Pulsed laser deposition and characterisation of perovskite-type LaTiO$_{3-x}$N$_x$ thin films

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Abstract

LaTiO$_{3-x}$N$_x$ films with high nitrogen contents ($x \approx 0.4–0.8$) have been grown on (001)-oriented MgO and LaAlO$_3$ substrates by pulsed reactive crossed-beam laser ablation from a La$_2$Ti$_2$O$_7$ target in a one-step process. These films have a perovskite-type structure, similar to bulk polycrystalline LaTiO$_2$N. The nitrogen content in the films can be changed by selecting the nitriding source, i.e. NH$_3$ or N$_2$ gas pulse, and by varying the substrate temperature. Films deposited on MgO show a preferential (001) and (112) orientation, whereas films on LaAlO$_3$ are predominantly (001) oriented. N(2p) orbitals contribute to the top of the valence band, leading to a considerable decrease in the band gap energy from $\approx$4.0 eV for the parent LaTiO$_3$ to $\approx$2.4–2.9 eV for LaTiO$_{3-x}$N$_x$ ($x \approx 0.4–0.8$) films. This results in a strong visible light absorption at wavelengths below $\approx$500 nm. The band gap energies in LaTiO$_{3-x}$N$_x$ films decrease with increasing nitrogen content. The values of the band gap energies for LaTiO$_{3-x}$N$_x$ as a function of the N content agree well with other titanate-based perovskite-type oxynitrides, which confirms the proposed band gap model.

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1. Introduction

Perovskite-type oxides with a general formula $ABO_3$ have been widely studied and are used for a large number of purposes and applications [1–7]. The properties of the perovskite-type oxides can be tuned and adjusted by chemical substitutions in the cationic $A$ and $B$ sublattices. This approach is widely used in many areas of application [5–7]. Substitution of oxygen with other non-metals in the anionic sublattice is much less explored, although it gives an additional path to change and tune the properties of perovskites [8–12]. For replacing oxygen the substitute anion should have similar electronic structure and ionic radius. One of the potential candidates is nitrogen, which contains one 2p electron less than oxygen and has a relatively similar ionic radius: $R$(N) $\approx$ 1.29 Å, $R$(O) $= 1.21$ Å [13]. Partial substitution of nitrogen for oxygen is, therefore, possible in perovskite-type oxides if the overall electroneutrality condition is maintained [9,10,14–18]. The resulting compounds are commonly called oxynitrides, and resemble oxides and nitrides. Incorporation of nitrogen leads to a change in the electronic and/or optical properties of the parent perovskite oxides. The oxidation state of the transition metal in the $B$-sublattice can be varied by partial substitution of oxygen with nitrogen due to the different negative charge of N$^{2-}$ and O$^{2-}$ anions. This leads to changes of the electrical properties of the initial oxide compounds [16,18–22]. Another important difference between oxygen and nitrogen is the energy of 2p orbitals: $-11.5$ eV for nitrogen compared to $-14.1$ eV for oxygen [23]. This gives rise to different optical properties of the

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oxynitrides compared to the corresponding oxides. The band gap energy, color and light absorption can be changed by incorporation of nitrogen into oxides [8,14,15].

Substitution of three oxygen ions (O$^2-$) with two nitrogen ions (N$^-$) in a layered perovskite La$_2$Ti$_2$O$_7$ yields a three-dimensional perovskite-type LaTi$_2$O$_2$N oxynitride, which matches to the general formula $ABX_3$, where the anionic sublattice $X$ is formed by oxygen and nitrogen ions [14,15]. The incorporation of nitrogen results in a reduction in the optical band gap energy, which allows visible light absorption [15,24]. This has been used to demonstrate the photocatalytic activity of the lanthanum titanium oxynitride powders for water decomposition under visible light irradiation [24,25].

