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Textured Manganite Films Anywhere

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Abstract:

New paradigms are required in microelectronic when the transistor is in its downscaling limit and integration of materials presenting functional properties not available in classical silicon is one of the promising alternatives. Here, we demonstrate the possibility to grow $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) functional materials on amorphous substrate with properties close to films grown on single crystalline substrate by use of a two-dimensional seed layer. X-ray diffraction and electron backscatter diffraction mapping demonstrate that $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheets (NS) layer induces epitaxial stabilization of LSMO films with a strong out-of-plane (001) texture, whereas the growth of LSMO films on uncoated glass substrates exhibit a non-textured polycrystalline phase. Magnetic properties of LSMO films deposited on NS are similar to those of the LSMO grown on SrTiO_3 single crystal substrates in the same conditions (which is used as reference in this work). Moreover, transport measurements take advantages of the texture and polycrystalline properties in order to induce low field magnetoresistance at low temperature and also a high value of 40%

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3 magnetoresistance from 10 to 300 K interesting for sensor applications. Therefore, NS seed
4 layer offers new perspectives for the integration of functional materials grown at moderate
5 temperature on any substrate which will be the key for the development of oxitronics.
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10 11 **1. Introduction** 12 13 14

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16 In the near future, new materials will be required beyond the mainly used CMOS
17 (Complementary Metal Oxide Semiconductor)-based electronics with new and dramatically
18 improved properties, providing innovative paradigms for information storage and data
19 processing (More-than-Moore approach)^{1,2}. Complex oxides are potential candidates thanks to
20 their exceptionally broad range of versatile functionalities, a number of them being not
21 present in classical semi-conductors. Among these oxides, the doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$
22 manganite (LSMO) is a reference material for its remarkable electronic and magnetic
23 properties³⁻⁵. The magnetic diagram of LSMO system has a large variety of phases depending
24 on the composition with outstanding magnetic and transport properties^{6,7}. LSMO has the
25 largest single electron bandwidth and the highest Curie temperature (T_C) among the
26 perovskite manganites, making it an interesting material for application in spintronic devices⁸.
27 The strontium content leads to hole doping of the manganite, controlling the charge density at
28 the Fermi level. Notably, LSMO exhibits a colossal magnetoresistance (CMR) and a
29 ferromagnetic-metallic state (FM-M) at room temperature with high T_C of 369 K for a
30 substitution rate of ~30% for La, rendering this oxide very interesting for applications as
31 sensor^{9,10}, in spintronics¹¹⁻¹⁴ and for magneto-optical and optoelectronic applications^{15,16}.
32 Moreover, LSMO exhibits a low resistivity at high temperature and can be used as an
33 electrode in solid oxide fuel cells-based devices^{17,18}. Also, its integration on flexible substrates
34 (mica, polymers...) represents of utmost interest for emerging applications in spintronics or
35 electronics in bending conditions⁸. Nevertheless, the magnetic and transport properties of
36 LSMO can be tuned by various factors, such as external hydrostatic pressure¹⁹, oxygen
37 stoichiometry^{20,21}, Sr doping level²², as well as the strain effect²³ because of the sensitive
38 lattice-spin-charge coupling. For example, epitaxial LSMO films exhibits lower T_C than
39 polycrystalline films of about 20 K^{24,25}. In this way, it may be possible to tune magnetic and
40 transport properties of films by inducing a texture or near-epitaxy of LSMO films on non-
41 adapted substrates. However, the coexistence of optimized properties and its integration onto
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3 low cost substrates as silicon for the electronics industry or amorphous materials as glass is a
4 current challenge required to overcome technological limitations. Indeed, growth of LSMO
5 directly on silicon is extremely complicated due to the incompatibility between their
6 respective crystalline structure and their reactivity with oxygen. This issue leads to very low
7 crystalline quality of LSMO thin films together with a large degradation of their properties.
8 This is due to the high reactivity of unsaturated silicon bonds at the surface of the substrate
9 leading to an oxidation of the surface and the formation of a SiO₂ layer. Even at low
10 deposition temperatures, this layer cannot be avoided, and may lead to problems regarding the
11 epitaxial growth^{26,27}.

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19 The main approach to circumvent these difficulties was the integration of high quality
20 functional oxides as LSMO films on Si with the growth of a buffer layer by using for example
21 TiN, CeO₂/Y₂O₃, SrTiO₃ (STO) and more recently SrRuO₃/TiN, by molecular beam epitaxy
22 or pulsed laser deposition²⁸⁻³⁴. Nevertheless, the process is generally tedious and not adapted
23 to large-scale production due to its complexity and high temperature process. Moreover, this
24 method requires necessarily the use of a crystalline substrate and cannot be transferred easily
25 to larger lattice mismatched or amorphous substrates as a-Si or SiO₂, for example. Therefore,
26 regarding the use of complex oxides in a large scale, new approaches are a necessary
27 prerequisite for the integration of complex oxides.

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34 Another approach for complex oxides integration onto non-adapted substrates is the
35 use of nanosheets (NS) as seed layer³⁵. In this approach, NS created by an exfoliation process
36 of layered oxides are transferred on low cost large-surface substrates as silicon or glass,
37 providing the seed layer for the growth of complex oxide thin films independently on the
38 bottom substrate material. These NS can be synthesized from precursors prepared by solid
39 state route, followed by an exchange reaction of protonation in solution and finally exfoliation
40 to obtain the colloidal dispersion suitable to transfer the NS on the substrate by Langmuir-
41 Blodgett method³⁶. These NS are exceptionally rich in structural diversity (cubic, rectangular,
42 hexagonal structures...) and can be used as seed layers to induce epitaxy of a wide range of
43 complex oxides. A large variety of layered oxides are dedicated to the perovskite structures.
44 The NS obtained by exfoliation of layered structures such as Ruddlesden-Popper phases (for
45 instance SrLaTi₂TaO₁₀²⁻ and Ca₂Ta₂TiO₁₀²⁻), Dion-Jacobson phases (for instance
46 (Ca,Sr)₂(Nb,Ta)₃O₁₀⁻ and LaNb₂O₇⁻) and Aurivillius phases (for instance (Sr,Bi)Ta₂O₇²⁻ and
47 Bi₄Ti₃O₁₂²⁻)³⁷ open new perspectives for the integration of oxides onto non-adapted
48 substrates. Among the NS obtained from these layered oxides, Ca₂Nb₃O₁₀⁻ (CNO) has been
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used for the growth of various materials as TiO_2 ³⁸, $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ³⁹, or $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ ⁴⁰, SrTiO_3 ⁴¹ and SrRuO_3 ^{35,42}. The Dion-Jacobson parent phase $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ crystallized in the monoclinic system ($a = 0.7741$ nm, $b = 0.7707$ nm, $c = 1.4859$ nm, $\beta = 97.51^\circ$, JCPDS card N°01-075-9853) and is usually described in a larger tetragonal unit cell with lattice constants $a = 0.7727$ nm and $b = 2.9466$ nm^{43,44}. Its structure consists in stacking of slabs of 3 perovskite layers laying in the (001) plane, separated by a cation (K^+) layer. After exfoliation, the two-dimensional lattice of the nanosheets has a square a-b plane with $a_{\text{NS}} = 0.384$ nm. Therefore, the use of CNO NS as seed layer is especially well-adapted for the growth of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ with a lattice parameter of 0.386 nm in the pseudo-cubic description, leading to a misfit of only -0.18 %. Moreover, CNO NS layer exhibits a good thermal stability. It has been reported to be stable up to 800°C in air³⁷, and segregates into a mixture of $\text{Ca}_2\text{Nb}_2\text{O}_7$ and CaNb_2O_6 above this temperature. Similarly, Kweon *et al.* report that the thermal stability of CNO NS is ensured up to ~600°C, depending on the number of layers⁴⁰. Thus CNO NS layer is expected to be suitable for the growth of epitaxial LSMO films by pulsed laser deposition since, in our deposition system, the optimal temperature was around 640°C on single crystals SrTiO_3 substrates^{25,45}, in a partial pressure of oxygen.

