Supplementary Material for

Ferromagnetic insulating epitaxially-strained La$_2$NiMnO$_6$ thin films grown by sputter deposition

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I. Experimental details and methods

La$_2$NiMnO$_6$ (LNMO) thin films were grown using off-axis radio-frequency magnetron sputtering. The ceramic target was a two inches single-phase commercially-available pellet. The TiO$_2$-terminated (001)-oriented SrTiO$_3$ substrates are used “as-received” because they are characterized by a sharp step-and-terrace surface. All the other (001)- and (110)-oriented substrates were annealed in a furnace at 1000 °C in a regulated oxygen flow to promote the formation of atomic steps$^1$. The films were grown at a substrate temperature of 720°C and a total pressure of 0.18 mbar in a controlled mixture of oxygen and argon. After the growth, the samples were cooled to room temperature in the same gas environment. The gun power was varied between 50W and 80W to control the growth rate. Under these conditions, we achieved growth rates in the order of 0.5-1 nm/min.

Before every growth, the heater was annealed in high vacuum (p < 10$^{-6}$ mbar) at 850 °C for 30 minutes. We find that this strategy allows to obtain a nearly reproducible growth of our films. Otherwise, films grown under exactly the same conditions are sometimes characterized by an island topography instead of a step-and-terrace morphology. Indeed, stabilizing the stoichiometric cation-ordered DP phase in thin-film form is very challenging, as observed by many authors$^{2-5}$. An additional source of complication for the growth of LNMO films might be related to the formation of a
lanthanum hydroxide layer on the surface of the target ceramic. We note that this hydroxide dissolves when heated at high temperature in vacuum.

The reflection high energy electron diffraction (RHEED) measurements were performed in situ during the sputter growth. In this RHEED-equipped chamber, we find that the optimal growth conditions are equal to the original growth chamber albeit at a lower temperature of 660°C. In this chamber, we also find no necessity to anneal the heater in high vacuum prior to the LNMO deposition. The RHEED gun was a differentially pumped Staib system operated at 35 keV.

The thickness, structure and orientation of the films were characterized by x-ray diffraction (XRD) using a Rigaku Smartlab diffractometer operating in line focus mode with a monochromated Cu Kα1 radiation. The XRD data is simulated using the InteractiveXRDfit software developed by Céline Lichtensteiger and from this the film thickness is derived. Surface topography was obtained using an Autoprobe CP atomic force microscope (AFM) operated in contact mode. The AFM data was analyzed using the WSxM software. Electron transparent cross-sectional samples for transmission electron microscopy were prepared by means of a FEO Helios NanoLab 600i focused ion beam operated at accelerating voltages of 30 and 5 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray (EDX) spectroscopy were carried out using a probe-corrected FEI Titan Themis microscope equipped with ChemiSTEM technology. The microscope was operated at an accelerating voltage of 300 kV, probe convergence semi-angle of 18 mrad and collecting semi-angles of 66–200 mrad. The EDX spectrum image was acquired using the Velox software with a 539 x 126 frame size, 25.36 pm pixel size, 16 µs dwell time and 128 nA probe current. The elemental maps were calculated from the EDX spectrum image using the Sr Kα, Ti Kα, La Lα, Ni Kα, Mn Kα and O Kα lines. The resistivity of the thin films was determined by standard four-point van der Pauw measurements. Au/Ti (50/5 nm) contact pads were fabricated by sputtering through a shadow mask and the sample was contacted by wire bonding using Al wires.
Magnetic measurements were carried out in a Quantum Design superconducting quantum interference device (SQUID) magnetometer operating in vibrating sample mode (VSM) with the magnetic field applied parallel to the plane of the sample. In isothermal curves, the diamagnetic contribution from the substrate is determined via a linear fitting in the two high magnetic field ranges (> 4 T). The average of these two slopes is then subtracted to the raw data. The magnetization units are then converted to $\mu_B$/f.u. using the total number of unit cells. A similar strategy is used to analyze the temperature-dependent magnetization data.

X-ray absorption measurements (XAS) were performed at the EPFL/PSI X-Treme beamline at the Swiss Light Source. The spectra were acquired by measuring the total electron yield (TEY) and total fluorescence yield (TFY) with an incidence angle (the angle between the x-ray beam direction and the sample normal) of 60°. In this geometry, the direction of the applied magnetic field is fixed at 30° in respect to the sample surface. The XAS curves are obtained as the sum of spectra measured with left and right circular polarization and are normalized to the peak of the respective L$_3$-edge. The x-ray magnetic circular dichroism (XMCD) is defined as the difference between spectra measured with left and right circular polarization and normalized to the L$_3$ maximum from the XAS. The XMCD asymmetry is defined as $\frac{L-R}{L+R}$ with $L$ ($R$) obtained as the difference between the L$_3$-resonant and off-resonant energies for left (right) circular polarization.

Film stoichiometry was determined using both Rutherford backscattering (RBS) and ex-situ x-ray photoemission spectroscopy (XPS) as shown in Figure S5 and S6, respectively. For the first method, LNMO films grown on MgO substrates have been measured by 2 and 5 MeV He ion beams with a silicon PIN diode detector under 168° and the spectral data was analyzed using the RUMP software. The XPS data were collected using the K$_\alpha$ radiation obtained from a non-monochromated Mg source, with a photon energy of 1253.6 eV. In this case, the elemental ratio between Ni and Mn was obtained comparing the total peak areas of the 3p core levels after the subtraction of a Shirley-type background, divided by the respective atomic cross-sections for photoionization and analyzer transmission.
function. Prior to XPS data acquisition, the surface of the LNMO//STO film was treated with a 30 minutes annealing at 400 °C in an oxygen pressure of $1 \cdot 10^{-4}$ mbar.

II. Supporting figures

**FIG. S1.** Reciprocal space maps around the (103)$_{pc}$ substrate diffraction condition certify the strained state of the circa 30 uc LNMO films grown on (a) LAO ($\xi = -2.1\%$), (b) NGO ($\xi = -0.5\%$), (c) LSAT ($\xi = -0.2\%$) and DSO ($\xi = +1.8\%$). $\xi$ represent the nominal epitaxial strain.

**FIG. S2.** Intensity of the RHEED specular spot during the growth of a 30 uc LNMO//STO film. The growth oscillations are characteristic of a layer-by-layer growth mode.
FIG. S3. HAADF-STEM images along the [110]_{STO} zone axis unveil a high crystalline quality of the LNMO//STO film.

FIG. S4. HAADF-STEM image and corresponding EDX elemental maps of Sr, Ti, La, Mn, Ni and O along the [110]_{STO} zone axis. The horizontal field of view is 3.2 nm. (b) The line profiles of the elemental maps were extracted over the full map widths and confirm a fairly homogeneous elemental distribution over the entire film thickness.
FIG. S5. (a) 2 MeV He RBS data of a circa 60 nm-thick LNMO film grown on a MgO substrate. The red solid line is a RUMP simulation. (b) Same as (a) using 5 MeV He. We observe that our films are stoichiometric within the measurement error.

FIG. S6. (a) ex-situ XPS results for the Mn 3p core level peaks of a 30 uc LNMO//STO film. (b) Same as (a) collected for the Ni 3p peaks. By comparing the total peak area (green) of the 3p orbitals after subtracting a Shirley-type background (red line), divided by the respective atomic cross-section and analyzer transmission function, a Ni/Mn ratio of 0.998 is estimated.
References