For many technical applications as well as for scientific studies it is necessary to produce thin films. Oriented epitaxial films can be used as model systems to investigate the material's properties as a function of its crystallographic orientation. Thin films are also necessary for solar cell technology and electronics [26]. Oxynitride thin films can be prepared by two different approaches. The first one involves deposition of the oxide film and its subsequent nitridation [27,28]. Alternatively, the oxynitride film can be deposited in a nitriding atmosphere in one step starting from the oxide or oxynitride precursor [16,29–31]. This approach is more preferable as it is less time consuming and allows to produce epitaxial thin films with homogeneous nitrogen distribution through the layer thickness [31]. Until now LaTi(O,N)$_3$ films have been prepared only using the two-step approach, i.e. through deposition of the oxide film and its following thermal ammonolysis [27,28] or starting from the oxynitride ceramic target [29]. In this paper we report the direct growth of LaTiO$_3$-$x$N$_x$ thin films by pulsed laser deposition (PLD) from the oxide target and the characterization of the composition, crystalline quality and optical properties of the films.

2. Experimental

2.1. Sample preparation

LaTiO$_3$-$x$N$_x$ films with the thicknesses ranging from 330 to 560 nm have been grown by pulsed reactive crossed beam laser ablation (PRCLA), a modification of the conventional PLD technique. PRCLA is based on the utilization of the pulsed injection of a reactive gas, which expands towards the substrate and crosses the ablation plasma plume close to its origin (Fig. 1) [32]. The gas pulse is synchronized with the laser pulse. This leads to a large number of collisions between the molecules from the gas pulse and the highly energetic ablation plasma species when the ablation plasma plume crosses the gas injection. The molecules from the gas pulse can therefore dissociate, providing additional reactive species, which can incorporate into the growing film. This approach has been successfully used for improving the oxygen content in the films. In this case oxygen-containing gases, such as O$_2$, O$_3$ or N$_2$O, can be used for the gas pulse [33–35]. Utilization of N$_2$ or NH$_3$ for the gas pulse allows nitrogen incorporation into the films. We have previously demonstrated the advantage of PRCLA compared to the classical PLD for the growth of N-substituted SrTiO$_3$N layers [36]. The same approach has been applied for deposition of LaTiO$_3$-$x$N$_x$ films described in this paper.

In our PRCLA experiments the gas pulse was simultaneously used with the same background gas. Ammonia and nitrogen have been tested as potential nitriding sources for the preparation of N-substituted LaTi(O,N)$_3$ films. The background gas pressure was kept at 8 × 10$^{-4}$ mbar by an adjustable leak valve. The operation conditions for the gas pulse were identical for all experiments. It is noteworthy that the background gas pressure in PRCLA experiments (8 × 10$^{-4}$ mbar) is considerably lower compared to typically reported oxide ablation conditions, which are in the 10$^{-1}$ mbar range [37]. The time difference between the gas pulse and the laser pulse was controlled. The ablation plasma was produced at the moment when the densest portion of the gas pulse emerging from the valve nozzle passes in front of laser focusing point on the target (Fig. 1). In our set-up the delay time of the laser pulse with respect to the gas pulse was 30 μs, while the gas pulse duration was 400 μs. This has been done in order to increase the energy transfer from the ablation plasma species to the gas pulse molecules via collisions when the plasma expands and propagates through the gas pulse.

All studied films were deposited using a KrF excimer laser (λ = 248 nm, pulse duration of ~30 ns) operating at a frequency of 10 Hz. A sintered cylindrical rod of La$_2$Ti$_2$O$_7$ was used as the target. During the deposition the target was rotated and translated vertically (with respect to the laser beam) to ensure that each pulse interacts with a “fresh” surface on the target, and that no cumulative heating of the target by the laser pulses occurs. During deposition the substrate holder was rotated continuously in order to
achieve a homogeneous film deposition. The target-to-substrate distance was fixed at 5 cm. The substrate was resistively heated using a doped Si plate. The substrate temperature \( T_S \) was varied over the range of 600–700 °C for the deposition with the NH\(_3\) gas pulse and fixed at 650 °C for the N\(_2\) gas pulse, respectively. The laser fluence was maintained at 5 ± 0.5 J cm\(^{-2}\) (for the ablation spot of \( \sim 1 \) mm\(^2\)). These conditions have been chosen to obtain the highest nitrogen content in LaTiO\(_3\)\(_{1-x}\)N\(_x\) films, according to our previous experiments on the SrTiO\(_3\):N model system \([31,36,38]\). The films were deposited on MgO(001) and LAO(001) substrates with 20,000–30,000 pulses to obtain thicknesses of 330–560 nm.

