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The role of oxygen vacancies on the weak localization in $LaNiO_{3-\delta}$ epitaxial thin films

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ABSTRACT

We report on the analysis of weak localization observed in epitaxial films of $LaNiO_{3-\delta}$ deposited coherently on $SrTiO_3$ (001) substrates using different oxygen pressures, controlling thus the oxygen stoichiometry δ. The structural and transport properties of 10 nm thick $LaNiO_{3-\delta}$ films were investigated. In the films deposited under the lowest oxygen pressures, we observe localization effects at low temperatures, indicating first a high structural quality of the films, and second an influence of the growth conditions on the quantum transport properties of the nickelate. We will discuss the origin as well as the dimensionality of this effect, giving insight into novel and accurate strategies for the design of ultrathin $LaNiO_3$ electrodes for improved next generation electronics devices.

1. Introduction

$LaNiO_3$ (LNO) is a widely used perovskite oxide as an electrode for next generation oxide electronic devices such as resistance random access memories, microsensors, capacitors, microbatteries and fuel cells etc. [1–3] Its perovskite crystal structure and the high conductivity make LNO suitable for integration with other functional oxides based on ferroelectric, ferromagnetic or multiferroic films [4,5] into multifunctional devices to fulfil modern industrial requirement of miniaturization, especially as the growth on Si is possible. In order to accomplish the thinnest possible electrode, high quality ultrathin oxide films with a uniform Ni^{+3} state for good metallic conductivity with a low strain budget have to be developed. LNO has been extensively studied both in its bulk state [6–10] and in thin films [11–16] due to a large effective mass and enhanced Pauli paramagnetism coupled with strong electronic correlations. LNO is renowned for its high sensitivity towards the degree of disorder originated from varieties of factors such as oxygen stoichiometry and changing dimensionality, growth conditions etc. Typically, the oxygen stoichiometry is a crucial factor; an increasing amount of oxygen vacancies leads to weak localization and metal-insulator (MI) transitions, antiferromagnetic ordering and spin-glass behavior etc. [9,10,13,15,17,18].

Recently, Scherwitzl et al. [15,19] have studied ultrathin films in the two dimensional (2D) limit by decreasing the film thickness (≤8 unit cells). They observe a weak localization regime at the crossover from the 2D strong localization phase and the three dimensional (3D) metallic state. As the dimensionality in the weakly localized regime is 2D, the unexpected isotropic magnetoresistance was attributed to spin fluctuations, maybe related to an oxygen deficiency of the films. Also in 3D, a weak localization phase was observed in thin films [12], but the influence of the oxygen vacancies on this phase was not studied to our knowledge. In order to disentangle the 2D effects from effects due to oxygen vacancies, we have chosen to study the weak localization in thicker films (a priori well above the 2D limit) in order to illustrate the role of the oxygen deficiency in these quantum effects. The present work is focused towards the systematic investigation of the weak localization of high-quality epitaxial LNO films as a function of their deposition oxygen pressure. The first part of the characterization will be dedicated to well establish the quality of the films, and reproduce the evolution of the electronic properties with the oxygen pressure already observed by other studies [11,13,14]. This will assure the general character of the results extracted from the second part of the characterization, which is dedicated to the weak localization effects. These effects on the resistivity and the magnetoresistance at low temperatures offer the possibility to identify the sources of the coherent backscattering of the charge carriers, allowing to distinguish between disorder related scattering and the scattering due to electron-electron interactions. Earlier studies were focused on the resistivity at higher

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temperatures, where the incoherent scattering mechanisms govern the temperature dependence, therefore the present study offers new insight into the influence of the oxygen vacancies on the coherent electronic transport in $LaNiO_{3-\delta}$.

2. Experimental details

2.1. Preparation of epitaxial $LaNiO_{3-\delta}$ thin films

Epitaxial LNO films were grown on (001) SrTiO3 (STO) substrates by pulsed laser deposition (PLD) using a KrF laser with a 248 nm wavelength. The growth conditions were 5 Hz repetition rate, and a fluency of around 2 J/cm2 on the stoichiometric LNO target at a substrate target distance of 3.5 cm. During all the depositions, the total number of shots (i.e. 2000 shots) on the target was kept constant. The deposition temperature of the sample was 720 °C. The oxygen pressure during the deposition process was ranging from 0.01 to 0.2 mbar.

2.2. Characterization of epitaxial $LaNiO_{3-\delta}$ thin films

The surface morphology was characterized by atomic force microscopy (AFM), the AFM images (not shown here) suggest densely packed large grains having 50–80 nm average grain size. The film roughness increases with low oxygen pressure (Table 1). Microstructure and crystallographic orientation of the films were characterized by θ–2θ scans of Cu Kα1 x-ray diffraction (XRD) using an Al filter. The film thickness was measured by x-ray reflectivity (XRR). Electrical resistivity was measured by the conventional four-probe method and temperature dependent transport measurements were carried out using a physical property measurement system (Quantum Design). In the magnetoresistance measurements, the magnetic field was applied perpendicular to the film plane.

