Supplementary information

Epitaxial $LaMnO_3$ films with remarkably fast oxygen transport properties at low temperature

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SIMS depth profiles

Fig. SI 1a and b correspond to one of the depth profile measurements carried out on the LMO/STO film and LMO/LAO film, respectively, after the ^{18}O exchange at 600 ºC. The ionic species corresponding to LaO_2^- ions ($La^{16}O_2^- + La^{16}O^{18}O + La^{18}O_2$), MnO^- ions ($Mn^{16}O^- + Mn^{18}O^-$), and TiO^- ions ($Ti^{16}O^- + Ti^{18}O^-$), as well as the $^{18}O^-$ and $^{16}O^-$ ions are visible across the LMO film. An abrupt interface between LMO and STO (LAO) is observed, characterized by the decay of LaO_2^- and MnO^- ions and the corresponding sharp increase of TiO^- (AlO_2^{2-}) ion signal. The dash-dot line at distance zero stands for the interface calculated as the midpoint of the decaying slope of the MnO^- ions. The distance between the LMO surface and the zero line corresponds to 12 and 11 nm for the LMO/STO and LMO/LAO thin films, respectively.

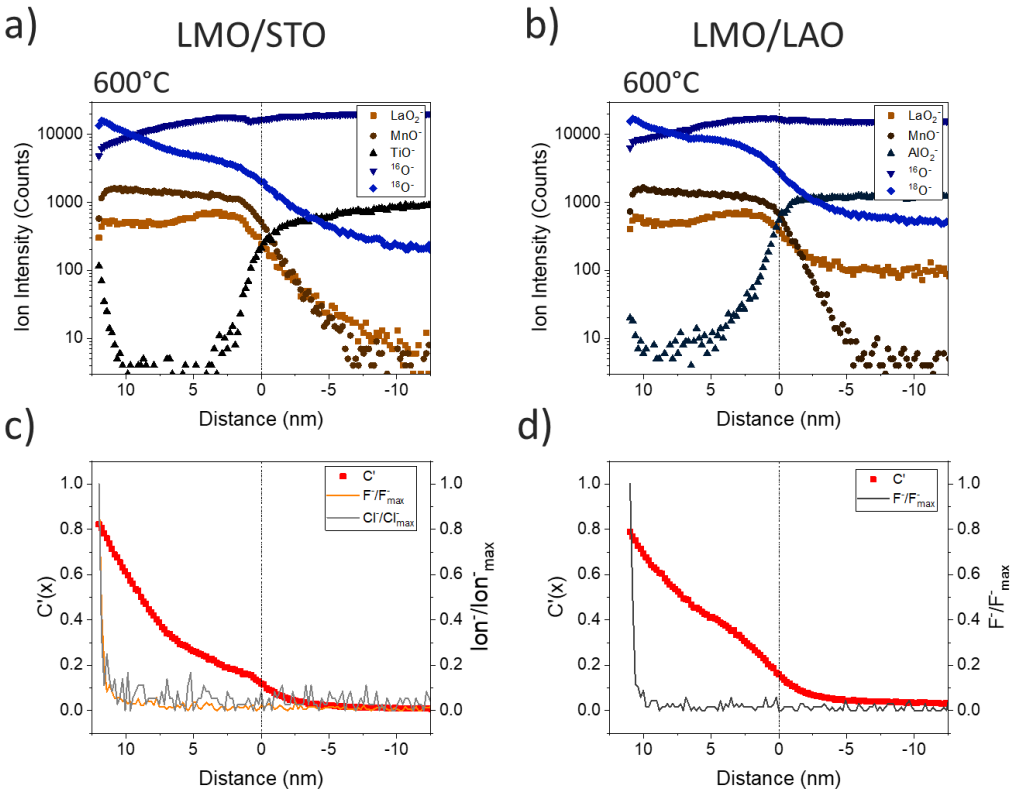

Fig.SI 1 SIMS ion depth profiles as a function of the distance for the a) LMO/STO and b) LMO/LAO films exchanged at 600°C/1h. The secondary ions plotted correspond to ^{18}O, ^{16}O, total LaO_2^- ions ($La^{16}O_2^- + La^{16}O^{18}O + La^{18}O_2$), total MnO^- ions ($Mn^{16}O^- + Mn^{18}O^-$) and a) total TiO^- ions ($Ti^{16}O^- + Ti^{18}O^-$) or b) total AlO_2^- ions ($Al^{16}O_2^- + Al^{16}O^{18}O + Al^{18}O_2^-$). Normalized ^{18}O isotopic fraction (red squares) and F^- ions (normalized to the maximum value) (continuous line) for the c) LMO/STO and d) LMO/LAO films exchanged at 600°C/1h. The zero position corresponds to the film/substrate interface.

In order to assess if the profiles are properly resolved, as done in ref [1], we have compared the tracer profiles with the ion profiles from surface contaminant species (such as F^- and Cl^-), which are expected to appear only in the first 1-2 monolayers. These species have a high concentration at the top surface, but very steeply decrease over the first nanometer of the film, as shown in Fig.SI 1c-d for the F^- ions. This fact strongly suggests that the profiles obtained across the LMO film corresponds to a real diffusion process, and not to the SIMS ion-beam mixing.