### 2.2. Sample characterization

The film thickness was obtained by profilometry. The measurements have been performed on a Dektak 8 profilometer with a tip size of 5 μm, a load mass of 3 μg and a scanning speed of 150 μm s\(^{-1}\). The thickness was determined at the film edges by measuring the step height between the uncovered part of the substrate and the deposited film.

The film composition has been obtained from a combination of Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA) \([39]\). The La:Ti:O concentration ratio in the films was determined by RBS, which is more sensitive to heavier elements compared to ERDA \([39]\). The measurements were performed using a 2 MeV \(^{4}\)He ion beam and a silicon surface barrier detector with an angle of 165°. The collected RBS data were simulated with the RUMP software \([40]\). The experimental uncertainty (accuracy) in cation and oxygen stoichiometries, determined by RBS, are ±3% and ±5%, respectively. The nitrogen content in the films was calculated from the combination of RBS results and N:O concentration ratio obtained from ERDA. For the measurements a 12 MeV \(^{12}\)I beam was used under an incident angle of 18°. The scattered recoils were identified by the combination of a time-of-flight spectrometer with a gas ionization chamber. The experimental uncertainty in the determination of the N concentration is about ±5%.

Grazing incidence X-ray diffraction (XRD) analysis was performed to check and confirm the phase composition of the grown films. The measurements were done on a Phillips X’Pert diffractometer using Cu K\(_\alpha\) irradiation at an incident angle of 5° (2θ range of 20–80°, step 0.05°, 0.5 s per step). The grazing incidence XRD reveals diffraction patterns similar to that of polycrystalline samples due to the small fixed incident angle of the X-rays of 5°. The penetration depth of X-rays at this small incident angle is considerably lower compared to a 0–2θ scan. The film roughness (i.e. topographic features at the film surface) and other possible non-idealities of the crystal structure within the probed layer of the film are therefore more important in grazing incidence XRD, resulting in a diffraction pattern of randomly oriented crystallographic planes. The film texture has been studied on a Siemens D5000 four-circle X-ray diffractometer by scanning in 0–2θ mode along the c-axis direction of the substrate, which provides information about the growth orientation in the out-of-plane direction (Cu K\(_\alpha\) irradiation, 20 range of 20–80°, step 0.005°, 0.3 s per step).

The transmittance of the films \((T)\) was measured by a Cary 500 Scan UV–Vis–NIR spectrophotometer in the wavelength range of 190–2000 nm (6.5–0.6 eV). The measurements were performed in a two-beam configuration using a blank substrate as a reference. The optical band gap energy \((E_g)\) was determined by linear extrapolation of \((A \cdot hν)^2\) vs. the photon energy in the appropriate linear region using the Tauc equation for direct electron transitions \([41]\):

\[
(A \cdot hν)^2 \sim (hν − E)
\]

where \(hν\) is the photon energy, \(E\) is the optical band gap energy or energy levels inside the band gap, and \(A\) is the film absorbance estimated from the film transmittance as:

\[
A = −\log(T)
\]

All the films studied were deposited on single-side polished substrates. The absolute value of the film transmittance can therefore be influenced by the different light scattering on the unpolished side of the film and the blank substrate, used as a reference. However, these effects do not affect the position and calculated energy of the absorption bands.

### 3. Results and discussion

#### 3.1. Target selection

All films were deposited from a sintered La\(_2\)Ti\(_2\)O\(_7\) ceramic target. The nominal metal:anion ratio in La\(_2\)Ti\(_2\)O\(_7\) is 1:1:3.5, i.e. it contains more oxygen than required for the three-dimensional perovskite-type structure (1:1:3). The motivation for selecting an anion overstoichiometric target was to avoid a large loss of oxygen during the PLD process. As mentioned in the literature, PRCLA yields films with high levels of oxygen deficiency \([31,34,35]\). We have previously shown that N-substituted SrTiO\(_3\):N thin films grown from the stoichiometric SrTiO\(_3\) target in reducing media reveal relatively high anionic deficiencies of up to 0.5 anionic vacancies per formula unit \([36,38]\). Therefore, an overstoichiometric initial oxygen content in the target can help to maintain the desired anionic stoichiometry in the perovskite-type films (i.e. 1:1:3).

