Doctoral Thesis

Pulsed laser deposition and characterisation of perovskite-type oxynitride thin films

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PULSED LASER DEPOSITION AND CHARACTERISATION
OF PEROVSKITE-TYPE OXYNITRIDE THIN FILMS

A dissertation submitted to ETH ZURICH

for the degree of
Doctor of Sciences

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SUMMARY

OUTLOOK

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ABSTRACT

In this work the one-step deposition of perovskite-type oxynitride thin films is presented and their optical and electronic properties discussed. Substitution of oxygen with nitrogen in perovskite-type oxides results in the formation of perovskite-type oxynitrides classified by the formula $AB(O,N)_3$. The continuous substitution of oxygen with nitrogen allows a fine tuning of the material’s properties such as band gap energy, dielectric permittivity and color. Perovskite-type oxynitrides exhibit promising electrical and optical properties and have been suggested as potential photocatalysts, dielectric materials and non-toxic inorganic pigments.

Epitaxial thin films can be used as model single crystalline samples for measurements of dielectric, optical and photocatalytic properties. Perovskite-type oxynitride thin films can be prepared by a two-step approach involving deposition of an oxide film and its subsequent thermal ammonolysis. However, this approach has several drawbacks, such as potential side reactions and inhomogeneities of the film composition. In this work a new approach for the one-step deposition of perovskite-type oxynitride thin films has been developed. Pulsed laser deposition (PLD) and two modifications of PLD have been applied for the film deposition.

The modification of conventional PLD by adding a synchronized gas pulse provides the possibility to control the anionic composition of the films by using N-containing gases. This technique, called pulsed reactive crossed beam laser ablation (PRCLA), has been applied for the one-step deposition of epitaxial SrTiO$_3$:N, LaTiO$_{3-x}$N$_x$ and SrMoO$_{3-x}$N$_y$ thin films. The utilization of NH$_3$ for the reactive gas pulse yields SrTiO$_3$:N films with N contents that are a factor of 3.5 higher compared to conventional PLD with an ammonia background. The use of NH$_3$ as the reactive gas yields SrTiO$_3$:N films with a N content of up to ~4 at. %, where the N concentration can be adjusted by changing the deposition temperature and laser fluence. Applying N$_2$ for the gas pulse yields SrTiO$_3$:N films with N contents of up to ~1.5 at. %.

The incorporation of nitrogen in SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$ films grown by PRCLA results in a change of the electronic structure when compared to the parent oxides. This enables the absorption of visible light, which may be interesting for potential photocatalytic applications. Introducing of 1–4 at. % of nitrogen into SrTiO$_3$ results in the formation of localized N(2$p$) orbitals located inside the band gap close to the valence band. A larger amount of nitrogen of ~8–16 at. % in LaTiO$_{3-x}$N$_x$ results in a contribution of the N(2$p$) levels to the valence band, which leads to a decrease of the band gap energy compared to LaTiO$_{3.5}$. Increasing the nitrogen content in LaTiO$_{3-x}$N$_x$ from $x = 0.4$ to 0.8 changes the band gap energy from 2.9 to 2.4 eV. Epitaxial SrMoO$_{3-x}$N$_y$ ($y = 0.6$–1.2) perovskite-type thin films
have also been successfully deposited from a SrMoO$_4$ target by PRCLA. The films exhibit electronic conductivity due to mixed Mo oxidation states of +4 and +5.

Another modification of conventional PLD, which has been tested to deposit perovskite-type oxynitride thin films is radio frequency plasma assisted PLD. Here, a continuous plasma beam is directed onto the surface of the growing film. The application of a N$_2$ RF-plasma beam allows to deposit SrTiO$_3$:N thin films. However, the N content in these films is ~1.6 times lower compared to films grown by PRCLA with the N$_2$ gas pulse. The deposition with the NH$_3$ RF-plasma beam yields films with a negligible amount of incorporated nitrogen. Optical emission spectroscopy has been performed in order to understand the role of N-containing species in the film growth process and to explain the observed difference between the NH$_3$ and N$_2$ plasmas in PRCLA and RF-plasma assisted PLD. On the basis of the experimentally determined N content and the results of optical emission spectroscopy, a mechanism for nitridation of the growing films in PLD has been proposed.