In this paper, we report the structural and physical properties of highly (001)-textured LSMO films deposited on CNO NS seed layer using glass as substrate (GS). The local epitaxy of LSMO resulting from the growth of the film on small crystalline domains formed by the juxtaposition of the buffer CNO NS offers the possibility to investigate the electronic and magnetic properties of textured film on amorphous substrate. The properties of these textured film were compared with those of polycrystalline⁴⁶ and fully strained films^{25,40}, using not covered glass and STO substrates, respectively. Furthermore, the influence of the growth temperature on the different type of substrates was also investigated in order to demonstrate the potential of NS for the growth of LSMO at intermediate temperature.

2. Experimental Section

First, powder of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ oxide was synthesised by solid state reaction. Precursors oxides K_2CO_3 (Acros Organics, 99 %), Ca_2CO_3 (R.P. Normapur, 99.5 %) and Nb_2O_5 (Alfa Aesar, 99.5 %) were ball-milled in ethanol during 5 h before a thermal treatment at 1100°C during 10 h. Following Ebina *et al.*'s method⁴⁷, the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ oxide was then proton-

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3 exchanged in 6 M HNO₃ for 3 days. The protonated phase was exfoliated by reaction with
4 tetra(n-butyl)ammonium hydroxide (TBAOH) in a molar ratio 1:1, during 14 days. The
5 obtained TBACa₂Nb₃O₁₀ nanosheets (NS) were deposited on fused silica substrates (glass
6 substrate (GS): 10 × 10 × 0.5 mm, Neyco, NEGS3) by Langmuir-Blodgett method with the
7 help of a KSV NIMA instrument. After that, deposited NS/GS samples were subjected to a
8 thermal treatment at 110°C during 90 min followed by an exposition to UV radiations during
9 45 min to enhance the adhesion of NS on GS and remove adsorbed residual solvents. TEM
10 characterizations of the NS are presented on Figure S1.

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17 Then, La_{0.67}Sr_{0.33}MnO₃ (LSMO) thin films have been grown on cut 5 × 5 × 0.5 mm³
18 NS/GS prepared samples, pristine GS and (001)-oriented SrTiO₃ (STO) substrates by pulsed
19 laser deposition (PLD). Prior to deposition of LSMO, GS and STO substrates were
20 successively cleaned in acetone and ethanol ultrasonic baths. A KrF excimer laser (λ = 248
21 nm) was used with a repetition rate of 2 Hz and a laser fluence adjusted to get a deposition
22 rate close to 0.1 Å per laser pulse. This beam laser is focused on a La_{0.67}Sr_{0.33}MnO₃
23 polycrystalline target prepared by standard solid-state reaction. The deposition was carried out
24 under oxygen ozone mixture²⁵. The deposition pressure at the growth temperature was 5 ×
25 10⁻⁴ mbar. The LSMO thickness was fixed to be around 40 nm for all samples by adjusting
26 the deposition time. In order to investigate the influence of the temperature on the
27 crystallization of LSMO films, the substrate temperature (T_G) was set at 550°C and 645°C. A
28 40 nm thick LSMO film grown on (001)-oriented STO in similar conditions sample was taken
29 as reference throughout this work (see Figures S3 and S4). All thicknesses have been
30 confirmed using X-ray reflectometry (see Figure S6).

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The structural properties were characterized by X-ray diffraction (XRD) with a Philips
X'Pert MRD diffractometer operating with monochromatic Cu K _{α 1} radiation (λ = 1.5406 Å)
and equipped with a Pixel detector. The morphology of films was investigated by scanning
electron microscopy (SEM) with a Zeiss Supra 55 (FEG source) and atomic force microscopy
(AFM) Pico SPM-LE of Molecular Imaging in tapping mode. The surface coverage of glass
substrates by NS is estimated around 90% by AFM imaging acquired on different large scale
areas of the samples (see Figure S2 (d)). In order to get better insight of the structural
dependence between LSMO and NS deposited glass, electron backscatter diffraction (EBSD)
mapping of sample surfaces were performed on the SEM microscope equipped with a ultra-
sensitive high resolution detector from Bruker at an accelerating voltage of 15 kV. Data are

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3 computed by means of Esprit Software. The phase identification and orientations of
4 LSMO/GS and LSMO/NS/GS samples are based on imposed starting structural references in
5 the computational method. The rhombohedral and hexagonal structure descriptions of LSMO
6 have been defined for the two respective samples.
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10 The magnetization of LSMO films was determined using a Squid MPMS XL Quantum
11 Design. The sample was placed in the sample holder with a parallel configuration to the
12 magnetic field H . The calculated error is $\sim 22 \text{ emu.cm}^{-3}$. This error takes into account the
13 measurement errors of the magnetization (Squid device error: $\Delta m = 5 \times 10^{-6} \text{ emu}$), the surface
14 of square samples determined by direct measurement ($\Delta L = 3 \times 10^{-5} \text{ m}$) and the thickness
15 determined by X-Ray reflectometry ($\Delta t = 1 \times 10^{-9} \text{ m}$). The main error originates from the
16 surface measurements of the sample. The temperature dependence of transport properties was
17 determined by the four probe method from 5 K to 370 K in a physical properties measurement
18 system (PPMS) by Quantum Design. The magnetoresistance was determined at 300 K and 5
19 K by applying successively a magnetic field of 0 and 9 T perpendicular to the film surface.
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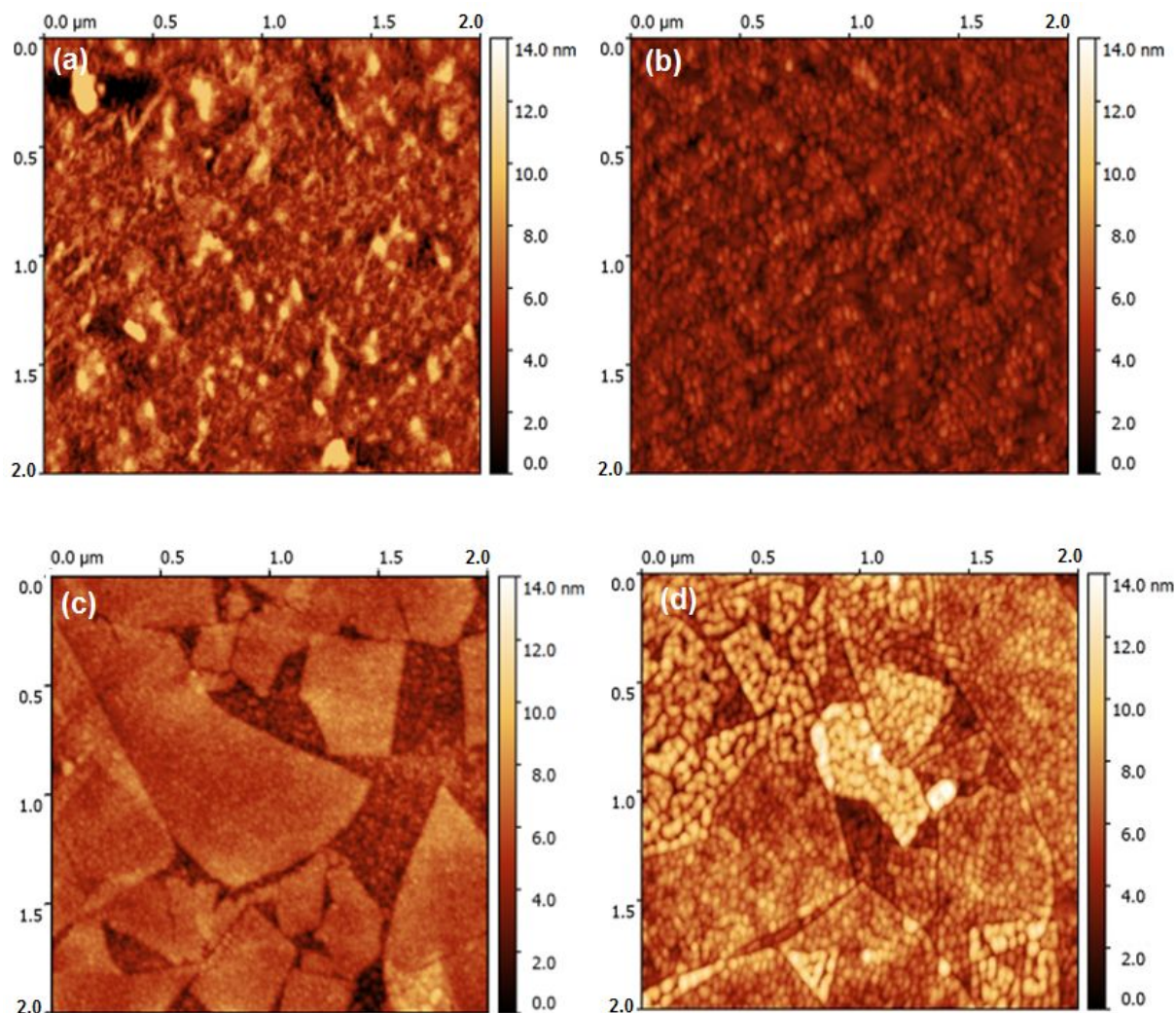
32 **3. Results and discussion**