La\(_2\)Ti\(_2\)O\(_7\) targets were prepared from the La\(_2\)Ti\(_2\)O\(_7\) powder, which has been synthesised through a conventional solid-state technique from La\(_2\)O\(_3\) and TiO\(_2\) (Aldrich) powders. The formation of the phase-pure La\(_2\)Ti\(_2\)O\(_7\) was confirmed by XRD analysis, and the powder was isostatically pressed and sintered in air at 1500 °C for 10 h. The XRD analysis of the ceramic target revealed the formation of a single-phase La\(_2\)Ti\(_2\)O\(_7\).
3.2. Phase composition of the LaTiO$_3$-$\text{N}_x$ films

The crystal structure of the product phase deposited as thin films was studied and identified by grazing incidence XRD. For this purpose a series of films deposited on MgO substrates was measured. Fig. 2 shows the respective diffraction pattern for the produced thin films. The diffraction patterns for all studied films reveal reflections corresponding to the reported perovskite-type structure reported for LaTiO$_2$N [42]. The reflections at 2$\theta$ of 26–29° are due to the substrate holder of the grazing incidence set-up. In addition, some patterns also reveal reflections of the MgO substrate because the substrates were not completely covered by the films and the X-ray beam size was larger than the samples. The results of grazing incidence XRD analysis confirm therefore the suitability of the target selection and LaTiO$_{3-x}$N$_x$ perovskite-type films were successfully grown.

3.3. Chemical composition of LaTiO$_3$-$\text{N}_x$ films

The chemical composition of the films shown in Table 1 was determined by combining RBS and ERDA measurements. All films exhibit a significant Ti deficiency, typically about 10% vs. the La content. This is most probably due to the larger atomic mass of La compared to Ti, which results in a stronger scattering of Ti species in the plasma plume during the deposition. Similar effects have also been observed during PLD of (La,Ca)MnO$_3$ and (La,Ca)CoO$_3$ thin films [34,35], where the concentration of La in the films was enhanced, whereas the concentration of Ca was reduced. Therefore, RBS analysis of the studied films suggests the formation of Ti vacancies in the B-sublattice of the perovskite-type structure $ABO_3$ and/or a formation of some prolonged defects with Ti deficiency. However, this does not change the film phase crystallographic structure, which remains a perovskite-type as confirmed by grazing incidence XRD.

Films deposited with the same conditions on different substrates (i.e. MgO and LAO) exhibit no significant difference in their composition. The nitrogen content in LaTiO$_{3-x}$N$_x$ films deposited at 650 °C with the N$_2$ gas pulse ($[\text{N}_x\text{N}_y]$) is lower than in films grown with the ammonia gas pulse ($[\text{N}_x\text{NH}_3]$) at the same substrate temperature, which is similar to our previous findings for SrTiO$_3$N layers grown with PRCLA [36,38]. The observed difference in the nitrogen content between the samples grown with nitrogen and ammonia gas pulses can be explained as follows.

Considering the different dissociation energies of N$_2$ and NH$_3$ molecules, N atoms are likely to be the most important species for the formation of oxynitrides [43]. During the deposition of thin oxynitride films by PLD, these species are mainly produced by the dissociation of the gas pulse and background gas molecules via collisions with the high-energy ablated species from the target. The N$_2$ molecule is thermodynamically very stable and has a dissociation energy of 945 kJ mol$^{-1}$ (~9.8 eV) [44], which is considerably higher compared to the average dissociation energy for one N–H bond in an NH$_3$ molecule of 391 kJ mol$^{-1}$ (~4.1 eV), [44]. Typical ion energies in PRCLA (close to the target) vary in the range of 5–15 eV [45]. Thus, it is possible to disproportionate both nitrogen and ammonia molecules and produce active N-containing species in the PRCLA process via collisions of the ablation plume species with the gas pulse molecules. However, smaller chemical bond energies and the possibility of a consecutive detachment of hydrogen atoms in NH$_3$ will make this process more likely if compared to N$_2$. This results in a higher concentration of atomic N species in the plasma, and hence increased nitrogen content in films grown with the NH$_3$ gas pulse. This is shown in Table 1 and Ref. [38], where LaTiO$_{3-x}$N$_x$ and SrTiO$_3$N thin films prepared by ammonia in the gas pulse show a significantly larger nitrogen content as compared to films prepared using a nitrogen gas pulse. A likely reason for this observation is the reducing properties of NH$_3$ and its decomposition products which result in an increase of the nitrogen content of the compound

