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Interface structure and strain relaxation in Nd_{0.96}MnO₃ epilayers grown on (001) SrTiO₃ substrates

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Abstract:

In this work we focus on the growth of highly oriented Nd_{0.96}MnO₃ (NMO) perovskite epilayers of different thickness on single-crystalline (001) SrTiO₃ (STO) template, using an injection metal-organic chemical vapor deposition process. X-ray diffraction revealed that the epilayers have an orthorhombic *Pnma* structure and were purely (101) oriented parallel to the (001) plane of the substrates. The orientation relationships between the film and substrate are rather well defined in the vicinity of the interface as [101]NMO//[001]STO (out-of-plane), [10 $\bar{1}$]NMO//[100]STO and [010]NMO//[010]STO (in plane). It can be concluded that the film thickness significantly influences the strain state of the NMO epilayers deposited on STO. There was a contraction of out-of-plane layer network spacing leading to a progressive relaxation in the growth direction. The out-of-plane lattice parameter is lower than the bulk value. As the film thickness increases, the NMO epilayer strain reduces so that out-of-plane lattice parameters tend towards their bulk values. The calculated strain goes from -0.4% (thickness of 150 nm) to 0% (thickness of 600 nm). These epilayers are therefore strained at the interface and relax with the thickness. The out-of-plane lattice parameter observed for the 600 nm thick epilayer relaxed toward the bulk NMO. No traces of extra phases are detected. An atomic model of interfaces has been built using cross-sectional transmission electron microscopy image, as well as a crystallographic simulation software CrystalMaker.

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Keywords: Epilayers, Metal-organic chemical vapor deposition, X-ray diffraction, Thickness, out-of-plane texture, Transmission Electron Microscopy.

1. Introduction

The particularity of perovskites-like oxides is their instability facing multiple intrinsic or extrinsic constraints. The known structure of an ABO_3 material, given at room temperature and at atmospheric pressure can change towards another more or less deformed structure under the effect of an external parameter like variations of pressure, temperature, but also with the application of constraints, chemical substitutions, the application of electric or magnetic field, an environment in a reducing or oxidizing atmosphere, etc... Depending on several factors, such as variable crystal structure and the nonstoichiometric chemistry, which influence the electronic structure, these materials exhibit various physical properties. They are under intensive study due to their interesting dielectric and magnetic properties such as ferromagnetic, antiferromagnetic, charge, and orbital ordering. Thus, these properties have potential applications in the fields of sensors and spintronic devices [1-4], or in the fields of chromogenic coatings and devices [5-6]. Even slight distortions of the perovskite structure can give rise to various changes in physical properties as a result of these variations. The richness of the perovskite physical properties directly results from the multiple possible distortions of their structure [7-11]. The chemical substitution on site A and/or B of a given perovskite or the existence of sub-stoichiometry in one of the elements constituting the compound, in particular, oxygen in the case of oxides, can modify significantly the physical and structural properties. In addition, having nanoparticles shape, thin layers, or multilayers can also modify the properties observed compared to solid materials [12-17]. The rare-earth manganite $NdMnO_3$ belongs to the group of orthorhombically-distorted perovskites $AMnO_3$, where A is a rare earth ion from La^{3+} to Dy^{3+} , with the $GdFeO_3$ structure. Research on some of these materials is still in its beginning and their properties are sometimes only partially understood or known. Among these materials, it can be noted that the neodymium manganites show crystallographic deformations yielding tilts of the octahedra MnO_6 , which play an essential role in the magnetic interaction between magnetic cation networks [18]. In the epilayer system, structural characterizations, other than the study of the effect of the thicknesses on the growth stabilization and texture of the neodymium lacunar manganite, was made in a rather concise and brief manner [19-22]. This paper aims to contribute to such topic, we present a systematic study of the thickness effect on the structure and growth stabilization of lacunars $Nd_{0.96}MnO_3$ (abbreviated hereafter as NMO) epilayers epitaxially

grown on (001) SrTiO₃ (STO) substrates by using an injection metal-organic chemical vapor deposition (MOCVD) process. We reported an X-ray diffraction (XRD) analysis and a transmission electron microscopy (TEM) study on the microstructure and interfacial atomic structure of such thin epilayers, representing one of the key steps to understanding its growth mechanism and structure-property relationships.

