High-temperature conductivity evaluation of Nb doped SrTiO₃ thin films: Influence of strain and growth mechanism

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Doped SrTiO₃ thin films, 55 nm thick, were epitaxially grown by Pulsed Laser Deposition with niobium contents ranging from 2 to 5 mol% on SrTiO₃ and LaAlO₃ substrates. The different templates result in different growth defects, film growth mechanism and therefore a different volume fraction of uniformly strained film under the critical thickness. The investigation of the conductivity reveals a significant difference between the two substrate choices, but only at elevated temperatures with conductivity values up to 30% larger for films on SrTiO₃ substrates compared with LaAlO₃. Whereas in bulk ceramics the niobium level dictates the total conductivity, here it was found that the substrate choice had a greater influence for thin films, in particular at temperatures over 400 °C. This finding provides important information on conductive layers in complex heterostructures where strain and defects could work cooperatively.

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1. Introduction

Highly conductive perovskite type thin films are attractive as bottom electrodes in heterostructures. Doped SrTiO₃ is an important candidate providing both high temperature stability and lattice compatibility with many functional materials. The electrical properties of SrTiO₃ can be tuned from insulating to semiconducting by intrinsic doping, through the control of the oxygen vacancy concentration in the perovskite structure, or by extrinsic doping, obtained from cation substitution producing either n- or p-type semiconducting behavior [1,2]. The most common n-type mechanism is typically achieved by substituting B site Ti⁴⁺ by Nb⁵⁺ [1.3–5] or A site Sr⁺⁺ by La³⁺ [1,2,6,7]. The extrinsic doping concentration level is usually proportional to the number of carriers present in the structure, which dictates the conductive and electric transport mechanism of the material. For bulk single crystals, niobium doped SrTiO₃ displays conductivity up to $3.5 \times 10^{-4}$ S/m for a 4 mol% Nb doping (carrier concentration measured to $3.3 \times 10^{20}$ cm⁻³) which reduces to $9.5 \times 10^{-3}$ S/m for 2 mol% (carrier concentration measured $1.6 \times 10^{20}$ cm⁻³) [6]. Commercial available SrTiO₃ based single crystals are grown by techniques at very high temperatures and expensive whereas nanostructured thin films would be a more cost-effective alternative for conductive layer or electrode structure.

In nanostructures, crystallographic arrangements and defects should be taken into account as films are often far from the ideal stoichiometry when grown by energetic and vacuum deposition techniques, such as pulsed laser deposition (PLD), which introduce various extra defects such as oxygen deficiency. Moreover, when growing the film on a substrate, a compressive or tensile interfacial strain at the substrate-thin film interface may be formed. The impact of this interfacial strain on the ionic and electric conductivity of metal oxide materials has recently been reviewed [8] and originates from the local off-centering of the ions which affects the bond strength between the oxygen ion and the nearest neighbour cation, and changes the migration space of ions and electronic charge carriers [9–13]. However, there are limits to the volume of the film, where strain can be induced. Over a critical thickness the epitaxial film cannot maintain its strained structure and tends to release its energy by generating defects such as misfit dislocations, defects or island formation increasing the surface roughness. In addition, it is reported for the case of thin films that the conductivity has a strong dependence on the thickness increasing by four orders of magnitude for films of 45 to 300 nm thick [14]. Tomio et al. [15] investigated and compared Nb doped SrTiO₃ with undoped SrTiO₃ films grown by PLD and put forward a relation of the level of charge carriers formed, proposing a presence of Sr-cation vacancies, co-existence of Ti⁺⁴/Ti⁺³, Nb⁵⁻ and oxygen vacancies in the Nb doped thin film. From above conclusions we find that there is no clear picture of how different growth templates affect the conductivity, particularly for elevated temperatures as conductivity for these type films are reported at room temperature or cryogenic temperatures.