LaTiO$_{3-x}$N$_x$ $\Rightarrow$ LaTiO$_3$ $\text{N}_x$ perovskite $\Rightarrow$ layered $A_4B_4O_{14}$ structure[46]
The reoxidation indicated in (3) under ideal conditions will result in the formation of the layered $A_4B_4O_{14}$ structure [46] with corresponding structural changes. Due to a small amount of oxygen available during the PLD process the formation of intermediate LaTiO$_{3.5-x}$ phases is more likely to occur [46].

The variation of the N content in LaTiO$_{3-x}$N$_x$ films grown with the NH$_3$ gas pulse at different substrate temperatures is shown in Fig. 3. The nitrogen concentration increases with increasing substrate temperature. This can be due to the enhanced kinetics of nitrogen incorporation at higher $T_S$, as well as for thermodynamic reasons, i.e. an increased stability of LaTiO$_{3-x}$N$_x$ oxynitrides at higher temperatures in ammonia [14,15]. Another possibility is the additional reaction of thermal ammonolysis of the growing films between laser pulses by NH$_3$ molecules from the background. This result is also similar to the SrTiO$_3$:N system, where the same trend has been observed [38]. The largest nitrogen content of $x \approx 0.8$ achieved for the studied LaTiO$_{3-x}$N$_x$ thin films deposited by PRCLA is comparable to the previously reported value of 0.75 in the films grown by radiofrequency sputtering in N$_2$ [29].

The oxygen content decreases with increasing $T_S$ for the same reasons, i.e. it is inversely linked to the N content, as shown in Fig. 4. A higher substrate temperature results in a better mobility of the species in the growing film, allowing an easier exchange of oxygen with nitrogen during a thermal ammonolysis reaction. It is worth pointing out that the overall anionic content in the films is very close to the ideal value of 3.0 for the perovskite phase (Fig. 4, Table 1). Despite selecting a LaTiO$_{3.5}$ target with a different crystalline phase and oxygen content compared to the final film composition, the loss of oxygen during growth of LaTiO$_{3-x}$N$_x$ is balanced by the nitrogen incorporation, yielding a good overall anionic stoichiometry. The appearance of a dark grayish color of the as-prepared films is also observed, and is indicative of Ti$^{3+}$/excess charge carriers in the compound.

### Table 1

<table>
<thead>
<tr>
<th>Gas pulse</th>
<th>$T_S$ (°C)</th>
<th>Substrate</th>
<th>Composition (±3% for cations; ±5% for anions)</th>
<th>Out-of-plane orientations$^a$</th>
<th>Out-of-plane cell parameter $(eV)$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>600</td>
<td>MgO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.55}$N$</em>{0.47}$</td>
<td>(001)</td>
<td>8.04</td>
<td>2.64</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>650</td>
<td>MgO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.40}$N$</em>{0.60}$</td>
<td>(001), (112)</td>
<td>8.03</td>
<td>2.47</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>700</td>
<td>MgO(001)</td>
<td>La$<em>{1.04}$Ti$</em>{0.96}$O$<em>{2.28}$N$</em>{0.72}$</td>
<td>(001), (112)</td>
<td>8.01</td>
<td>2.36</td>
</tr>
<tr>
<td>N$_2$</td>
<td>650</td>
<td>MgO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.33}$N$</em>{0.51}$</td>
<td>(001), (112)</td>
<td>7.94</td>
<td>2.63</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>600</td>
<td>LAO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.52}$N$</em>{0.42}$</td>
<td>(001), (011)</td>
<td>8.13</td>
<td>2.95</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>650</td>
<td>LAO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.44}$N$</em>{0.61}$</td>
<td>(001), (011)</td>
<td>8.11</td>
<td>2.69</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>700</td>
<td>LAO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.13}$N$</em>{0.82}$</td>
<td>(001), (011)</td>
<td>8.10</td>
<td>2.40</td>
</tr>
<tr>
<td>N$_2$</td>
<td>650</td>
<td>LAO(001)</td>
<td>La$<em>{1.05}$Ti$</em>{0.95}$O$<em>{2.64}$N$</em>{0.52}$</td>
<td>(001), (011)</td>
<td>7.99</td>
<td>2.74</td>
</tr>
</tbody>
</table>