2. Experimental procedure

NMO epilayers were grown by an injection metal-organic chemical vapor deposition process [23] on single-crystalline (001) STO substrates. In this system, the solid precursors Nd(tmhd)₃ (Nd(C₁₁H₁₉O₂)₃) and Mn(tmhd)₃ (Mn(C₁₁H₁₉O₂)₃) are dissolved in a solvent exhibiting optimum compatibility which is 1,2-dimethoxyethane (DME), denoted "monoglyme". The obtained solutions with a concentration of 0.02 mol.l⁻¹ were then mixed in the appropriate proportions to form the only liquid source used for the synthesis. We note that the solubility limit for each precursor was found to be between 0.05 and 0.1 mol.l⁻¹. The solution is retained at room temperature in a pressurized vessel (1 to 2 bar of argon) fixed to an injector. Droplets of few microliters are injected into the reactor on a moving belt maintained at room temperature. They are immediately evaporated and eliminated *in-situ* by a small back pumping. The remaining micro-amount of solid precursors on the belt is mechanically carried into the evaporation zone (heated at 230°C) where the precursor vapors are produced and transported by an O₂ gas into the reaction zone where the classical CVD reaction ensues on the substrate. In comparison to the standard MOCVD [24-26], the injection MOCVD presents some interesting particularities: unstable precursors can be used because they are kept at room temperature under inert gas. Furthermore, the control of the precursor vapour pressure and the growth rate are very precise through the control of the injected volume. Moreover, at the same time as a solvent is needed for solid precursors, only a mixture of carrier gas / precursor vapour, without solvent, reaches the substrate because of the small back pumping of the evaporated solvent. This is a great advantage compared to traditional bubblers and can be useful in order to avoid the cracking of solvent which can occur in some deposition conditions leading to the incorporation of carbon or metal carbonates in the films. To control the nominal composition of our epilayer as concerning initial Nd/Mn proportion, we realized lacunar perovskite-type manganese oxides Nd_{1-x}MnO₃ epilayers of about 200 nm thickness on STO with a different Nd/Mn ratio. The substrate temperature was at 680 °C. The growth rate was 0.72 μm.h⁻¹, in terms of one injection per second. The as-deposited samples were then heat-treated, in an in situ manner, at 680 °C for 30 min under an O₂ flow. [Figure 1](#)

shows linear dependence of The Nd/Mn proportion of the Nd_{1-x}MnO₃ epilayers, measured by Wavelength Dispersive Spectroscopy (WDS) technique about the Nd/Mn proportion in the beginning solution, which allows us to possibly control the nominal composition of the epilayer by adjusting the Nd(tmhd)₃ and Mn(tmhd)₃ starting precursor ratio. To attain lacunar perovskite-type manganese oxides with Nd_{0.96}MnO₃ (NMO) formula, we used a starting precursor proportion of 0.79. The thickness of the epilayer varies from 150 to 600 nm. X-ray diffraction (XRD) measurements were performed using a BRUKER D8 advance research diffractometer with a Cu anode ($\lambda=1.5406$ nm) and LynxEye 1 dimension detector. Transmission electron microscopy (TEM) observations were carried out at 200 kV with a JEOL 2010 microscope (0.19 nm resolution). Crystallographic images have been made with the program CrystalMaker [27].

3. Results and discussion

The structure of STO, at room temperature, is a Pm $\bar{3}$ m cubic perovskite with $a_{STO} = 3.905 \text{ \AA}$. Compared to the STO structure (figure 2(b)), the NMO bulk material presents deformations which correspond to orthorhombic distortions according to the space group *Pnma* (equivalent to *Pbnm*, space group # 62). Figure 2(a) shows the geometrical relations between an orthorhombic cell parameters *Pnma*; $a_o = 5.4972 \text{ \AA}$, $b_o = 7.6647 \text{ \AA}$ and $c_o = 5.4340 \text{ \AA}$ [28] characterized in a ($\vec{a}_o, \vec{b}_o, \vec{c}_o$) base (where “o” refers to orthorhombic) and the small pseudo-cubic cell, characterized in ($\vec{a}_{pc}, \vec{b}_{pc}, \vec{c}_{pc}$) base (where the index “pc” refers to a pseudo-cubic) with $a_{pc} = c_{pc} = \frac{\sqrt{a_o^2 + c_o^2}}{2}$, and $b_{pc} = b_o/2$ [29]. Along this study we consider the fact that the *b*-axis of *Pnma* corresponds to the *c*-axis of *Pbnm* [30]. The relationship between the two systems of structural symmetry is given by Eq. (1).