It is obvious that the thin film processing history and resulting growth mode and structural order and disorder plays an important role in the...
the data from 40 to 110°, which were processed using the X planes of LaAlO3 and SrTiO3 substrates. Short 2 was realised by tilting the sample by 45° in order to diffract the (220) plane. The crystallographic orientation of the samples was determined by X-ray diffractometry (Philips Xpert Pro Diffractometer) using Cu Kα radiation with monochromator and a nickel filter was added to remove the Kα2 wavelength. A high speed X’celerator detector was used to collect the data from 40 to 110°, which were processed using the X’pert HighScore Plus software. The Nelson Riley formula was used to evaluate the lattice parameters of the thin films [18]. Reciprocal space mapping was realised by tilting the sample by 45° in order to diffract the (220) planes of LaAlO3 and SrTiO3 substrates. Short 2θ – ω scans were then performed at Ψ angles between 43 to 47° and the data were plotted using commercial data processing software after calculating the reciprocal vector values. The surface of the sample was analysed using Atom Force Microscopy (AFM, Veeko Dimension) mounted with a silicon nitride cantilever.

For high resolution transmission electron microscopy (HRTEM) studies the films were prepared using an FEI Helios focused ion beam (FIB). To minimize the ion beam damage, low energy argon ions final thinning was performed at an accelerating voltage of 2 kV and a beam current of 28 pA, which prevent surface damage from the FIB preparation. HRTEM micrographs were acquired at 300 kV using a FEI Titan 80-300 equipped with a Cs corrector at the image plane.

2.2. Conductivity measurements

The conductive properties were measured with a high temperature dedicated measurement system by in-plane four point measurements in air. Electrodes of platinum strips of roughly 150 nm thickness were sputtered (SCD 050 Sputter Coater, Bal-Tec) through a stainless steel shadow mask. Platinum wires were then fixed to the sample with platinum paste (C 3605 P, Heraeus GmbH) and a two-component ceramic binder outside the film as more accurately described [19]. Electrical measurements were performed using a digital multimeter by DC four-point conductivity measurements (197 A, Keithley multimeter). The DC four point conductivity experiments were performed at a given single voltage of maximal 4 V across the thin film as a function of temperature in air. Measurements were done for 2 cycles between approximately 150 and 820 °C with heating and cooling rate of 3 °C/min and dwell time of 30 min. The first cooling curve was chosen for comparison between samples, since it is in thermal equilibrium upon cooling and no irreversible transformation was observed during the different thermal cycling.

3. Results and discussion

3.1. Microstructure and strain of Nb-SrTiO3 films relative to substrate lattice misfit

The microstructures of the 3.5 mol% Nb doped SrTiO3 thin films prepared on SrTiO3 and LaAlO3 substrates were investigated by TEM and HRTEM. The structure of the two films is shown in Fig. 1a and e. The micrographs confirm the good reproducibility of the film thickness of 55 nm on the two different growth templates. In addition, a difference in texture aspect can clearly be observed between the two films. Fig. 1b and f depict close-ups of the films’ regions. Both films exhibit regular damage caused by cross-sectional specimen preparation by focused ion beam which however has a minimum impact on the overall microstructure. When SrTiO3 serves as the template (no lattice mismatch with the film), the film grows uniformly on the substrate as evidenced by the minimum interfacial contrast (denoted by the white line in Fig. 1b). However, when LaAlO3 is used as the template high interfacial contrast exists. This indicates a high defect density at the substrate-film interface as can be noted in Fig. 1f. Planar defects propagate from the LaAlO3/Nb-SrTiO3 interface to the top of the thin film in a kink band boundary aspect. Selected area electron diffraction (SAED) analysis (inset of Fig. 1e) of the film on the pseudo cubic LaAlO3 substrate shows diffraction spots splitting mainly along the out-of-plane direction. This is directly related to lattice distortion and strain due to the crystallographic incompatibility between the film and the substrate.