$^a$ Small font used for crystallographic orientations indicates that this orientation is minor compared to the main orientation.
3.4. Texture of LaTiO$_{3-x}$N$_x$ films and their unit cell parameters

Lanthanum titanium oxynitride exhibits a photocatalytic activity for water decomposition under visible light irradiation [24,25]. It is interesting to study the influence of the surface orientation, since it can affect photocatalytic properties [4]. Oriented thin films can be used as model systems for these investigations. The film orientation can be controlled by a proper selection of substrates with a minimal lattice mismatch with the film unit cell parameters. We have achieved a deposition of (001)-oriented SrTiO$_3$:N on a variety of substrates with different lattice mismatches (MgO, LAO, STO). The same approach was tested for LaTiO$_{3-x}$N$_x$. The chosen substrates were cubic MgO(001) with $a = 4.212 \text{Å}$ and pseudo-cubic LaAlO$_3$(001) with $a = 3.79 \text{Å}$.

The reference compound for our films, LaTiO$_2$N, was reported to be an orthorhombic perovskite with the following unit cell parameters: $a = b = 5.578$ and $c = 7.888$ [42]. The $a$ and $b$ constants are approximately a factor of $\sqrt{2}$ larger than the lattice constants of the chosen substrates. Therefore, the expected epitaxial relationship is tilted by 45° in the $a$-$b$ plane with respect to the substrate. In this case the $c$-axis of the film points in the out-of-plane direction, indicating a (001) orientation.

The θ–2θ diffraction patterns of the studied LaTiO$_{3-x}$N$_x$ films grown on MgO substrates are shown in Fig. 5. The films grown at $T_S$ of 600 and 650 °C exhibit a relatively low intensity of their reflections, which increases considerably for the films grown at 700 °C. This indicates that fairly high temperatures of ~700 °C are necessary for deposition of the oriented films.

The diffraction patterns reveal the presence of reflections from the (00X) series and (112) reflections, indicating that there are two predominant out-of-plane orientations: (001) and (112). Grazing incidence XRD analysis of these films revealed no detectable phase impurities, therefore excluding the possibility that the observed (112) reflection on the θ–2θ patterns belong to another phase. The mixed oriented growth most probably results from the relatively large lattice mismatch (LM) between $\sqrt{2}a$ of the MgO substrate and $a$ of LaTiO$_2$N:

$$\text{LM(MgO)} = \frac{\sqrt{2}a(\text{MgO}) - a(\text{LaTiO}_2\text{N})}{a(\text{LaTiO}_2\text{N})} \approx +6.8\%$$
LaAlO$_3$ substrates have a better lattice matching: the negative lattice mismatch is about $-3.9\%$, suggesting that these materials may be potentially better for the deposition of single (001)-oriented films:

$$\text{LM(LaAlO}_3) = \sqrt{2}a(\text{LaAlO}_3) - a(\text{LaTiO}_2\text{N}) \approx -3.9\%$$

Diffraction patterns of the LaTiO$_3$$_x$N$_x$ films deposited on LAO substrates are shown in Fig. 6. These films reveal a series of relatively intense (00 $X$) reflections. Weak (022) reflections can also be observed. This suggests a mixed oriented growth with predominant (001) orientation along the substrate’s c-axis. To obtain perfectly oriented films, another substrate with a better matching of the cell parameters should be selected. The perfect matching requires a cubic cell parameter of 3.94 Å (for 45° tilted epitaxy) or 5.58 Å (for “cube-on-cube” epitaxy). Possible substrates are rare-earth scandate substrates REScO$_3$ ($RE = Dy$, Tb or Gd) with in-plane lattice parameters ranging from 3.946 to 3.970 Å [47].