33 **3.1. Structural analyses**

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39 Scanning electron microscopy (SEM) micrographs of LSMO films deposited on GS
40 and NS/GS samples are displayed in Figure S7. For uncoated GS samples, the deposition of
41 LSMO leads to a flat and homogenous surface over the entire sample surface, independently
42 of the growth temperature (T_G). In contrast, SEM micrographs taken on GS samples coated by
43 NS show a tessellated surface due to the juxtaposition of NS. The size of the NS in an
44 equiaxed-shape description is between 100 nm to 2 μm for the largest ones. The darker areas
45 between well-delimited nanosheets are related to LSMO deposited on not covered glass
46 zones. An analysis of the images provides a surface coverage level of the substrate with NS
47 close to 90% (see Figure S2 (d)).
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55 To get better insight of the morphology of LSMO films, Atomic Force Microscopy
56 (AFM) characterizations are displayed in Figure S8 and Figure 1 for $10 \times 10 \mu\text{m}^2$ area and a
57 zoom of $2 \times 2 \mu\text{m}^2$ area, respectively. For the NS/GS samples, the NS are juxtaposed
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3 alongside each other even if small overlapping is revealed in some places. As it is observed
4 above by SEM analyses, AFM images confirm the excellent coverage level of the surface by
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47 **Figure 1.** $2 \times 2 \mu\text{m}^2$ AFM images of LSMO films grown on GS (a-b) and NS/GS (c-d) at
48 550°C and 645°C respectively. A granular structure of films appears at high deposition
49 temperature.
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53 However, important differences are observed in the morphology of films as function
54 of the substrate and the growth temperature (T_G). Without NS, the surface is uniform and
55 exhibits an apparent roughness due to the presence of long-tipped streaks ascribed to the glass
56 substrate. The root mean square (RMS) roughness increases from 0.35 nm up to 0.70 nm for
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3 growth temperature at 550 and 645°C, respectively. For the NS coated glass substrates, the
4 films cover the NS and the interstices. The RMS roughness increases from 0.20 up to 0.47 nm
5 when T_G rises from 550°C up to 645°C. Interestingly, small domains identified by a granular
6 morphology are discernible (Figure 1 (d)). The estimation of the average particle size with the
7 rise of T_G gives an increase from ~20 to ~40 nm for LSMO/GS samples and 20 to 50 nm for
8 LSMO/NS/GS samples. The swelling of grains is correlated to the apparent roughness of
9 films determined above and the T_G increase. The roughness of LSMO films is considerably
10 lower than the values (between 14 and 56 nm) reported by Nguyen et al.⁴⁸ for 2 μm -thick
11 columnar $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ films grown on $\text{LaNiO}_3/\text{CNO}$ nanosheets. In our case, the growth
12 of LSMO films carried out with a lower repetition rate of the laser and growth rate (2 Hz and
13 0.1 Å per pulse, respectively) and significantly lower thickness (40 nm) lead to lower surface
14 roughness.
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25 The structural characterizations of LSMO films have been carried out by X-ray
26 diffraction in specular θ - 2θ configuration. The corresponding diffractograms at different T_G
27 are shown in Figure 2. First, LSMO films grown directly on amorphous glass substrate exhibit
28 a polycrystalline structure indexed according to the rhombohedral structure (space group $R\bar{3}c$)
29 known to be the structure of LSMO deposited by pulsed laser deposition or by sputtering
30 magnetron onto non-adapted substrates^{46,49}. According to the required energy for the
31 crystallization of films, a significant increase in the crystallinity is observed between 550 and
32 645°C due to a higher thermal activation. The lattice parameters, hexagonal setting, are found
33 to be $a = 0.550(2)$, $c = 1.337(8)$ nm and $a = 0.546(7)$ nm, $c = 1.331(8)$ nm for $T_G = 550^\circ\text{C}$ and
34 645°C, respectively. These values are in good agreement with data reported by Hibble *et al.*
35 for bulk rhombohedral LSMO⁵⁰. In the absence of an adapted template layer provided by
36 CNO NS, the growth temperature is sufficient to induce the spontaneous crystallization of
37 LSMO in the rhombohedral structure identified as the structure of the bulk material with a
38 complete relaxation of intrinsic strains. For LSMO films deposited on NS/GS, a strong
39 increase in the intensity related to the (001), (002) and (003) reflections (pseudo-cubic setting)
40 is observed which means that the presence of the CNO NS induces a texturation of LSMO on
41 NS with a 001 out-of-plane direction as for the LSMO film grown on single crystal (001)STO
42 substrate. The out-of-plane lattice parameter of the LSMO phase is found to be close to
43 0.384(5) nm (550°C) and 0.383(6) nm (645°C) (pseudo-cubic setting). It can be mentioned
44 that no reflection related to the NS layer is evidenced in XRD scans because of the too small
45 diffraction volume. Nevertheless, the values of LSMO films match closely with CNO
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3 reported in the literature ^{38,43,44,51}, thereby confirming the epitaxial stabilization of the LSMO
4 cell on the CNO one. A slight increase in the peak intensity is observed between 550 and
5 645°C indicating that the crystalline quality is enhanced with the increase of T_G . Finally, for
6 LSMO grown on (001)STO, the out-of-plane lattice parameters determined from the high
7 resolution θ - 2θ scans (Figure S4) are $c = 0.383(8)$ and $0.385(2)$ nm at 550 and 645°C,
8 respectively which are very close to the values observed for the films deposited on NS. For
9 LSMO films grown on GS, NS/GS and STO substrates at 645°C, full width at half maximum
10 (FWHM) values obtained from the rocking curves of the (002) peak (not shown here) are
11 2.85, 1.33 and 0.04°, respectively. Hence, the mosaicity of LSMO films is dependent on the
12 nature of the substrate with an enhancement of the structural quality of films grown on glass
13 thanks to the NS seed layer.
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23 The average size of the crystallite domains was determined using the Scherrer's
24 formula⁵². The size increases with T_G from 14 to 34 nm and from 21 to 40 nm for LSMO/GS
25 samples and LSMO/NS/GS, respectively. These values match closely with the ones of
26 granular domains determined above in enlarged AFM scans (see Figure 1). Therefore, the
27 increase of T_G as well as the use of NS enhances the size of crystallite domains and the
28 structural quality of films. For LSMO deposited on GS, the thermal energy promotes the
29 diffusion of adatoms on the surface resulting in the increase of the grain size. For LSMO
30 grown on NS/GS, a similar behavior is observed as function of T_G but grains are larger than
31 on GS showing that diffusion of the add-atoms seems more important on NS than on only GS.
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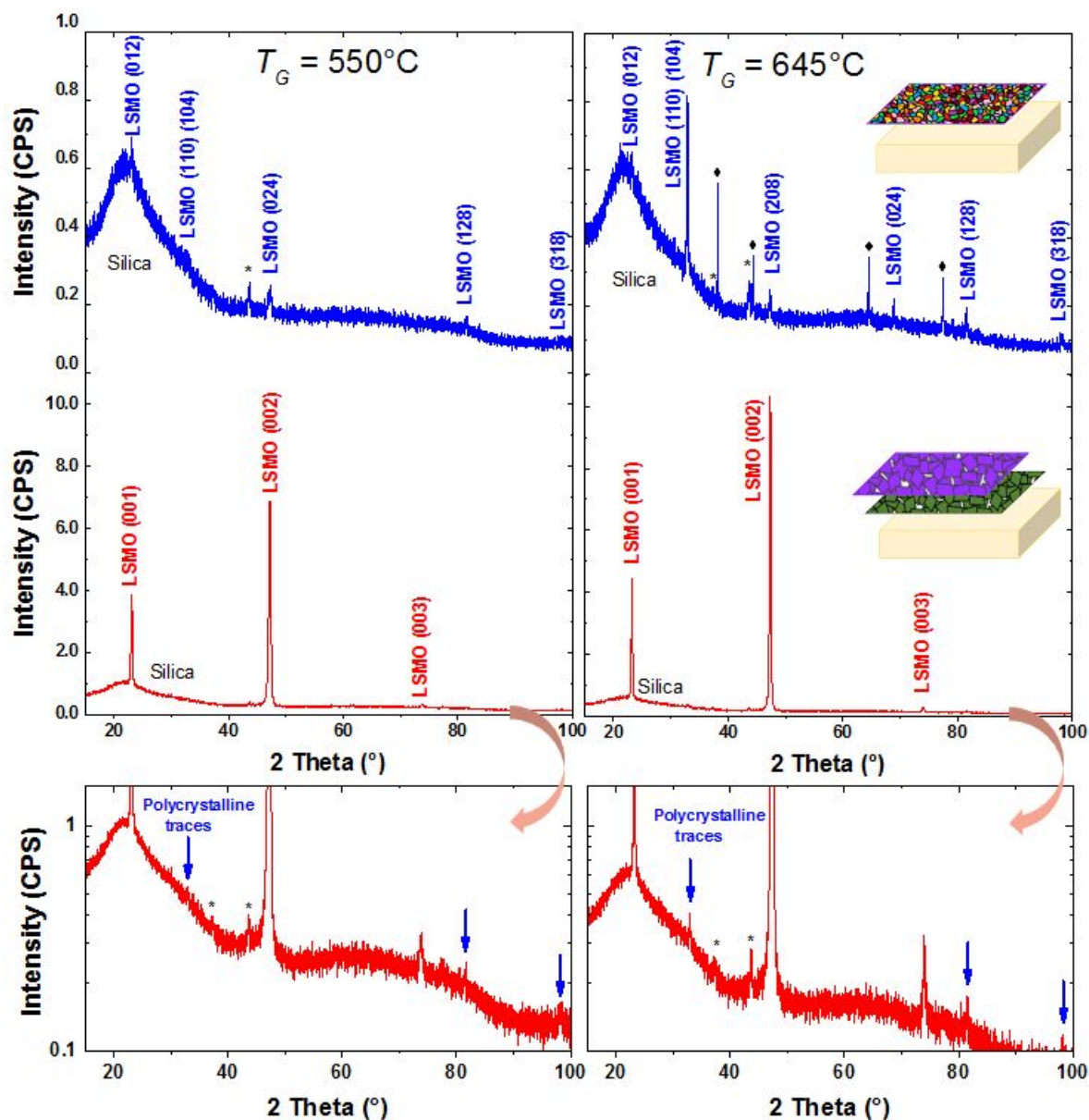