The detailed parametric study on the one-step deposition of perovskite-type oxynitride thin films by PLD and its modifications has allowed to determine the best deposition conditions, which yield epitaxial films with controlled nitrogen concentration. As a result, we obtained films with the highest nitrogen content possible with these deposition techniques. These results can be used as basis for the deposition of other perovskite-type oxynitride thin films.
ZUSAMMENFASSUNG

Gegenstand der vorliegenden Arbeit war die Realisierung einstufiger Prozesse zur Abscheidung sub-μm dünnner Schichten von Oxynitriden des Perowskitstrukturtyps und eine Untersuchung der optischen und elektronischen Eigenschaften der Filme. Oxynitrirde des Perowskittyps welche durch die allgemeine Summenformel \( AB(O,N)_3 \) beschrieben werden können, entstehen mittels partieller anionischer Substitution des Sauerstoffs in oxidischen Perowskiten durch Stickstoff. Der kontinuierliche Ersatz von Sauerstoff- durch Stickstoffatome ermöglicht eine präzise Einstellung der Materialeigenschaften wie z. B. der Bandlückenenergie, der dielektrischen Charakteristika oder der optischen Absorptionseigenschaften, d. h. implizit der resultierenden Farbe. Oxynitride des Perowskittyps zeigen vielversprechende elektrische und optische Eigenschaften, die sie für potentielle Anwendungen als Photokatalysatoren und Dielektrika sowie als nicht toxische anorganische Pigmente interessant machen.


Eine Modifikation des konventionellen PLD Prozesses durch Zusatz eines synchronisierten Gaspulses ermöglicht eine effektive Kontrolle der anionischen Filmstöchiometrie durch Verwendung stickstoffhaltiger Gase. Diese, als gepulste reaktive Kreuzstrahl laserablation (engl.: Pulsed Reactive Crossed Beam Laser Ablation, PRCLA) bekannte Technik wurde zur einstufigen Abscheidung epitaktischer dünner Schichten von SrTiO\(_3\):N, LaTiO\(_3\):xN\(_x\) und SrMoO\(_3\):xN\(_y\) eingesetzt. Die Verwendung von NH\(_3\) als reaktiven Gaspuls ergibt SrTiO\(_3\):N Filme mit um einen Faktor von 3.5 höheren Stickstoffgehalten verglichen zu konventioneller gepulster Laserablation in einer Ammoniakrestgasatmosphäre. Der mittels NH\(_3\) Gaspuls in den SrTiO\(_3\):N Schichten erreichbare Stickstoffgehalt beträgt bis zu 4 at. % und kann durch die Wahl der Substrattemperatur und die Laserenergiedichte gezielt
eingestellt werden. Die durch Verwendung von Stickstoff als Gaspulskomponente erzielbaren Stickstoffgehalte liegen niedriger und betragen maximal 1.5 at. %.


Die detaillierte parametrische Studie über eine einstufige Abscheidung von Oxynitridschichten des Perowskitstrukturtyps durch den PLD Prozess und dessen Varianten
ermöglichte eine Bestimmung der optimalen Abscheidungsbedingungen für ein epitaktisches Wachstum bei Optimierung und präziser Kontrolle des in das Gitter eingebauten Stickstoffgehaltes. Die erzielten Resultate können als Basis für die Abscheidung dünner Schichten anderer Oxynitridsysteme dienen.
1. INTRODUCTION

1.1. Perovskite-type structure

Crystalline solids reveal specific types of crystallographic structures depending on the composition, ion size, and bonding nature [1,2]. The distinct structure types are generally characterized by the coordination geometry around cations and the type of polyhedral linkage. The crystallographic structure is one of the main factors, defining chemical and physical properties of a material. Even for ternary solid-state systems several unique crystal structure types exist [3]: perovskite ($ABX_3$), spinel ($A_2BX_4$), $K_2NiF_4$ and Ruddelsden-Popper ($A_{n+1}B_nX_{3n+1}$), pyrochlore ($A_2B_2X_7$), scheelite ($ABX_4$), etc... Each of these types represents a family of compounds with a similar arrangement of ions in the crystal lattice. The relative abundance of each structure group is mainly determined by the thermodynamical stability of cation-anion packing. The perovskite-type structure is one of the most abundant crystal structures due to its high thermodynamic stability [1-3].