The out-of-plane unit cell parameters ($c$) were calculated from the positions of the film (00 $X$) series of reflections. The results are summarized in Table 1. The $c$-axis lattice parameter in the studied LaTiO$_3$$_x$N$_x$ ($x \approx 0.4-0.8$) films ranges within (7.94–8.11) ± 0.05 Å. This is higher compared to the reference LaTiO$_2$N powder ($c = 7.888$ Å), but also larger than the $c$-axis parameter of LaTiO$_3$$_0$ ($c = 7.906$ Å) with a crystalline structure similar to that of LaTiO$_2$N. In addition, the chemically reducing deposition conditions for the deposition of LaTiO$_2$N from a La$_2$Ti$_2$O$_7$ target are expected to affect the film lattice parameters because the target composition is the thermodynamically stable phase [46]. The studied LaTiO$_3$$_x$N$_x$ films are quite thick (330–560 nm). At these thicknesses the films are already relaxed and the strain induced by the lattice mismatch with the substrate is small [31]. Therefore unit cell parameters are expected to be strongly influenced by the chemical composition of the films. There are at least two main aspects that affect the lattice constants in the studied LaTiO$_3$$_x$N$_x$ films:

- The N content, since nitrogen has a larger crystallographic radius compared to oxygen. A decrease in the nitrogen content in LaTiO$_3$$_x$N$_x$ from 1.0 (reference compound) to 0.4–0.8 (studied films) should therefore result in a decrease in the unit cell parameters.
- The Ti oxidation states, since Ti$^{3+}$ and Ti$^{4+}$ have different crystallographic radii, i.e. $R(\text{Ti}^{3+}) = 0.81$ Å, $R(\text{Ti}^{4+}) = 0.745$ Å [13]. The LaTiO$_3$$_x$N$_x$ films reveal mixed titanium oxidation states of +3 and +4, whereas titanium in LaTiO$_2$N exhibits an oxidation state of +4. Films with a mixed oxidation state of Ti should therefore exhibit larger unit cell parameters.

The actual out-of-plane $c$ parameters in the LaTiO$_3$$_x$N$_x$ films are slightly larger than in the LaTiO$_2$N reference powder due to these two counteracting trends, i.e. a decrease in the cell constants with decreasing N content and an increase due to the mixed Ti oxidation states.

### 3.5. Optical properties of LaTiO$_3$$_x$N$_x$ films

In a previous paper we proposed that nitrogen incorporated into the SrTiO$_3$ lattice results in the formation of localized N(2$p$) levels located inside the band gap of SrTiO$_3$ (Fig. 7 right) [38]. In this case, the transmittance spectra of the corresponding SrTiO$_3$:N films with 1–4 at.% N reveal...
an absorption shoulder near the band gap absorption edge [38]. For the LaTiO$_3$–N$_x$ system the situation changes, as the amount of incorporated nitrogen is considerably larger, i.e. 8–16 at.%. The N$(2p)$ orbitals in this case contribute to the top level of the valence band, resulting in a decrease of the band gap in these materials compared to the parent oxide (Fig. 7 left). The transmittance spectra of the studied LaTiO$_{3–x}$N$_x$ films are shown in Fig. 8. A spectrum of a reference LaTiO$_{3.5}$ film deposited in oxidizing conditions on MgO substrate is shown for comparison.

Transmittance spectra of the studied LaTiO$_{3–x}$N$_x$ films reveal a considerable absorption in the visible (at $\lambda > 500$ nm) and IR region. Absorption of these low-energy photons is attributed to the electronic transitions within the conduction band of perovskites [48], and occurs due to the presence of free electrons (i.e. Ti$^{3+}$) in the films. The LaTiO$_{3.5}$ oxide film grown in oxidizing conditions on MgO (the upper dashed curve in Fig. 8a) exhibits almost 100% transmittance in this wavelength range, indicating a minor amount of Ti$^{3+}$.