Model describing oxygen exchange and diffusion

A model of an infinite solid slab extending over the region of thickness 2l is assumed. This plane sheet model gives a symmetrical solution for the plane sheet occupying the region -l<z<l. This solution applies also to the sheet 0<z<l when the face z = 0 is non-permeable (see Figure SI 2). In our case the impermeable surface corresponds to the film-substrate interface, through which no oxygen diffusion occurs.

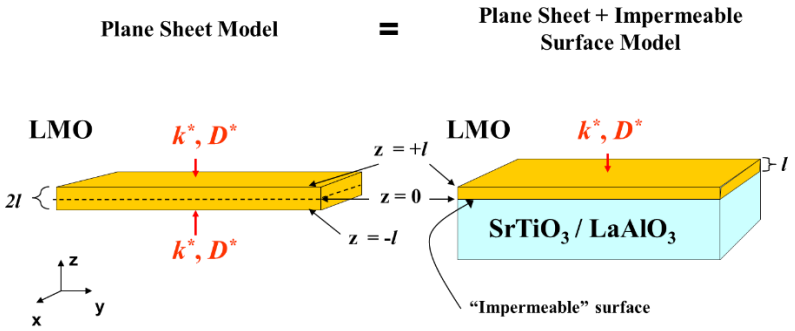

Fig.SI 2 Schematics of the plane sheet model used for the solution to the diffusion equation

The first boundary condition is related to the rate of transfer of the oxygen species across the surface. The assumption made is that the rate of exchange is proportional to the difference between the concentration in the gas and the concentration in the surface at any time:

$$-D^* \frac{\partial c^*(l,t)}{\partial z} = k^*[c_g^* - c^*(l,t)] \qquad \text{Equation (1)}$$

The initial boundary condition is expressed by:

$$c^*(z,0) = c_{bg}^* \qquad \text{Equation (2)}$$

while the second boundary condition is:

$$\frac{\partial c^*(l,t)}{\partial z} = 0 \qquad \text{Equation (3)}$$

where $c^*(z,t)$ is the isotopic concentration at depth z, c_{bg}^* is the background isotopic concentration, c_g^* is the ^{18}O concentration in the gas phase, k^* and D^* are the tracer surface exchange and diffusion coefficients, respectively.

Then, the solution to the diffusion equation given by Crank[2] for a plane sheet is as follows:

$$\frac{C^* - C_{bg}^*}{C_g^* - C_{bg}^*} = 1 - \sum_{n=1}^{\infty} \frac{2Lcos(\beta_n z/l)\exp(-\beta_n^2 D^* t/l^2)}{cos\beta_n(\beta_n^2 + L^2 + L)} \qquad \text{Equation (4)}$$

where β_n (n=1, 2,...) are the nonnegative roots of $\beta tan\beta = L, L = lk^*/kD^*$. This analytical solution is only applicable in the case of a homogenous diffusion coefficient throughout the film, as well as ideal oxygen diffusion blocking at the substrate interface.