![Fig. 1.1. Atomic arrangement in an ideal $ABX_3$ perovskite. The ion sizes are not to scale.](image)

The name “perovskite” was first associated with the mineral CaTiO$_3$, but nowadays is universally used for all compounds that have the structural characteristics described below [4]. The composition of a regular three-dimensional perovskite is defined as $ABX_3$, where $A$ and $B$ are cations and $X$ is an anion. Typical elements for the $A$-site are alkali, alkaline earth, and lanthanide cations. The $B$-site is usually occupied by the transition metal cations in higher
oxidation states (≥ +3). In most cases \( X \) is oxygen, but can also be a halogen [5], chalcogen [6] or nitrogen [7,8].

The ideal perovskite consists of a close-packed network of corner-shared \( BX_6 \) octahedra with \( A \) cations occupying the interstitials (Fig. 1.1). The \( A \) and \( X \)-sites have the 12- and 6-fold coordination, respectively [3,4]. To describe deviations of the real crystal structures from the ideal structure a parameter called tolerance factor \( (t) \) is used, which can be expressed as [3]:

\[
t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)} \tag{1.1},
\]

where \( R \) is the crystallographic radius of the corresponding species.

For an ideal cubic perovskite \( t = 1 \), which indicates the perfect matching of the ionic sizes. However, this situation is realized very rarely (e.g. in the high-temperature modification of SrTiO\(_3\)). When the size of the \( B \)-site cation is too large \( (t < 1) \), then stress is introduced into the lattice, which is relaxed by a tilting of the \( AB_6 \) octahedra, i.e. the \( B-X-B \) angle becomes <180° (Fig. 1.2A) [9,10]. This results in a lowering of the crystallographic symmetry. When the \( A \)-site cation is too large \( (t > 1) \), then the resulting stress leads to a displacement of the \( B \)-site cation or to the formation of hexagonal perovskite-type structure, where the \( BX_6 \) octahedra are face-shared (but not corner-shared as in the ideal structure) [11,12], as shown in Fig 1.2B. Distortions of the ideal perovskite-type structure correlate with the electronic and magnetic phenomena centered on the \( B \) cations, which enables the application of perovskites as ferroelectrics, piezoelectrics, high \( T_c \) superconductors, magnetoresistant materials etc… [4].

![Fig. 1.2](image.png)

**Fig. 1.2.** Possible distortions of the ideal perovskite-type lattice: A) rotation of \( BX_6 \) octahedra \( (t < 1) \), B) formation of the face-shared network of \( BX_6 \) octahedra \( (t > 1) \).
Beside these possible distortion in the perovskite structure, there are other possibilities to change the crystal structure: e.g. cation ordering in the A- or B-sublattices can result in the formation of layered perovskites. The introduction of the additional \( AX \) planes results in the formation of intergrowth perovskite-related structures [2,3].

1.2 Electronic structure of perovskite-type oxides

Transition metals, which usually occupy the B-sublattice of the perovskite-type structure, have their frontier \( d \)-orbitals close in energy to the \( O(2p) \) orbitals. The electronic structure of the perovskite-type oxides near the Fermi level is therefore dominated by the hybridization of these orbitals (Fig. 1.3) [13]. The top of the valence band is predominantly formed by the \( O(2p) \) orbitals, whereas the bottom of the conduction band consists mainly of the \( d \)-orbitals of the transition metal.

![Fig. 1.3. Electronic structure of the perovskite-type oxides near the Fermi level.](image)

The band gap energy is one of the important properties of functional materials for photochemical applications [14]. In \( d^0 \) perovskite-type oxides the band gap energy is determined by the difference between the energy of the \( d \)-orbitals of the transition metals and \( O(2p) \) orbitals. The band gap increases therefore with increasing the electronegativity of the B-site cation for isostructural compounds. It has also been shown, that the band gap energy in the distorted perovskites increases with an increase of the tilt of the \( BO_6 \) octahedra, i.e. with a decrease of the \( B-O-B \) angle. The band gap in \( d^0 \)-perovskites decreases with an increase of the A-site cation radius [15]. These empirically-established relationships between the crystal and
electronic structure of the perovskite-type oxide and the band gap allow to predict and design materials with the required band gaps for specific applications.