To clarify the origin of these defects, HRTEM images were acquired close to the interface of the two structures. Fig. 1c and d depict well the coherency of the lattice-matched Nb-SrTiO3/SrTiO3 interface. This suggests a two dimensional (2D) nucleation process taking place throughout the 55 nm thick film. The strain associated energy seems to be relieved by local lattice distortions (black arrows in Fig. 1c and d). On the contrary, a high density of misfit dislocations is observed for the lattice-mismatched Nb-SrTiO3/LaAlO3 interface (Fig. 1h and g). These misfit dislocations provide an incomplete strain relief for the film which further relaxes by producing stacking faults (Fig. 1h) or defect
dislocation lines (Fig. 1g). Thus, a typical Stranski-Krastanov growth mode is very likely to occur for both film sets but with different strain releasing mechanisms. As a result, dissimilar lattice defects are associated with each and in the following we will probe electrical conduction properties of these two differently strained substrate-film sets. Moreover, the roughness of the thin film surface observed during the TEM analysis was confirmed by AFM measurements. Rougher surfaces with larger islands were observed on the films prepared on the LaAlO3 substrate compared to the surface of the films on SrTiO3 substrate. The surface of the thin films was confirmed by AFM as illustrated in Fig. 2a and b, representing the surface of the 5 mol% Nb doped SrTiO3 samples on LaAlO3 and SrTiO3, respectively. The low root mean square (Rms) of the surface of these films indicates a low roughness of the sample and therefore low impact on the conductive properties are expected.

The XRD analysis of the samples (Fig. 3a and b) show sharp diffraction peaks belonging to the same family of planes (00 l), indicating epitaxial growth in the out-of-plane direction. The same epitaxial growth is observed regardless the substrate and the dopant concentration. Films on SrTiO3 substrate, Fig. 3b and inset, reveal peaks slightly separated from the substrate and clearly separated in the case of highest niobium dopant. This shift of the 2θ peaks indicates that despite a lattice mismatch ~0.2%, the out-of-plane lattice parameter appears expanded.

For LaAlO3 substrates, where film peaks for all dopant levels are clearly visible, a shift towards lower 2θ values with increasing niobium dopant was seen, representing an increase in the c-direction by increasing the Nb content (seen in Fig. 3c). For identical 5 mol% Nb doped film on the two substrates, the shift of their respective 2θ values (002 peak) was greater for the films on SrTiO3, which would mean a smaller in-plane cell parameter in average (towards bulk values) when that substrate was used, if assuming a constant cell volume of the perovskite as also observed elsewhere by ref. [20].

Additional cell parameter and lattice information was obtained by reciprocal space mapping (RSM) around the scattering angles of the (220) diffracted planes of SrTiO3 and LaAlO3. This measurement technique consists of successive 2θ XRD scans around a diffracted peak by varying the ψ angle by a step size of 0.15°. The measured distribution of intensity for 3.5 mol% doped films on LaAlO3 and SrTiO3 substrates seen in Fig. 4a and b, where the centre of the spot is inversely proportional to the lattice parameter.

In Fig. 4a, it can be observed that the spot originating from Nb-SrTiO3 signal is off-centred compared with the dotted red line, which serves as a visual guide line for the cubic structure position. This off-centring of the spot reveals that the film has lost its cubic symmetry towards a more distorted structure with a = b ≠ c. From the RSM, an in-plane lattice constant of 3.900 Å was determined for the 3.5 mol% doped thin film on LaAlO3 substrate which means a slight compression when compared with bulk, which confirms the increase of out of plane parameter evaluated from the 2θ XRD above.

For the same doped film but on SrTiO3, the spot detection becomes harder due to the similar lattice parameters, but a higher resolution scan reveals a slight distortion not originating from the system distortion, which could further be identified via a 20 scan at ψ = 44.47°, shown as inset in Fig. 4b. This scan identifies the diffraction of (220) planes of Nb-SrTiO3 films separated from the substrate. The low intensity of the signal and the proximity with the substrate peak do not allow any
Further identification of cell parameters but the observation of the lattice distortion reveals that the films on SrTiO₃ are also slightly compressed in-plane and expanded out-of-plane. The low lattice mismatch between Nb (3.5 mol%) doped SrTiO₃ and the SrTiO₃ substrate enables the film lattice to accommodate easily to the template in a cube-on-cube growth seen in the TEM diffraction pattern (SAED Fig. 1a) and this slight compression would produce few relaxational interfacial defects and an observed increase of the out-of-plane lattice parameters. A small compressive strain in-plane for similar films on SrTiO₃ substrate was previously reported by Ramadan et al. [14]. Furthermore, localized strain originating by the defects in a typical PLD film is known to be significantly larger than expected only by the unavoidable deviations in the stoichiometry [21].