In addition to the plane sheet homogeneous film model fit, the oxygen concentration profiles were simulated by the finite element method (FEM) using the Chemical Reaction Engineering module of COMSOL Multiphysics. A 1D model was built up from 2 or 3 line segments (sample on STO and LAO, respectively) with different D_i within the LMO layer and one diffusion regime for the substrate. The diffusion equation was considered for all the solid domains. On the top boundary (*e.g.* surface) of the LMO, a convection type boundary condition was imposed (Equation 1). The bottom surface of the substrate was set as adiabatic (diffusion flux equal to zero). Finally, the solution was computed in time dependent mode, setting the solution time equal to the exchange time of the isotope exchange experiments. The model parameters (surface exchange and diffusion coefficients, k_{ex} and D_i, as well as region boundary positions z_i) were fitted to the experimental data via the optimization module using a least square objective.

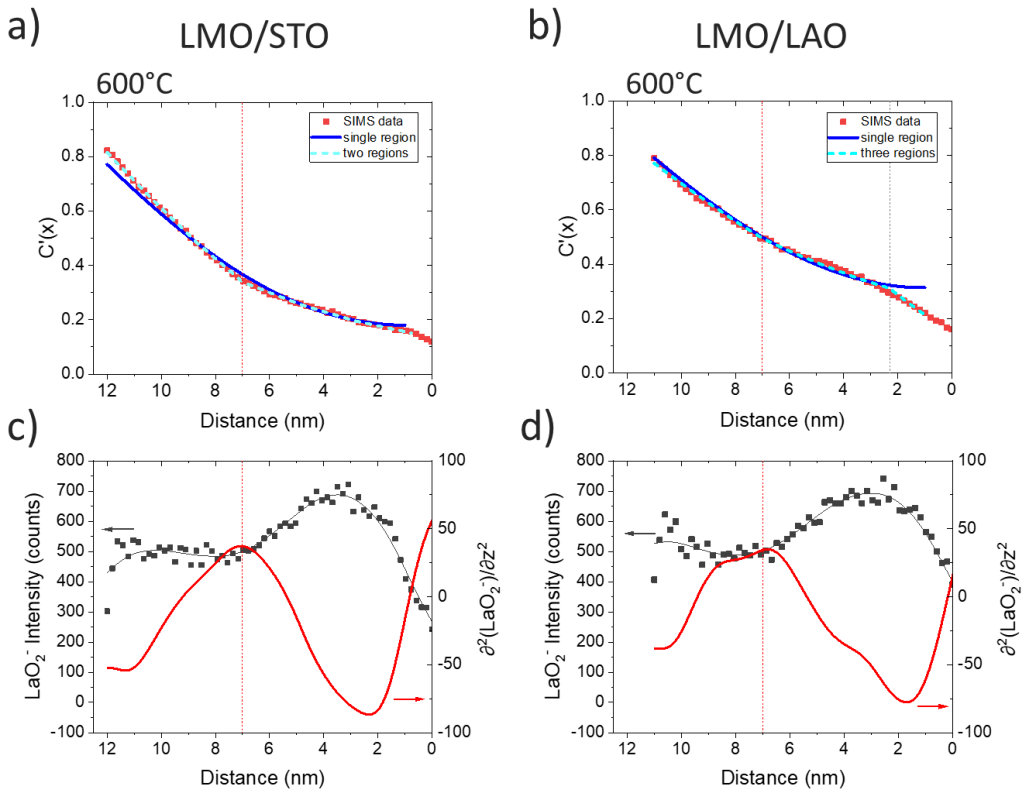

Fig.SI 3 Comparative SIMS depth profiles for the thin LMO films exchanged at 600°C for 1h. Normalized ^{18}O isotopic fraction as a function of the distance for the films grown on a) STO and b) LAO. The blue straight lines correspond to the best fit to Crank's solution to the diffusion equation for a solid slab, while the cyan dashed lines correspond to the solution obtained by the FEM modelling and fitting using 2/3 different regions with different D. Total LaO_2^- ions ($La^{16}O_2^-$+$La^{16}O^{18}O$ +$La^{18}O_2$) depth profiles for the thin LMO films grown on c) STO and d) LAO. Smoothed curve in black, and its second derivative in red. The optimized position for the change from region 1 to region 2 (at 7 nm) coincides with the maxima of the second derivative of the total LaO_2^- ions counts. The zero position corresponds to the film/substrate interface.*