The properties of the $B$-site cation (such as electronegativity, size, electron configuration, Jahn-Teller character, lone electron pairs, etc...) play an important role in deriving the crystal structure and the physicochemical properties such as electronic conduction, magnetism, ferroisms, etc [16]. For example, the $B$ cation can often be chosen to have a magnetic moment to develop new materials for magnetic applications. For many years the diverse and novel physicochemical properties of perovskite phases have stimulated intense studies on this subject, which resulted in various industrial applications in different areas [16-18], such as capacitors and dielectrics (BaTiO$_3$, SrTiO$_3$), piezoelectrics (Pb(Ti,Zr)O$_3$), giant magneto-resistance materials ((Ca,La)MnO$_3$), conducting electrodes and interconnects (SrRuO$_3$, LaCrO$_3$), NO$_x$ sensors (LaFeO$_3$), catalysts (La(Co,Mn)O$_3$), superconductors (layered cuprates), materials for fast ionic transport ((La, Sr)(Ga,Mg)O$_3$, (La,Sr)CoO$_3$), etc…

1.3 Anionic substitutions in perovskites. Perovskite-type oxynitrides

The properties of any material can be changed and tuned by chemical substitutions. For perovskite-type oxides the most common way to change the properties is cationic substitution in the $A$- or $B$-sublattices. The high thermodynamic stability of the perovskite-type structure provides a large degree of flexibility for chemical substitutions, which allows fine tuning of the properties according to the required specifications.

Anionic substitution in perovskite-type oxides is a much less explored approach, which is probably due to the difficult synthesis of these materials. However, this type of substitution is considered to be a promising approach to modify properties of perovskites. To replace oxygen in a perovskite-type oxide, the potential non-metal candidate should fulfill several requirements, such as similar crystallographic radius ($R$), electronegativity and electronic configuration. Several elements, which are located nearby oxygen in the periodic table, can be considered as promising candidates (Table 1.1).

Sulfur and chlorine are located in the 3rd period of the periodic table. They exhibit therefore larger crystallographic radii and considerably smaller electronegativities, as compared to oxygen. The ionic radii for N$^3-$ and F$^-$ are close to O$^{2-}$, likewise the electronegativity (Table 1.1). Nowadays, most research activities are focused on the substitution of oxygen in perovskites with fluorine or nitrogen, although synthesis of the perovskite-type oxysulfides and oxychlorides is also possible [5-8]. In these compounds the
crystal and electronic structures of the parent oxide are modified according to the distinctive properties of $O^{2-}$ and the substitute anion. Especially the anionic substitutions are attractive since they can be used simultaneously with cationic substitutions, thus providing an additional possibility for modification of certain properties of perovskites.

Table 1.1. Suitable ions to substitute oxygen in perovskites.

<table>
<thead>
<tr>
<th>ion</th>
<th>$S^{2-}$</th>
<th>$N^{3-}$</th>
<th>$O^{2-}$</th>
<th>$F^-$</th>
<th>$Cl^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$, Å</td>
<td>1.70</td>
<td>1.29</td>
<td>1.21</td>
<td>1.145</td>
<td>1.67</td>
</tr>
<tr>
<td>$\chi$</td>
<td>2.60</td>
<td>3.07</td>
<td>3.50</td>
<td>4.10</td>
<td>2.83</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>$3s^23p^6$</td>
<td>$2s^22p^6$</td>
<td>$2s^22p^6$</td>
<td>$2s^22p^6$</td>
<td>$3s^23p^6$</td>
</tr>
</tbody>
</table>

Our research activities were focused on the substitution of oxygen with nitrogen in perovskite-type oxides resulting in the formation of perovskite-type oxynitrides. The differences between nitrogen and oxygen anions, listed in Table 1.1, result in the following differences of the oxynitrides compared to the parent oxides:

- a more covalent bonding in oxynitrides due to the smaller electronegativity of nitrogen,
- a smaller band gap due to the higher energy of $N(2p)$ orbitals (-11.5 eV compared to -14.1 eV for oxygen [19]),
- a lower thermodynamic stability due to the weaker metal-nitrogen bonding,
- different cationic composition or oxidation state of the $B$-site cation due to the larger formal anionic charge for $N^{3-}$ anions compared to $O^{2-}$,
- potentially different polarization properties due to the higher polarisability of nitrogen.