Figure 2. θ - 2θ X-ray diffractograms of LSMO thin films grown on GS (blue) and NS/GS substrates (red) at 550°C and 645°C. Zoom in diffractograms of LSMO/NS/GS films reveal peaks attributed to the polycrystalline phase. Stars (*) and diamond (♦) symbols refer to instrumental artefact and silver traces, respectively.

In order to study the texture of the film in more details, electron backscatter diffraction (EBSD) mapping is reported in Figure 3 for LSMO films deposited onto NS/GS at 550°C (a and b) and 645°C (c and d) for out-of-plane and in-plane configuration, respectively. The mapping of the surface highlights the tessellated areas similar to SEM imaging (see Figure S7) corresponding to the size of the NS. All the electron backscattered beam signal is considered to be assigned to the LSMO film since the thickness of NS is too small to be detected. LSMO films are showing a preferential orientation along the [001] direction as seen

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3 with the standard stereographic triangle (see Figure 3). The texturation is induced by the NS
4 crystalline structure and confirms our previous XRD measurements. In-plane analysis
5 reported in Figure 3 (b) and d reveals a mixed contribution between the [100] and [110]
6 crystallographic directions of the LSMO and confirms the full disorientation of in-plane
7 domains. Furthermore, some areas also appear in black and can be ascribed to areas being not
8 covered by NS (see Figure S7 and S8). To understand this phenomenon, EBSD mapping was
9 also performed on polycrystalline LSMO films deposited on GS (not shown here).
10 Unfortunately, the polycrystalline domains size seems to be too small and do not allow a
11 sufficient diffracting volume to be indexed in the limit of resolution of our device and appears
12 black. Considering this along with the spontaneous crystallization of LSMO on GS, the areas
13 between NS seems to be covered by polycrystalline LSMO. The observation in XRD scans of
14 additional reflections at 32.8° , 81.5° and 98.2° on LSMO films deposited on NS/GS substrates
15 (red enlarged scans in Figure 2) supports the EBSD observations. These additional reflections
16 can be attributed to the rhombohedral phase but their low intensity indicates that the
17 corresponding diffraction volume is small and could arise from the interstitial gaps between
18 NS. In other words, NS induce LSMO epitaxial growth along the out-of-plane direction but
19 does not induce the texture around the NS. For that reason, it is important to reach a high
20 coverage level of the GS surface by NS. The orientation of LSMO on NS does not seem to
21 depend strongly on the growth temperature but actually on the presence or absence of NS.
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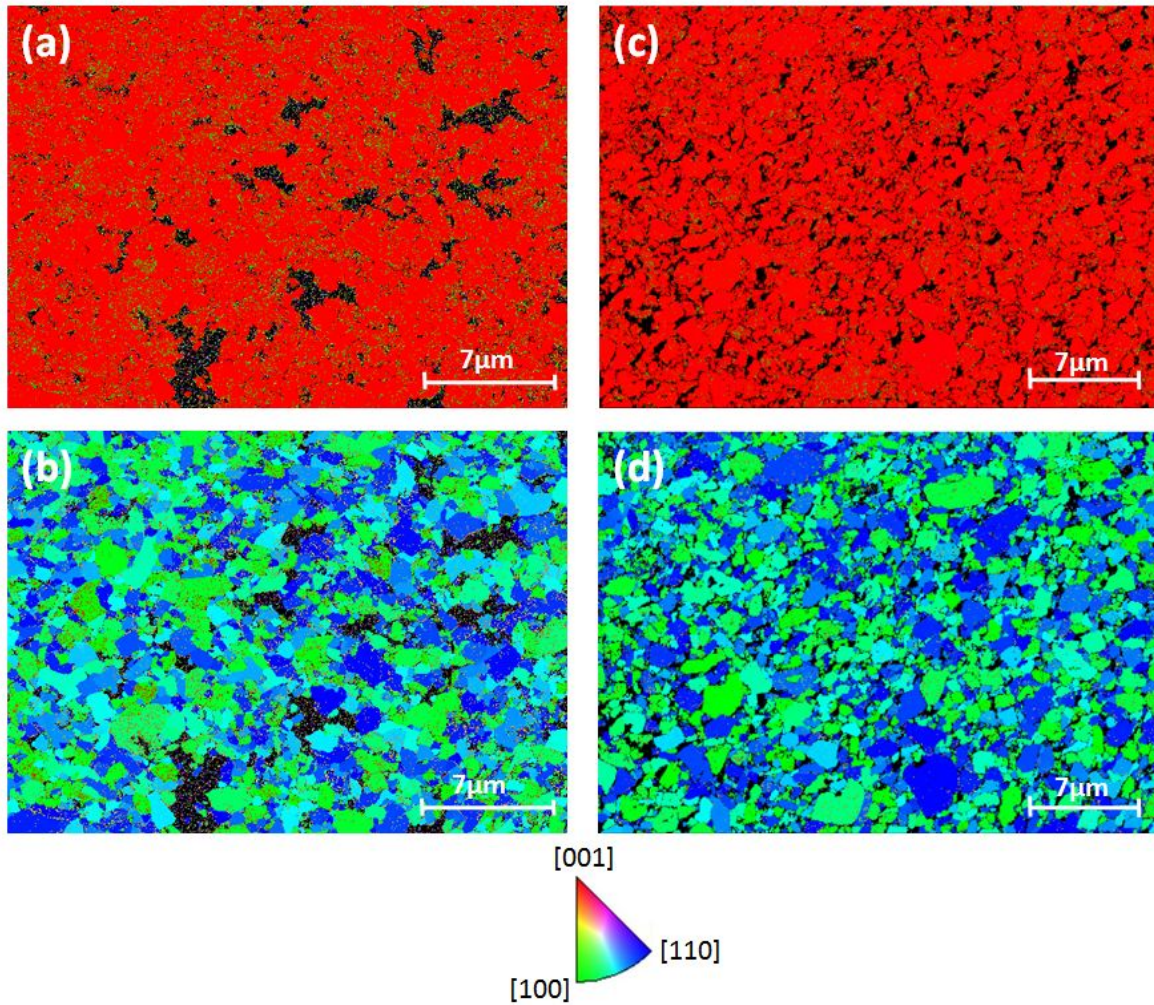