In Fig.SI 3a-b the normalized ^{18}O concentration profiles for LMO/STO an LMO/LAO (600°C exchange) are shown. Additionally, a fit of the plane sheet model as well as the optimized numerical simulation is plotted. We observe a slow diffusion region at the top, followed by a fast diffusion region below (boundaries of diffusion regions are indicated by dashed lines as obtained by the COMSOL fit). For the LMO/LAO film an additional interface region close to the substrate is required for an optimized fitting.

Structural characterization of the films after the isotopic exchanges

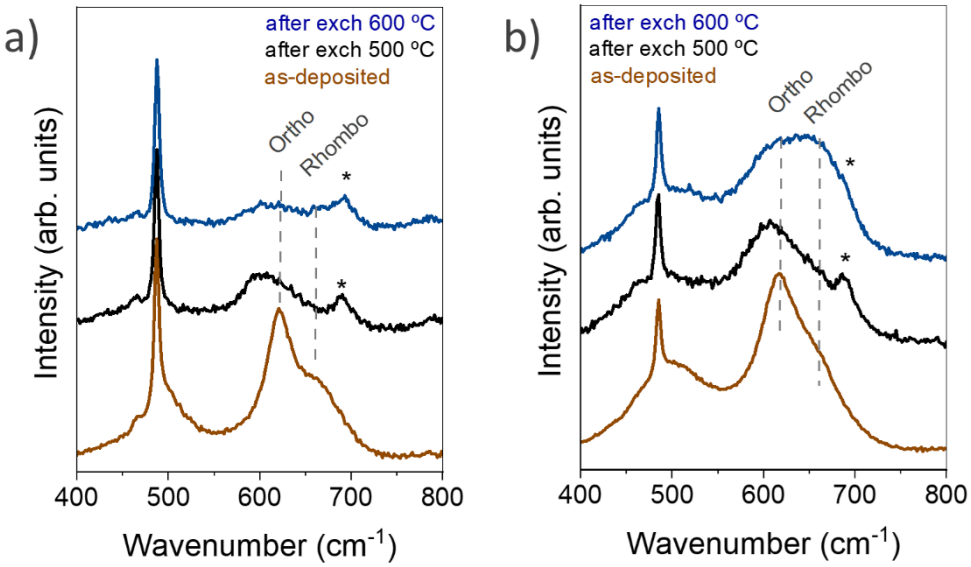

*Fig.SI 4 Raman spectra of the pristine and exchanged a) thin (11 nm) and b) thick (~ 66 nm) LMO/LAO films. The positions of the orthorhombic and rhombohedral lines in the pristine spectrum are indicated by the grey dashed lines. The narrow line at 487 cm^{-1} is related to the LAO substrate. The exact assignment of the peak * is not clear, and might correspond to the Mn_2O_3 or to the $LaMnO_3$ phase. For both figures, the pattern in brown corresponds to the as-deposited (pristine) LMO film, the black one was obtained after annealing (exchange) at 500 °C and the blue one after annealing (exchange) at 600 °C.*

References

(1) De Souza, R.; Zehnpfenning, J.; Martin, M.; Maier, J. Determining Oxygen Isotope Profiles in Oxides with Time-of-Flight SIMS. *Solid State Ionics* **2005**, *176* (15–16), 1465–1471.

(2) Crank, J. *The Mathematics of Diffusion*; Clarendon Press, 1979.