The lattice parameters, where obtained, are compared with bulk lattice parameters as shown in Table 1. Due to resolution limitation, only comparison of the lattice constants of the films of 5 mol% Nb doped SrTiO₃ on both substrates is possible. This shows that the film deposited on LaAlO₃ possesses an out-of-plane lattice parameter of 3.925 Å, which is smaller than the film deposited on SrTiO₃, which is 3.944 Å, but both are larger than the bulk value of 3.9137 Å. This, as well as the RSM results, suggests a compressive in-plane strain. A previous report has also shown a compressive strain for niobium doped SrTiO₃ films on SrTiO₃ substrates [17]. The figure of merit for the strain out-of-plane can be calculated by:

\[
\text{strain} = \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}}
\]

where \(c_{\text{film}}\) is the film lattice parameter in the out-of-plane direction and \(c_{\text{bulk}}\) represents the lattice parameter of the doped powder used as a target.

The two parameters affecting the lattice are: the insertion of niobium into SrTiO₃ lattice and the growth template which imposes a lattice mismatch. The increased cell volume with increasing niobium was attributed to the larger ionic radius of Nb⁵⁺ (64 pm) substituting for Ti⁴⁺ (60.5 pm) on the octahedrally coordinated B-site [1] and to the ionic repulsions around the formed cationic vacancies.

By comparing the 5 mol% Nb-doped film on LaAlO₃ and SrTiO₃ substrates, a lower out-of-plane lattice strain of +0.29% is found on LaAlO₃ (with a lattice mismatch of 3.29%) compared with SrTiO₃ of +0.77% (with a lattice mismatch of 0.3%).

In summary we have shown that a different growth mechanism is evident for films grown on different lattice matched substrates. Films grown on substrates with high lattice mismatch, such as LaAlO₃, produce defects in a close proximity to the interface, which propagates throughout the film to release the strain energy which further is accompanied by an island growth mode. Therefore a smaller out-of-plane strain compared with SrTiO₃ substrate was observed.

In contrast, films on SrTiO₃ exhibit a high volume fraction of coherent strain with a higher critical thickness before different relaxation mechanism appears. These different amounts and nature of defects can be used for enhancing the material performance where charge and ionic transport are possible along these defects. For the strained section, in particular in low doping concentrations as here, carrier mobility could be enhanced by the induced interatomic distances which may lower diffusion and transport energy barriers.

Fig. 3. XRD of 55 nm 5 mol% niobium doped SrTiO₃ film on LaAlO₃ (001) (a) and SrTiO₃ (001) (b) grown epitaxial in (001) direction. The inset in (b) focuses on the (002) peaks of film and substrate clarified by logarithmic scale. (c) Peak shift of the (002) diffracted plane with increasing niobium on LaAlO₃ substrate.

Fig. 4. Reciprocal space mapping of 3.5 mol% niobium doped SrTiO₃ on LaAlO₃ (a) and SrTiO₃ (b) around the (220) diffracted peak of the substrates. The red line is a guide line for a cubic structure. The inset in (b) represents the 2θ scan measured along the pink dashed line at φ = 44.47°.
3.2. Electric conductivity of Nb-doped SrTiO3 thin films

The electrical conductivity of Nb-doped SrTiO3 thin films was measured with respect to substrate (LaAlO3 or SrTiO3) and extrinsic doping concentration for temperature ranging from 300 to 800 °C. In-plane DC electric measurements along the surface of the films have been carried out using a four-probe electrode geometry. This geometry allows us to separate voltage and current for resistance determination as detailed in Ref. [22]. Measurements over a range of temperature provides important information on the difference in conductivity from a thermodynamic point of view, where charge mobility resulting from defects, different thermal carrier excitations, impurities, strain can be addressed.