Figure 3. EBSD maps of LSMO thin films deposited at 550°C (left panel) and 645°C (right panel) on glass substrates coated by NS, (a, c) out-of-plane and (b, d) in-plane configuration. The out-of-plane images single-red color demonstrate that LSMO films are highly textured along the [001] direction.

3.2. Magnetism

The temperature dependence of the magnetization (M) of LSMO films is shown in Figure 4 (a) and (b) for films grown at $T_G = 550^\circ\text{C}$ and 645°C , respectively. A magnetic field of 0.05 T is applied parallel to the film surface. Two LSMO/STO samples grown at 550°C and 645°C in similar conditions than on GS and NS/GS are taken as references to compare the magnetic properties. For all the curves, the magnetization increases below T_c around 300 K to reach a plateau in the low temperature range (below ~ 150 K) but some differences are observed both in the amplitude of the magnetization and T_c of films.

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3 Interestingly, the magnetization of LSMO/NS/GS films approaches closely the single
4 crystal films for both T_G . At the contrary, a difference of M of around 170 emu cm^{-3} is
5 observed between the films grown on GS and the buffered NS film for both T_G (all data are
6 reported in Table 1). Furthermore, for LSMO grown directly on GS, M tends to slightly
7 increase with T_G of about 15 emu.cm^{-3} (from 256 up to 271 emu.cm^{-3}) but remains
8 substantially lower than values of LSMO films on NS/GS and STO due to the polycrystalline
9 structure of the films. The same trend is observed for films deposited on NS/GS with a rising
10 of M up of 18 emu.cm^{-3} (425 (550°C) to 443 emu.cm^{-3} (645°C)). By comparison, the
11 magnetization of LSMO/STO samples tends also to increase from 453 and 463 emu.cm^{-3} with
12 the T_G raising. These results are consistent with values reported in references^{25,45,53} for
13 LSMO/STO thin films above the critical LSMO thickness of about 10 nm for which magnetic
14 and electrical properties are altered. In this regard, the growth temperature does not affect
15 critically the magnetization and can be related to the improvement of the crystallinity with T_G .

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17 In order to accurately measure the Curie temperature (T_C) of the films by the derivative
18 method (see Figure S9), the $M(T)$ was measured with a magnetic field of 0.005 T around the
19 magnetic transition after applying a field of 1 T at low temperature (see inset Figure 4 (a) and
20 (b)). For LSMO films grown directly on GS at 550 and 645°C, they exhibit a T_C equal to 333
21 and 348 K, respectively. These values are somewhat greater than LSMO grown on a single
22 STO crystal where a sharp magnetic transition occurs around T_C of 304 and 332 K for
23 increasing T_G . Therefore, the T_C measured for LSMO/GS films is very consistent with data
24 reported by Navasery *et al.*⁴⁹ in the case of polycrystalline LSMO. For LSMO on STO, the
25 LSMO film is clamped on the crystalline substrate. The induced tensile strain driven by the
26 lattice mismatch between the substrate and the film (-1.15%) leads to a deformation of the
27 perovskite structure accompanied by a tilting of the O–Mn–O bonds and a diminution of T_C
28 compared to the bulk^{54,55}. In contrast, the crystallization of LSMO deposited on GS leads to
29 polycrystalline structure with the complete relaxation of strains which explains the
30 displacement of T_C close to the bulk LSMO one (T_C is within the range between 360 and 370
31 K). For textured LSMO films deposited on NS, the T_C found at 318 K and 337 K at 550°C
32 and 645°C, respectively, is between the values measured for LSMO films deposited on GS
33 and on (001)STO because of the combined contribution of both polycrystalline structure and
34 local epitaxy on NS.