The different formal charge for $N^{3-}$ and $O^{2-}$ requires a charge compensation to keep the electroneutrality condition when nitrogen is substituting oxygen. There are four main possible charge compensation mechanisms:

1. Cross-substitutions in the cationic sublattices with cations having higher oxidation states [20,21]. For example, a simultaneous substitution of $Sr^{2+}$ with $La^{3+}$ and $O^{2-}$ with $N^{3-}$ can be realized for SrTiO$_3$, resulting in the formation of LaTiO$_2$N:

$$Sr^{2+}TiO_3 \Rightarrow La^{3+}TiO_2N \quad (1.2)$$
$$SrTi^{4+}O_3 \Rightarrow SrTa^{5+}O_2N \quad (1.3)$$

2. Increase of the oxidation state of the $B$-site cation [8,22]:

$$SrMo^{4+}O_3 \Rightarrow SrMo^{5+}O_2N \quad (1.4)$$
$$LaV^{3+}O_3 \Rightarrow LaV^{4+}O_2N \quad (1.5).$$
3. Formation of anionic vacancies [23,24]:

\[
\text{SrTi}^{4+} \text{O}_3 \rightarrow \text{SrTi}^{4+} \text{O}_{3-3x/2} \text{N}_x \quad (1.6),
\]

\[
\text{SrMo}^{4+} \text{O}_3 \rightarrow \text{SrMo}^{4+} \text{O}_{3-3x/2} \text{N}_x \quad (1.7).
\]

4. Change of the crystal structure due to the change of the cations-to-anions ratio [7,25]:

\[
\text{La}_2 \text{Ti}^{4+} \text{O}_7 \rightarrow \text{LaTi}^{4+} \text{O}_2 \text{N} \quad (1.8),
\]

\[
\text{SrMo}^{6+} \text{O}_4 \rightarrow \text{SrMo}^{6+} \text{ON}_2 \quad (1.9).
\]

Mixed charge compensation mechanisms are also possible:

\[
\text{SrMo}^{6+} \text{O}_4 \rightarrow \text{SrMo}^{5+} \text{O}_2 \text{N} \quad (1.10).
\]

The selection of the charge compensation mechanism allows to control the amount of incorporated nitrogen and the oxidation state of the B-site cation.

1.4 Potential applications of perovskite-type oxynitrides

1.4.1 Visible light driven water splitting

The possibility to decrease the band gap energy by substituting of O with N in perovskite-type oxides is promising for potential applications of the perovskite-type oxynitrides as photocatalysts for water splitting:

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2 \quad \Delta G = +237 \text{ kJ/mol}^{-1} \quad (1.11).
\]

Photocatalytic systems for this process should fulfill several requirements, such as stability under the operation conditions, good electron-hole pair capacitance to avoid the charge carrier recombination, appropriate energies for the conduction and valence bands and the band gap energy [26] (Fig. 1.4). In the case of a single semiconductor system (Fig. 1.4A) for photochemical water reduction it is necessary that the potential of the bottom of the conduction band is lower than the proton reduction potential (0.0 V at pH = 0). For water oxidation, the potential of the top of the valence band must be higher than the oxidation potential of water (+1.23 V at pH = 0). The minimum theoretical band gap of 1.23 eV is therefore necessary for a semiconductor to drive the water splitting reaction (1.11). Semiconductors with a smaller band gap or a higher conduction band potential or a lower valence band potential would require external red-ox reagents (sacrificial electron acceptors and donors) to drive the reaction, as illustrated in Fig. 1.4B/C. Alternatively, two semiconductors with small band gaps, but appropriate potentials for the conduction and valence bands can be combined in a tandem system for separated water oxidation/reduction using a red-ox mediator (Fig. 1.4D).
Fig. 1.4. Potential diagrams for photochemical water splitting at pH = 0 [14]: A) single semiconductor system, B) with a sacrificial electron acceptor, C) with a sacrificial electron donor, D) dual semiconductor system.