A broad absorption band in the UV and near-UV–visible (at $\lambda < 500$ nm) regions is attributed to the band gap in perovskites, and occurs through excitation of the valence band electrons to the conduction band by the high-energy photons. The spectra of the LaTiO$_{3–x}$N$_x$ films clearly reveal a strong shift of the absorption edge towards longer wavelengths compared to the parent oxide film (Fig. 8), which indicates a decrease in the band gap energies. An increase in the nitrogen content results in a stronger shift, suggesting that the band gap energy depends on the nitrogen concentration in LaTiO$_{3–x}$N$_x$ films, whereas for SrTiO$_3$:N no pronounced influence of the N content on the energy of localized N$(2p)$ states was found [38]. This can be due to the formation of the continuous band involving interacting N$(2p)$ orbitals which broadens with increasing nitrogen content in LaTiO$_{3–x}$N$_x$ films. For SrTiO$_3$:N the N concentration was relatively low compared to LaTiO$_{3–x}$N$_x$ and thus the orbitals of the localized N$(2p)$ states do not interact. The transmittance spectra (Fig. 8) show a difference in the measured transmittance with respect to the deposition conditions. Films grown with a N$_2$ background show a larger transmittance compared to films grown in NH$_3$. Distortions of the cation–anion bond angles as a result of the different growth conditions are a possible explanation for the observed differences. These distortions are expected to influence the optical properties of the films.

The band gap energies were calculated from the Tauc plots for direct electronic transitions. The results of these calculations are summarized in Table 1 and plotted in Fig. 9a. The optical band gap energies in the studied LaTiO$_{3–x}$N$_x$ films ($E_g$) range within (2.36–2.95) ± 0.10 eV, which is considerably smaller than for the parent LaTiO$_{3.5}$ oxide film ($E_g$ of 4.02 ± 0.10 eV) due to the nitrogen incorporation and the change of the crystal structure. Respectively, the optical band gap energies in the LaTiO$_{3–x}$N$_x$ films are larger than for the LaTiO$_2$:N powder (2.2 ± 0.1 eV) [15] due to the smaller nitrogen content in the films. The increase in the nitrogen content in the films results in a gradual decrease of the $E_g$ (Fig. 9a). Similar results have been previously found for Ca$_{1–x}$La$_x$TiO$_{3–x}$N$_x$ powders synthesized by thermal ammonolysis [15]. It is noteworthy, that the optical band gap energies of the films grown on LAO are generally slightly larger than for films deposited on MgO, although the corresponding films have similar compositions (Table 1), for reasons that are not yet understood. One possible reason may be the different texture and lattice distortion in films grown on MgO.
MgO and LAO, which may affect the band gap, as discussed elsewhere [49]. The values of the band gap energies for the studied LaTiO$_{3-x}$N$_x$ films as a function of the N content agree well with the trend found for Ca$_{1-x}$La$_x$TiO$_{3-x}$N$_x$ powders (Fig. 9b) [15]. This is a quite interesting result, which shows that the composition of the $\alpha$-sublattice in the $\alpha$TiO$_{3-x}$N$_x$ family of perovskite-type titanates has a minor influence on the $E_g$, which depends mainly on the nitrogen content. This confirms the appropriateness of the band diagrams suggested for $d^0$ perovskite-type oxynitrides (Fig. 7), i.e. that the top of the valence band is formed by $N(2p)$ orbitals and that the bottom of the conduction band is formed by $d$-orbitals of the transition metal.

4. Conclusions

LaTiO$_{3-x}$N$_x$ films with high nitrogen contents ($x \approx 0.4$–0.8) have been grown on MgO and LAO substrates by PRCLA from a La$_2$Ti$_2$O$_7$ target. The films exhibit a perovskite-type structure, similar to orthorhombic LaTiO$_2$N. Deposition with an NH$_3$ gas pulse yields films with larger nitrogen contents compared to the films deposited with a N$_2$ gas pulse. The N content for the films grown with ammonia increases with increasing substrate temperatures in the range of 600–700°C. The films deposited on MgO substrates reveal a mixed oriented growth with preferential (001) and (112) orientations, whereas the deposition on LAO yields films that are predominantly (001) oriented with a minor (011) orientation. The nitrogen incorporation leads to a considerable decrease in the band gap energy from $\sim$4.0 eV for LaTiO$_{3.5}$ to $\sim$2.4–2.9 eV for LaTiO$_{3-x}$N$_x$ ($x \approx 0.4$–0.8) films. This results in a strong visible light absorption at wavelengths below $\sim$500 nm, which should be promising for possible photocatalytic applications as suggested for LaTiO$_2$N powders [24,25]. The band gap energy in LaTiO$_{3-x}$N$_x$ films decreases with increasing nitrogen content, which is the same trend observed for Ca$_{1-x}$La$_x$TiO$_{3-x}$N$_x$ powders [15].

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