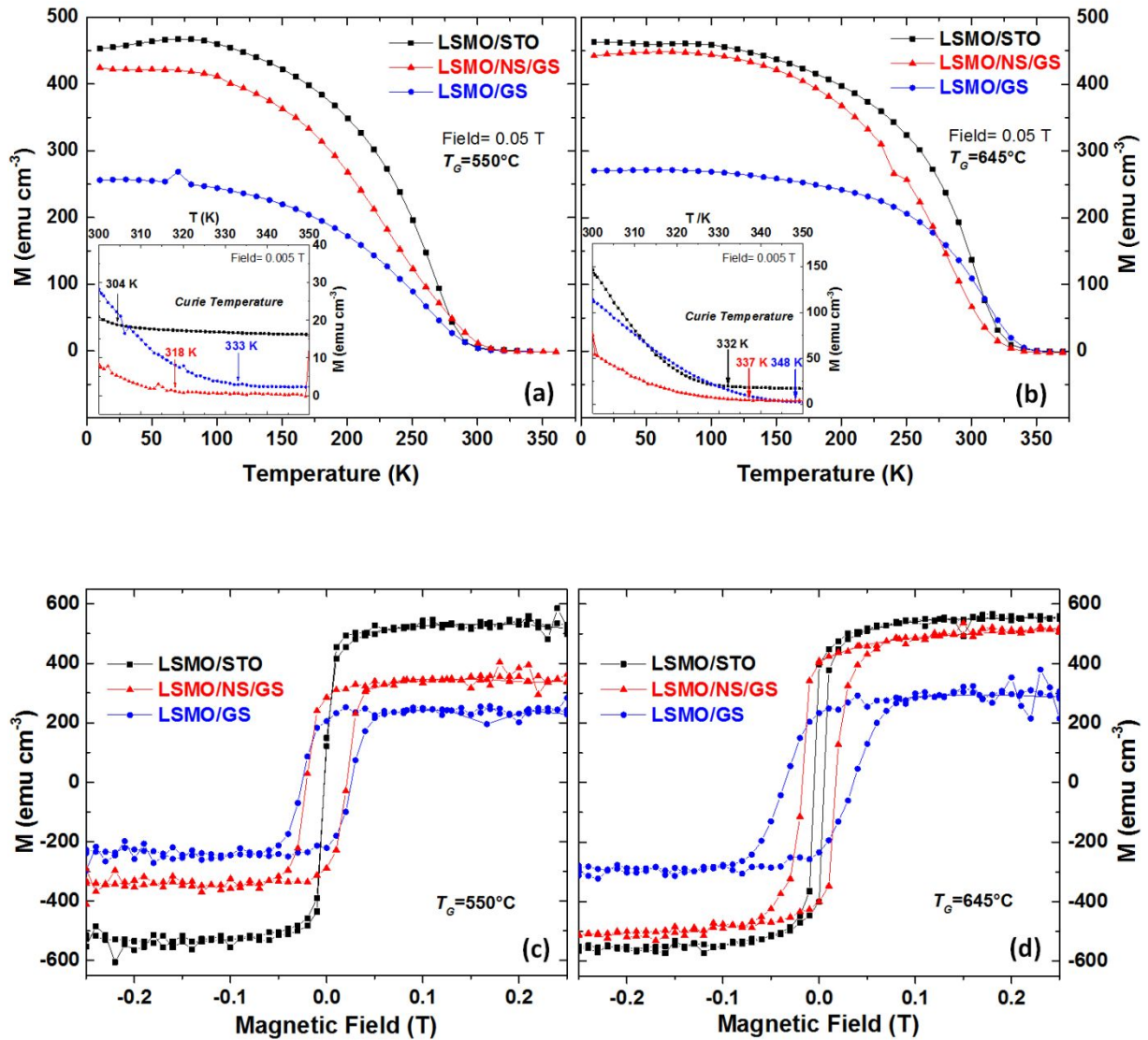


Figure 4. Temperature-dependent magnetization curves of LSMO films grown at 550°C (a) and 645°C (b) on GS (blue), NS/GS (green) and (001)STO (black). A magnetic field of 0.05 T and 0.005 T (in insert) was applied parallel to the surface for all the zero field cooled. Hysteresis loops acquired at 100 K of LSMO thin films grown at 550°C (c) and 645°C (d) for GS, NS cover GS and (001)STO substrates.

The hysteresis loops displayed in Figure 4 (c) and (d) are acquired at 100 K, just below the decrease of the magnetization (~ 150 K). Overall, the variation of the magnetization is consistent with the temperature-dependent magnetization curves described above. The remanent magnetic field B_R and the saturation magnetic field B_{Sat} gradually increase for LSMO films deposited on GS, NS/GS and STO substrates, respectively (see values summarized in Table 1). The influence of the growth temperature on B_{Sat} is also visible with

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3 an increase up to 182 emu.cm^{-3} for LSMO/NS/GS sample with the increase of T_G . The rise in
4 the saturation magnetization is somewhat lower for the polycrystalline and the single-crystal
5 LSMO films (63 and 35 emu.cm^{-3} , respectively). For LSMO/NS/GS samples, the
6 magnetization is between the values measured on the two other samples at $T_G=550^\circ\text{C}$ but is
7 similar to LSMO on (001)STO at $T_G=645^\circ\text{C}$. This behavior confirms the enhancement of the
8 structural quality of LSMO films provided by NS. The coercivity H_C is subjected to a similar
9 behavior as function of the nature of the substrate. The lower value of H_C is observed for the
10 LSMO films on STO with 27 and $52 \times 10^{-4} \text{ T}$ at $T_G=550$ and 645°C . Thus, H_C is divided by 2
11 as function of T_G . These low values of the coercivity reflect the single crystal structure and
12 large magnetic domains. In contrast, the hysteresis loops suffer a spreading for LSMO/GS
13 with values increasing up to ~ 350 and $\sim 250 \text{ Oe}$ for $T_G = 550^\circ\text{C}$ and 645°C . In the
14 polycrystalline LSMO samples, the formation of magnetic domains is driven by the particle
15 size influenced by the growth temperature. As suggested by Lecoer *et al.*⁵⁶, the domains
16 switch mostly independently each in a narrow range of fields and since the distribution of
17 switching fields is large, it provides a higher macroscopic coercivity when the particle size
18 decreases. For (001)-textured LSMO/NS/GS, the value of H_C decreases noticeably compared
19 to polycrystalline LSMO/GS films. This change is consistent with the improvement of the
20 structural quality and the particle size evidenced by AFM and XRD measurements for the
21 textured films.

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37 Nevertheless, the combination of shape and magnetocrystalline anisotropy in epitaxial
38 (001)-oriented LSMO films induces a magnetic anisotropy along preferential crystallographic
39 orientations which minimize the magnetostatic energy when an external field is applied⁵⁷. As
40 such, the [110] and [100] directions are identified to be easy and hard axes, respectively.
41 When the magnetization change over from the [100] to the [110] axis, the hysteresis loop
42 becomes larger and the coercivity increases. In polycrystalline films grown on glass, the full
43 misorientation of grains leads to the statistical distribution of the easy and hard axis of the
44 individual grains in all directions of space, and therefore to a random orientation in the
45 macroscopic measurements. The shape anisotropy is no longer relevant and the more likely
46 easy axis take place in the [111] axis of respective oriented grains^{58,59}, resulting in the
47 weakening of the square-shape hysteresis loop. For (001)-textured LSMO/NS/GS films, both
48 [110] and [100] orientations are randomly in-plane distributed leading to a more narrowed
49 magnetic response.

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3 Therefore, the presence of NS improves greatly the coercivity of LSMO films with
4 respect to the polycrystalline films by inducing larger magnetic domains. The LSMO films
5 undergo a magnetic transition from magnetically hard to a magnetically soft material as
6 function of the substrate.
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10 11 12 13 **3.3. Transport properties** 14 15 16 17