$$\begin{cases} \vec{a}_{pc} = \frac{\vec{a}_o + \vec{c}_o}{2} \\ \vec{c}_{pc} = \frac{\vec{a}_o - \vec{c}_o}{2} \\ \vec{b}_{pc} = \frac{\vec{b}_o}{2} \end{cases} \quad (1)$$

When grown on STO, along with the [101] orientation, with the *b*-axis in the plane (figure 2(a), a blue unit cell), it would have a lattice mismatch of $\epsilon_m \approx 1\%$.

$$\varepsilon_m = \frac{a_{\text{substrate}} - a_{hkl}^{\text{bulk}}}{a_{hkl}^{\text{bulk}}} \quad (2)$$

Where $a_{\text{substrate}}(a_{\text{STO}})$ and $a_{hkl}^{\text{bulk}} = a_{pc} = c_{pc}$ is the bulk value calculated using lattice constants from the literature [28]. They are respectively the no-strained cell parameters of the substrate STO and the bulk NMO. With these defined parameters, we can describe the strain state anticipated by NMO epilayer along a $[hkl]$ direction as:

$$\varepsilon_{\perp} = \frac{a_{hkl}^{\text{film}} - a_{hkl}^{\text{bulk}}}{a_{hkl}^{\text{bulk}}} \quad (3)$$

Where a_{hkl}^{film} is the epilayer lattice parameter in the out-of-plane direction ($[101]$). Thus, a contraction behavior induced by the out-of-plane strain could be expected for NMO on STO due to the relative difference of the parameter. This occurred strain was observed for the best part of stoichiometric oxide-like compounds [31]. Figure 3 represents the diffractograms in $\theta/2\theta$ configuration obtained for epilayers at different thicknesses (indicated on the right of each diagram). A single-family of substrate planes diffracted by XRD in 2θ -scans: the lines(001), (002), and (003) in the range of 20° - 80° . In addition to STO substrates, we show that the stabilization of the NMO phase is not realizable on Si (001) with our synthesis orders; a mixing of MnO_2 and Nd_2O_3 single oxides is obtained. Unlike the epilayer deposited on silicon, the NMO phase is present in these epilayers. It diffracts essentially along with the same family of plan (00 l) of the pseudocubic perovskite cell as the substrate. The phase, therefore, appears to be textured in the direction vertical to the substrate plane. Furthermore, the NMO diffraction peaks roughness for 150, 300, and 600 nm thick epilayer, and their emplacement close to the (00 l) Bragg peaks of STO, indicates a good crystallinity and an out-of-plane [001] texture. The analysis at large angles allows for better separation of the peaks. Figure 4 groups together the diffraction diagrams $\theta/2\theta$ obtained for $45^\circ < 2\theta < 50^\circ$ on the NMO/STO. We deduce from these 2θ -scans the interreticular-distance (d_{002}) between the planes parallel to the interface of the substrate owing to Bragg's law. We thus obtain directly the value of the cell parameter perpendicular to the interface of the substrate by applying equations Eq. (4).

$$\begin{cases} \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \\ a_{\perp} = 2 \cdot d_{002} = \frac{\lambda}{\sin\theta} \end{cases} \quad (4)$$