3. Results and discussion

3.1. Structural investigation of epitaxial $LaNiO_{3-\delta}$ thin films

Fig. 1 shows x-ray diffraction scans through the (002) symmetric reflections of all films. No impurity phases are observed, neither superstructure peaks related to a possibly ordered oxygen vacancy phases of LNO. The crystalline quality of the films has a maximum for an oxygen pressure of 0.1 mbar (Sample C) as indicated by the intense peak of the thin film, rocking curve and the Laue fringes. Stoichiometric LNO ($\delta = 0$) is a pseudocubic perovskite with small rhombohedral distortion with the pseudocubic lattice constant a = 3.838 Å [20]. The LNO films when grown on STO (a = b = 3.905 Å) are under tensile strain due to the 1.7% lattice mismatch between the two materials. If oxygen vacancies are introduced, the mean Ni–O distance is enlarged and Ni–O–Ni bond angle is broadened, both directly due to the oxygen vacancies, but also as a result of the higher ionic radius of Ni^{2+} ions compared to Ni^{3+}. As a consequence of the increase of volume of the NiO_6 octahedra, the LNO unit cell is expanded. Hence, the observed variation of the out-of-plane lattice constant (c_{LNO}) with the oxygen atmosphere (Table 1) can be easily understood by the poorer oxygen incorporation into the film for a low oxygen pressure (Sample A) and high oxygen content for a large background pressure (Sample E). In addition, cation stoichiometry is also playing a central role in all the observed differences between the samples. Cation off-stoichiometry appears to be the most likely cause for the poor quality of samples D and E.

With increasing oxygen pressure, the energy of the plume species from the target gets smaller due to enhanced collisions with the background atmosphere. Consequently, the increasing background oxygen pressure slows down the deposition rate correspondingly. Hence the thickness has decreased from 17.41 nm to 10.01 nm with increasing oxygen pressure from Samples A to E. As will be shown later on, the varying thickness of the films does not have an influence on the conclusions of this study.

In order to investigate the relaxation of the LNO thin films, high resolution x-ray reciprocal space maps for an 82.5 nm LNO film grown at 0.1 mbar were recorded in the vicinity of the STO (101) (not shown) and (103) reflections (Fig. 1). The ratio between the reciprocal distances of the STO substrate and LNO thin film in the H direction is 1.0004 (see the vertical bar on Fig. 1(right)). Neglecting this 0.04% difference, the in-plane lattice parameter (a_{LNO}) of the LNO film is considered being the same as the value of STO substrate (3.905 Å), which also provides the quantitative evidence for the enlargement of the synthesized LNO unit cell (about 2.9%) with no relaxation in the in-plane direction. Since the 82.5 nm-thick LNO thin film is the thickest one among all the films investigated in this study, the thickness of films A to E are far below the critical thickness of strain relaxation, so that we can infer that all films have the same, coherent a_{LNO}. This leads to a tetragonal distortion of the pseudo-cubic unit cell, with $c/a < 1$, as expected for tensile strain.

Thus, all investigated films in this study, independent on their thickness, have the relatively negligible strain influence. The observed changes in the lattice parameters and in the structure of the film are very small both compared to the bulk structure as well as along the oxygen pressure series, so that we can reasonably exclude strain effects as being the driving forces behind the observed changes of the properties. However, this fact may also allow us to estimate the oxygen deficiency of the films.

From reduction experiments on coherent LNO thin films on Si [18], the enhancement of the out-of-plane lattice parameter from stoichiometric $LaNiO_3$ to $LaNiO_{2.5}$ can be estimated to be 0.9 Å for $\delta = 0.5$. However, δ was derived from a phase change and not a direct measurement, so the error bar of this value is not known. The evolution between these two points can be assumed as linear, as both proposed mechanisms at the origin of this enhancement are directly related to the number of oxygen vacancies of Ni^{2+} ions. The coherent growth of the LNO films both on Si and on STO allows to ascribe the observed change of c_{LNO} solely to the introduction of oxygen vacancies, and therefore to estimate in the films of this study from c_{LNO}. Sample D and E show the same c_{LNO}, so we assume that these films have no oxygen deficiency and they serve as the origin of the linear extrapolation. The deduced values of δ are 0.26 for Sample A, 0.1 for Sample B and 0.04 for Sample C. These values have to be taken carefully, as a high number of assumptions are needed. The comparison of the resistive properties of the films

Table-1
The growth conditions i.e. oxygen partial pressure and a related physical property of LNO samples A to E.

Sample Name	Deposition O_2 Pressure (mbar)	Film Thickness (nm)	Resistivity at Room Temp. (μΩcm)	Out of Plane Lattice Constant (Å)	Oxygen deficiency (δ) from lattice volume	RMS Roughness (nm)
A	0.01	17.41	914	3.864	0.26	1.54
A-2	0.01	30.95	893	3.866	–	–
B	0.05	16.28	315	3.832	0.1	1.32
C	0.1	12.57	225	3.820	0.04	1.22
D	0.15	10.71	616	3.813	0.009	0.67
E	0.2	10.01	576	3.812	0.008	0.59