18 The temperature dependence of the electrical resistivity measured at 0 and 9 T is
19 plotted in Figure 5, for $T_G = 550^\circ\text{C}$ (a) and 645°C (b). Contrary to magnetic measurements,
20 the magnetic field applied in the PPMS system is perpendicular to the film surface. At first
21 glance, the zero-field resistivity at 300 K of polycrystalline LSMO films grown on GS is
22 always higher than the resistivity of films deposited on STO and NS/GS. The global
23 difference in the resistivity level observed for polycrystalline LSMO/GS samples compared to
24 LSMO on STO is explained by the effective incorporation of grain boundaries acting as a
25 local blockage to the electron delocalization across the crystalline domains. This behavior can
26 be correlated to our AFM and XRD structural characterizations for which a smaller grain size
27 is observed in the case of the complete polycrystalline films grown on GS (see Table 1 for
28 more details). However, the discrepancy is weaker between LSMO deposited on NS and STO,
29 especially for $T_G = 645^\circ\text{C}$. Hence, the improvement of the transport is explained by two
30 independent contributions driven by the structural quality of films. First, the growth
31 temperature leads to a better film crystallinity with larger crystalline domains. Secondly, NS
32 enhance greatly the structural quality of short range-epitaxial LSMO films by inducing the
33 high texturation along the [001] direction and an increase of the grains size with a different
34 growth mechanism on the scale of NS. Therefore, the use of NS promotes the carriers
35 delocalization and the lowering of the resistivity. Moreover, in the low temperature region
36 below 50 K, a resistivity minimum appears for LSMO films grown on GS and NS/GS and not
37 present for LSMO/STO one. The nature of this effect is H -dependent as evidenced by the
38 resistivity minimum shift toward lower temperature and flattens out when a magnetic field of
39 9 T is applied (see Figure S10). This effect is related to the presence of grain boundaries
40 which act as diffusion scattering for the transport carrier which are not present for film
41 deposited onto single crystal substrates^{60,61}. Numerous models based on the electronic
42 localization have been proposed to explain the appearance of the resistivity minimum within
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3 the low-temperature range observed in other manganites^{61–65}. The first one is a Coulomb
4 blockade effect related to weak localization and strong electron-electron interaction in a
5 disordered metallic state. Localized charge carriers need to overcome the Coulomb barrier and
6 the magnetic tunnel barrier to tunnel from a grain to the other. With the reduction of particle
7 sizes, the contribution of the Coulomb barrier increases and leads to a steeper rise in
8 resistivity. This effect is presumed to prevail for small grains (below 50 nm)⁶¹.
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12 The second model consists in the contribution of intergranular spin-polarized
13 tunneling (ISPT) between antiferromagnetically coupled grains through the grain
14 boundaries⁶³. The transport across the grain boundaries is sensitive to the applied magnetic
15 field. Under zero external H -field, the neighboring grains align in such a way that the charge
16 carriers of the grains have opposite spins and remains immobile. Such anti-ferromagnetic
17 interaction results in a gap between the charge carriers of the neighboring grains. With
18 increasing temperature, the grains reorient themselves and the carriers have enough energy to
19 overcome the barrier (resistance decreases). Application of external magnetic field forces the
20 grains to orient such that the spins carrier from the neighboring grains aligns favorably to
21 reduce the energy gap. According to this model, the resistivity minimum should flatten out
22 gradually with increasing field and vanish at some critical field. In this way, the resistivity
23 minimum is nearly suppressed at $H = 9$ T for the LSMO film grown at 645°C on NS/GS and
24 largely reduced for other polycrystalline substrates (see Figure S10).
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36 Another important part resulting from the transport curves in Figure 5 (a) and (b) is the
37 maximum of resistivity identified as the metal-insulator transition (T_P) usually correlated to
38 the magnetic transition from ferromagnetic–metal (FM-M) to paramagnetic–insulator (PM-I).
39 This effect can also be seen on the minimum of magnetoresistance MR defined as $MR = 100$
40 $\times (\rho_0 - \rho_H) / \rho_0$, where ρ_0 is the zero-field resistivity and ρ_H is the resistivity in the applied field
41 H is plotted versus the temperature dependence in Figure 5 (c) and (d).
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46 LSMO films show T_P around the temperature range of 225–312 K for the different type of
47 substrates (see Table 1 for more details). By comparing the difference in temperature between
48 the magnetic and the electrical transition $\Delta T = T_C - T_P$, we observe a rise in the discrepancy
49 between the two distinct transitions in polycrystalline films. The variation of ΔT is
50 specifically more important at $T_G = 645^\circ\text{C}$. In a perfect LSMO single crystal, the difference
51 must stay near zero^{13,66}. However, the existence of grain domains in LSMO films deposited
52 on GS and a lesser extent, in LSMO films grown on NS/GS influences the transport
53 mechanisms. The electrical transition in polycrystalline films is strongly dependent on the
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percolation threshold between neighboring grains in such a way that conduction path have to be established to ensure the carrier delocalization. On the reverse, the magnetic transition is statistically dependent on the commutation of each domain, leading to an average contribution around the observed T_C . Finally, the magnetic transition is more influenced by the structural properties of films such as the crystallographic phase or strains modifications than the particle size. In consequence ΔT is more representative of the morphology of films. This effect is clearly highlighted here in Figure 5 (c) and (d) with the displacement of dash lines stand for the metal-insulator transition, leading to a lower apparent T_P for polycrystalline films. Therefore, the presence of NS on GS enhances the morphology of LSMO films (larger particle size and preferential orientation) and results in the displacement of the metal-insulator transition by stabilizing the metallic state at higher temperature.

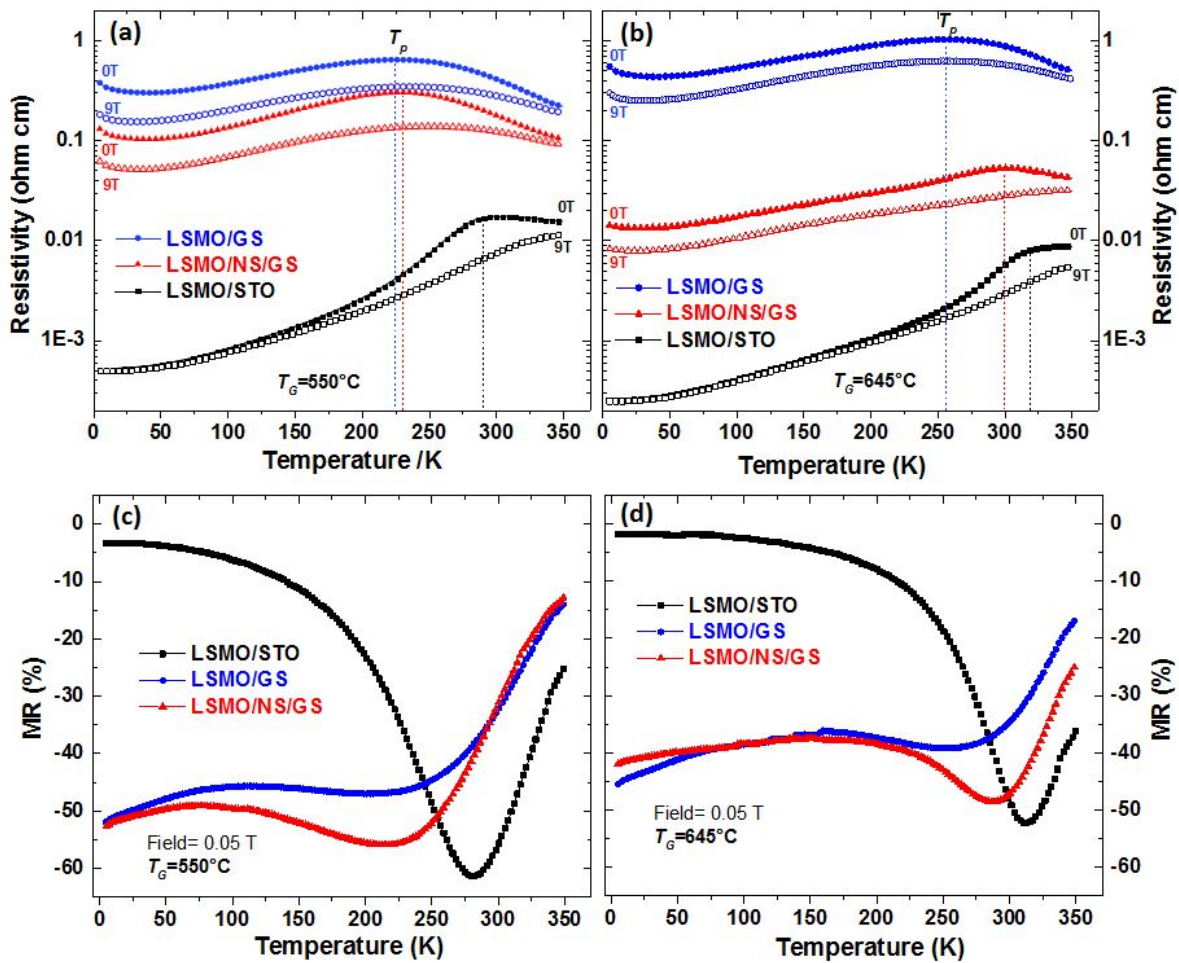
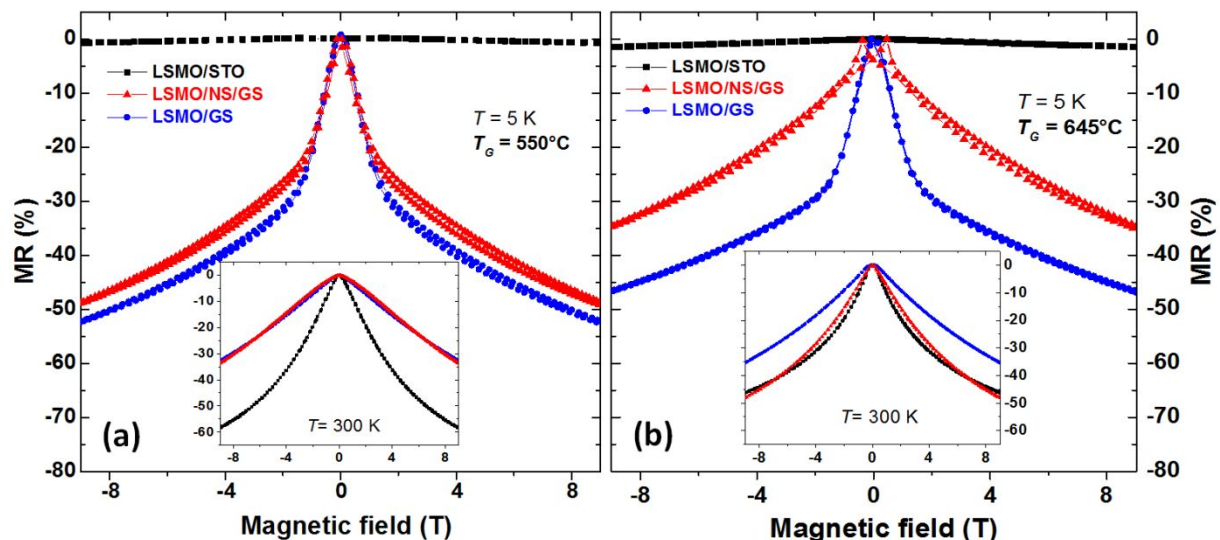