An apparent change in the cell parameter is observed as a function of the epilayer thicknesses on these diffractograms. These parameter values are a little bit lower than that of the bulk one. Hence, the epilayers exhibit an increase of the out-of-plane lattice distances from $a_{\perp} = 3.850 \pm 0.005 \text{ \AA}$ for a thickness of 150 nm up to $a_{\perp} = 3.866 \pm 0.005 \text{ \AA}$ for a thickness of 600 nm. These results could be explained by a gradual relaxation of the contraction strain of out-of-plane layer network spacing. The calculated strain (Eq. (3)) to be contraction (negative) goes from -0.4% (thickness of 150 nm) to 0% (thickness of 600 nm). These epilayers are therefore strained at the interface and relax with the thickness. The thickness-dependent out-of-plane lattice distances and strain is plotted in [figure 5](#). Transmission electron microscopy (TEM) observations were realized to better understand the nature of the different phases identified by X-ray diffraction. [Figure 6\(a\)](#) well shows the quality of the geometry structure (interface) and elemental distribution within the epilayers. The orientation relationships in the area of the interface between epilayer and substrate can be identified as:

$$\begin{aligned} &\text{Out-of-plane } [101]_{NMO} \parallel [001]_{STO} \\ &\text{In plane } \begin{cases} [010]_{NMO} \parallel [010]_{STO} \\ [10\bar{1}]_{NMO} \parallel [100]_{STO} \end{cases} \end{aligned}$$

The thickness of the treated epilayer revealed from TEM is about 150 nm. The morphology of the growth can generally be described as a repartition of well-structured domains that arrange themselves regularly. For more details on the quality of the geometric structure and elemental distribution in the interface within the epilayers, we showed in the enlarged red squared area ([figure 6\(b\)](#)), the schematic representation of the MnO_6 octahedral distortions and the regular distribution of TiO_6 octahedra in the cubic symmetry in the $[001]$ and $[100]$ substrate basis orientation. The crystal structure of both NMO and STO as well as a schematic description of hetero growth of NMO (101) layer on STO (001) substrate is showed in [figure 6\(b\)](#), (c), and (d). We can note that in direct space the phase orientations are compatible with the TEM maps. These observations, therefore, show a structuring of the epilayers with oriented growth along the (101), with the long b -axis in the interface plane. The structural representation and the associated models are carried out by crystallographic simulation software CrystalMaker.

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2 This famous behavior has been cited before by several studies on systems deposited on STO
3 specimens [31-34].

4. Conclusion

7 In conclusion, using an injection metal-organic chemical vapor deposition process, we
8 successfully prepared at different thicknesses a lacunar NMO perovskite manganite epilayers
9 and achieved growth of the epilayers on an STO(001) substrates. X-ray diffraction revealed
10 that the epilayers have an orthorhombic *Pnma* structure in the preferred (101) growth
11 orientation. All our epilayers are with out-of-plane direction texture. There was a contraction
12 of out-of-plane layer network spacing leading to a progressive relaxation in the growth
13 direction. The out-of-plane lattice parameter observed for the 600 nm thick epilayer relaxed
14 toward the bulk NMO. No traces of extra phases are detected. Cross-sectional transmission
15 electron microscopy investigations, as well as a schematic depiction constructed by
16 crystallographic simulation software CrystalMaker, showed stabilization and texture
17 characterized by evident cube-on-cube stacking with a distinct orientation nearby the
18 interface.
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Figure captions

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Figure 1. The Nd/Mn ratio measured by (WDS) plotted versus Nd/Mn ratio of starting solution for the growth of NMO/STO epilayers.

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Figure 2. Schematic of the crystal structure of: (a) orthorhombic NMO film, (b) cubic STO substrate, produced by the CrystalMaker software.

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Figure 3. X-ray diffraction patterns of as-deposited NMO/STO epilayers for $20^\circ < 2\theta < 80^\circ$.

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Figure 4. X-ray diffraction patterns of as-deposited NMO/STO epilayers for $44^\circ < 2\theta < 50^\circ$.

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Figure 5. The out-of-plane lattice distances and strain as a function of NMO/STO epilayer thickness,

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Figure 6. Cross-sectional TEM images showing: (a) close to the interface between NMO film and substrate revealing the presence of epitaxial perovskite NMO phase. (b) Enlarged red squared area; schematic reconstruction of the MnO_6 octahedral distortions in the $[101]$ and $[10\bar{1}]$ orientation and the regular distribution of TiO_6 octahedra in the $[001]$ and $[100]$ cubic symmetry at the vicinity of the interface between film and substrate. (c) Schematic diagram

showing crystal structure of NMO and STO. (d) Schematic representation of the epitaxial growth of orthorhombic NMO/STO epilayers.

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