In Fig. 5a to c, the electrical conductivity is presented for the various doping level for films on both substrates; b and c are close ups for selected temperature of 650–800 °C. For all Nb-SrTiO3 thin films electrical conductivity increases exponentially with increase in temperature. A classic semiconducting behaviour is observed due to increased thermal carriers’ excitation with temperature (Fig. 5a). Nb-doped SrTiO3 thin films exhibit a lower conductivity for deposition on LaAlO3 substrate compared to the films on SrTiO3 substrates, i.e. film conductivity is by 30% higher with 1600 S/m for depositions on SrTiO3 relative to conductivity of 1140 S/m measured for LaAlO3 substrates at 800 °C (Fig. 5b and c). Interestingly, the Nb-doping variation between 2 to 5 mol% does not affect conductivity despite the fact that microstructural evaluation revealed the insertion of niobium into the lattice. The contribution of the conductivity of the substrates was then evaluated by measuring bare substrates in identical conditions and their influence on the films conductivity was eliminated due to their low conductance.

Related conductivity evaluation was undertaken by Ramadan et al. [14] on LaAlO3 and MgAl2O4 and SrTiO3 substrates finding that 300 nm films showed orders of magnitude increased electrical conductivity for the case of SrTiO3. The authors highlighted that in case of compressive strain as for deposition of Nb-doped SrTiO3 on LaAlO3, Ti-O-Ti bonds of film locally tilt and electron orbital overlapping of Ti 3d–2pg gets reduced. It is known from structural field maps relating orbital overlap and semiconducting properties in perovskites relative to cation size and their valence that this would lead to a reduction in electrical conductivity.

Table 1
Calculated lattice parameters and lattice strain of Nb-doped SrTiO3 at various doping concentrations for 55 nm thick films. Calculations were conducted from the position of the observed (002) and (004) XRD peaks and using the Nelson Riley formula to eliminate the systematic errors.

<table>
<thead>
<tr>
<th>Nb (2 mol%) SrTiO3</th>
<th>Nb (3.5 mol%) SrTiO3</th>
<th>Nb (5 mol%) SrTiO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (bulk)</td>
<td>Lattice parameters (bulk)</td>
<td>Lattice parameters (bulk)</td>
</tr>
<tr>
<td>LaAlO3</td>
<td>SrTiO3</td>
<td>LaAlO3</td>
</tr>
<tr>
<td>3.789 Å</td>
<td>3.905 Å</td>
<td>3.905 Å*</td>
</tr>
<tr>
<td>film c-axis on LaAlO3</td>
<td>3.918 Å</td>
<td>3.924 Å</td>
</tr>
<tr>
<td>lattice strain</td>
<td>+0.32% +/-0.03%</td>
<td>+0.42% +/-0.03%</td>
</tr>
<tr>
<td>film c-axis on SrTiO3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Lattice strain</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Lattice parameters calculated by Rietveld refinement on powders before sintering the PLD targets.

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Fig. 5. (a) Temperature dependence of the electrical conductivity of Nb doped SrTiO3 films for different niobium content and prepared on SrTiO3 (001) and LaAlO3 (001) substrates. Evolution of the conductivity between 600 °C and 800 °C for different Nb content films deposited on LaAlO3 substrate (b) and SrTiO3 substrate (c). The experimental error on the conductivity value is determined to be 1.8 % in this region of temperature.
...It was also confirmed that these effects become strongest for small film thicknesses as strain per film volume increase. However, no structural proof of the hypothesis that for different growth and changes in associated defect densities per volume of film was given by authors and there was no study of activation energies of conductivity relative to film growth on different substrate materials. We observe that electrical conductivity is lower for case of Nb-doped SrTiO$_3$ on LaAlO$_3$ substrates due to a significant presence of film defects. The highest conductivities are observed for films deposited on SrTiO$_3$ substrates in this study. Interestingly, we observed lower conductivity for films deposited on LaAlO$_3$ substrates associated with an increased concentration of defect lines and stacking faults per film volume as detected by HRTEM (see Fig. 1e-h). The defects are observed to grow from the substrate to the air interface of the film in accordance to Stranski-Krastanov growth. Electrical conductivity is measured in-plane whereby charge carrier transport is lowered across these dislocation lines for the case of Nb-doped SrTiO$_3$ films on LaAlO$_3$ substrates. In the case of lowered concentration of defects per film volume, Nb-doped SrTiO$_3$ films on SrTiO$_3$ substrates, we observe an increased conductivity due to an easier conductivity path.