Figure 5. (a) Resistivity of LSMO films measured in parallel configuration at $H = 0\text{ T}$ and 9 T for $T_G = 550^\circ\text{C}$ (a) and 645°C (b) and different substrates (STO, NS/GS, GS). (b)

Dependence of the magnetoresistance of films as function of the temperature at $T_G = 550^\circ\text{C}$ (c) and 645°C (d).

The amplitude of the MR is also very different with temperature depending on the different substrates (see Figures 5 (c) and (d)). In LSMO/STO samples, the low temperature MR is almost suppressed in good agreement with result reported by Yang *et al.* for single crystals substrates⁶⁷. At the contrary, from low temperature to the apparent metal-insulator transition around 200 K, the MR of LSMO films on GS and NS/GS is constant with a value between 40 to 50%. Also, it is interesting to note that a strong MR is preserved within the low temperature range far below the transition for polycrystalline and textured films. In the case of textured LSMO films on NS/GS, this remarkable behavior represents of interest given that textured films have a high magnetization close to films of high quality deposited onto SrTiO₃. The presence of MR at low temperature for the textured LSMO film on NS is due to the grain boundaries of the textured polycrystalline structure. Furthermore, the presence of small polycrystalline domains on not covered GS zones confirmed by the presence of polycrystalline LSMO traces detected by XRD measurements (Figure 2) and AFM characterizations (Figure S2 (d)) can also amplify this low temperature MR.

To investigate deeper the transport response of films when a magnetic field is applied, we present in Figure 6 (a) and (b), the MR at 5 K versus H . For LSMO/STO samples, the MR is very weak, whereas LSMO/GS and LSMO/NS/GS samples show a high negative MR at 5 K of about -55 and -45 % for $T_G = 550$ and 645°C , respectively.



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3 **Figure 6.** Magnetoresistance of LSMO films measured with magnetic field applied
4 perpendicular to the surface at 5 K and 300 K (in insert), for $T_G = 550^\circ\text{C}$ (a) and 645°C (b) on
5 STO (black), NS/GS (red) and GS (blue).
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10 Interestingly, the MR increases rapidly in the low-field region. This behavior known
11 as low-field effect is only observed for polycrystalline and textured LSMO films and is
12 suppressed at 300 K (inset of Figure 6). The low-temperature MR in the polycrystalline films
13 at low fields can be understood in terms of magnetic domain scattering at the boundary
14 regions. Since the conduction electrons are almost completely polarized inside a magnetic
15 domain, electrons are easily transferred between pairs of Mn^{3+} and Mn^{4+} ions^{60,68}. However,
16 when these electrons travel across grains, strong spin-dependent scattering at the boundaries
17 will lead to a high zero-field resistivity. Application of a moderately low field can readily
18 align the domains into a parallel configuration causing the resistivity to drop substantially.
19 This phenomenon is very important for sensor applications⁶⁹ and we are showing the
20 possibility to tune this behavior with the different type of substrate and temperature growth.
21 This is particularly interesting because with the different type of substrate, we are able to
22 stabilize highly-textured LSMO films deposited on CNO NS while limiting the resistivity
23 threshold unlike pure polycrystalline films.
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Table 1. Magnetic and electrical properties of LSMO films deposited on different substrates at 550 and 645°C.

Substrate	T_G [°C]	Grain size [nm]	T_C [K]	T_P [K]	$\Delta T = T_C - T_P$ [K]	$M(0.05T)$ [emu cm ⁻³]	$\pm B_{Sat}$ [emu cm ⁻³]	$\pm H_c(100\text{ K})$ [$\times 10^{-4}$ T]	ρ_{300K} (00e) [Ω cm]	CMR (300K) [%]	MR low field [%]
GS	550	14	333	227	106	256	278;-274	252;-255	2.7×10^{-1}	30	30
NS/GS	550	21	318	230	88	425	390;-422	248;-212	1.2×10^{-1}	35	20
STO	550	-	304	281	23	453	569;-575	23;-47	7.0×10^{-3}	60	-
GS	645	34	348	257	91	271	329;-331	357;-357	5.7×10^{-1}	35	30
NS/GS	645	40	337	300	37	443	581;-575	172;-173	2.8×10^{-2}	50	-
STO	645	-	332	312	20	463	596;-600	52;-52	2.9×10^{-3}	45	-

4. Conclusion

Chemical synthesis and deposition of homogeneous CNO NS layer on GS have been achieved with a coverage level close to 90%. Then, highly (001)-textured LSMO films on NS/GS have been grown with a high structural quality by taking advantage of randomly dispersed CNO NS used as seed layer. In contrast, LSMO on glass without NS result in fully polycrystalline films without any texturation, as confirmed by XRD and EBSD analyses. The preferential growth of LSMO on NS leads to magnetic and transport properties between the polycrystalline and single crystal LSMO ones used as reference in this work. As example, B_{sat} and increase by 250 emu cm^{-3} while T_C , H_C and ρ_{300K} are reduced by 10 K, $180 \times 10^{-4} \text{ T}$ and $5.67 \times 10^{-4} \Omega \text{ cm}$, respectively when the buffer NS seed layer is deposited on GS. Hence, the coercivity of the textured LSMO/NS/GS films is divided by 2 compared to LSMO on GS, thus allowing to switch between a hard magnetically ferromagnetic LSMO on glass to an easier magnetically tuning LSMO on NS. Finally, the magnetization and the coercivity of textured films are very close to the single crystal ones. A further advantage is that a low field MR appears for textured films, which is absent for single-crystalline films but present for polycrystalline films. Accordingly, structural and physical properties are widely improved by the use of NS in the case of the integration of LSMO on glass and combine the properties of monocrystalline and polycrystalline films.

Another notable advance is the possibility to preserve interesting physical properties of LSMO films grown at 550°C on NS/GS, which is not the case for polycrystalline films on GS. The reduction of the growth temperature opens new opportunities to integrate readily textured LSMO of high quality on silicon at lower temperature, without to consider the formation of native SiO_2 . Also, the reduction of the temperature preserves more thermally sensitive substrates. In the near future, a fine adjustment of the coverage level of the surface by NS should also allow to tune the physical properties of deposited films on more complicated surfaces.

To summarize, $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheets open new perspectives and opportunities for integration of perovskite structures like LSMO on various templates besides single crystal substrates. Thereby, diverse non-adapted substrates such as amorphous substrates (glass...) or crystalline substrates (silicon...) can be now considered while maintaining good structural and physical properties of films. This approach overcomes technological limitations for the use of complex oxides into CMOS-based applications.

Supporting Information

TEM brightfield micrograph of NS, AFM images, RHEED patterns, High-resolution θ - 2θ diffractograms, X-Ray Reflectometry, SEM micrographs, Determination of Curie Temperature, Transport properties at low temperature

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