magnitude was observed in field effect experiments performed on $SrRuO_3$.[24] As can be seen, the resistance increases when a positive voltage is applied to the gate, which indicates that positive charge carriers are being removed from the $LaNiO_3$ layer, therefore agreeing with the p-type conduction observed in Hall measurements. A small hysteretic behavior appears, most likely due to charge trapping/detrapping in the substrate, but the device presents reproducible sheet resistance versus voltage and temperature characteristics. As mentioned above, 6 u.c. thick $LaNiO_3$ films exhibit a M-I transition at around 40 K. The sheet resistance versus temperature curves shown on Fig. 3 for different gate voltages reveal a shift of the transition temperature of up to 24 K. Defining T_{MI} as the temperature at which the resistance exhibits a minimum, T_{MI} is found to increase consistently with increasing the gate voltage from 42 K at 0 V to 56 K at 300 V, and to decrease down to 32 K at -300 V, showing that the metallic phase can be stabilized by the electric field over a relatively large temperature range. At higher temperatures, the decrease in the $SrTiO_3$ dielectric constant leads to a reduced charge modulation and the resistance is found to depend only weakly on applied voltage.

In conclusion, high-quality epitaxial $LaNiO_3$ thin films with thicknesses down to 4 u.c. were grown epitaxially and coherently on (001) $SrTiO_3$. It was found that the $LaNiO_3$ films are metallic down to 30 mK for films thicker than 7 u.c. Below this critical thickness, a M-I transition appears at 20 and 40 K for the 7 and 6 u.c. thick films, respectively, while a 5 u.c. thick film already displays a negative dR_{sheet}/dT at room temperature. Field-effect experiments performed on ultrathin films reveal a large resistivity and charge modulation of about 10% and directly indicate that coherent $LaNiO_3$ films grown on $SrTiO_3$ display p-type conduction, a result confirmed by Hall measurements. Finally, the M-I transition could be tuned by up to 24 K using an applied electric field.

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[25] The scattering length l was calculated as follows: $l=(mv_F)/(ne^2\rho) = (\hbar k_F)/(ne^2\rho)]$, where $k_F=(3\pi^2 n)^{1/3}$. Using the values measured at 4.2 K for a 30 u.c. film ($\rho=100$ $\mu\Omega$ cm and $n=1.5\times 10^{22}$ cm^{-3}), we obtain $l \approx 20$ Å.

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