To estimate the conductivity thermodynamics, the activation energies of the total conductivity were extracted from the conductivity measurement using the modified Arrhenius formula, which enables to explicitly emphasize on the temperature dependence of the conductivity:

$$\sigma = \sigma_0 \cdot \exp \left( \frac{-E_a}{RT} \right)$$

where $\sigma$ is the conductivity, $\sigma_0$ a constant pre-exponential factor and $E_a$ the activation energy of the electrical conductivity.

In Fig. 6 the activation energies for films with 5 mol% niobium doping on the two different substrates are shown exemplarily. All activation energy fits relative to temperature regions are summarized with respect to doping concentration of defect lines and stacking faults per film volume, as presented here. In the case of low lattice mismatch between film and substrate, smaller concentration of defect dislocation lines is formed and the motion of carriers is facilitated. This indicates that the impact of the substrate should be refrained on the thin film and suggests for applications that a large lattice mismatch between the deposited film and substrate is to be avoided to reduce the defect densities and facilitate carrier mobility in order to obtain better conductive properties.

### Table 2

<table>
<thead>
<tr>
<th>Activation energy for Nb-doped thin films</th>
<th>On LaAlO$_3$ (eV)</th>
<th>On SrTiO$_3$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 to 300</td>
<td>800 °C</td>
<td>555 °C</td>
</tr>
<tr>
<td>5 mol%</td>
<td>0.72 ± 0.06</td>
<td>1.31 ± 0.10</td>
</tr>
<tr>
<td>3.5 mol%</td>
<td>0.68 ± 0.06</td>
<td>1.33 ± 0.11</td>
</tr>
<tr>
<td>2 mol%</td>
<td>0.68 ± 0.06</td>
<td>1.32 ± 0.12</td>
</tr>
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</table>

![Fig. 6](image.png)

**Fig. 6.** Modified Arrhenius plot of total conductivity for 5 mol% Nb-doped SrTiO$_3$ thin films deposited on LaAlO$_3$ and SrTiO$_3$ substrates. The straight red lines are the fitting for activation energy calculation and used as eye guides.
4. Conclusion

Thin films of niobium doped SrTiO₃ with doping level between 2 to 5 mol% were grown on single crystal LaAlO₃ and SrTiO₃ substrates. The crystallographic analysis comparing bulk and thin film lattice parameters confirmed complete solubility of the niobium dopant into the lattice. Depending on the lattice mismatch of film and substrate, the two different substrates resulted in different growth defects, film growth mechanism and therefore a different volume fraction of uniformed strained film under a critical thickness. From DC conductivity measurements a significant difference between the two substrate choices was observed when the samples were annealed up to 800 °C in air, but only at elevated temperatures with conductivity values up to 30% larger for films on SrTiO₃ substrates compared with LaAlO₃. Here we compared equal thick films of 55 nm present a plausible reason for difference in conductivity over temperature.

The conductivity of the differently doped films grown on the different substrates was evaluated by the activation energy of total conductivity, where it was found that the degree of substitution did not vary the conductivity as much as the choice of substrate, unlike in reported bulk ceramics and single crystals where the niobium level dictates the total conductivity. It was shown that the higher the volume fraction of the defect and film relaxation mechanisms, like found for films on LaAlO₃, the more energy barriers exist for charge transfer and most likely alters the phonon vibrations negatively. The findings in this manuscript provide important information of conductive layers in complex heterostructures where strain and defects could work beneficial, in particular for stable high temperature electrodes.

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