A variety of different oxide materials, including perovskites, have shown catalytic activity for the light driven water splitting [14]. The best quantum efficiencies were reported for BaO-doped La$_2$Ti$_2$O$_7$ modified with a NiO co-catalyst in the base solution (50%) [27] and for La-doped NaTaO$_3$ with a NiO co-catalyst for pure water (56%) [28]. However, both catalyst systems (as well as most others) work well only for UV irradiation due to the large band gaps (~3.8 eV for La$_2$Ti$_2$O$_7$ and ~4.1 eV for NaTaO$_3$). For practical application, it is required that the catalyst works under visible light irradiation. The best visible light driven catalyst system that splits water without external red-ox agents is Cr/Rh-GaN:ZnO with a quantum efficiency of just 2.5% [29-31], which is well below the 10% efficiency required for commercial applications [32]. The main drawback of most oxide photocatalysts for water splitting is their very large band gap, which allows to capture only the small fraction of UV from the solar light spectrum.
Substitution of O with N in oxynitrides allows to decrease the band gap of oxide materials due to the higher energy of the N(2p) orbitals as compared to O(2p) orbitals, which contribute to the top of the valence band (Fig. 1.5). This can be a promising approach to improve the properties of the oxide photocatalysts. Perovskite-type oxynitrides have recently attracted attention for this application, since in 2002 it has been reported that LaTiO$_2$N and La$_{0.75}$Ca$_{0.25}$TiO$_{2.25}$N$_{0.75}$ titanium-based perovskite-type oxynitrides exhibit a photocatalytic activity for water splitting under visible light irradiation ($\lambda > 420$ nm) [33]. It has been shown, that fine powders of these materials photo-oxidize water into O$_2$ in the presence of Ag$^+$ acting as sacrificial electron acceptor (Ag$^+ + e^{-} \rightarrow$ Ag) and photo-reduce H$^+$ into H$_2$ in the presence of methanol, acting as a sacrificial electron donor, when both reactions have been carried out in aqueous solutions. However, LaTiO$_2$N was photo-oxidized at the experimental conditions resulting in a nitrogen evolution: 2N$^{3-} + 6h^+ \rightarrow$ N$_2$ [33,34]. This process has been avoided for La$_{0.75}$Ca$_{0.25}$TiO$_{2.25}$N$_{0.75}$ by the deposition of IrO$_2$ as co-catalyst (~2 wt. %). The initial quantum efficiency of this system for the O$_2$ evolution was about 5%, which is significantly larger as compared to 1.5% for the pure LaTiO$_2$N. The reported quantum efficiency of LaTiO$_2$N co-loaded with 3 wt. % of Pt for the H$_2$ evolution is ~0.15%. The overall water splitting using the LaTiO$_2$N-based perovskite-type oxynitrides has not been achieved, most probably due to the low efficiency of the H$_2$ evolution. The demonstrated possibility of separated visible-light driven photo-oxidation and photo-reduction of water in the presence of sacrificial reagents, however, indicates the appropriate position of the bands for the overall water splitting. The highest evolution rate of H$_2$ of 190 $\mu$mol·h$^{-1}$·g$^{-1}$ among all oxynitrides was reported for LaTaON$_2$, which has been co-loaded with 0.15 wt. % Pt and 0.25
wt. % Ru co-catalyst [35]. The tantalum-based perovskite-type oxynitrides revealed however no activity for water photo-oxidation [35,36]. The relatively low quantum efficiencies exhibited by perovskite-type oxynitrides can be related to the complex defect chemistry of their surfaces, e.g. partial reduction of $d^0$ perovskites during ammonolysis results in formation of recombination centers, which lower the catalyst efficiency [14,34].

1.4.2 Perovskite-type oxynitrides as pigments

Another potential application of perovskite-type oxynitrides related to the decrease of the band gap energy are non-toxic inorganic pigments. For certain materials, such as glasses, glazes or ceramics, there is no alternative for inorganic pigments for coloring. However, most inorganic pigments contain heavy metals or transition metals that can effect the environment and human health. In 2000 it has been suggested to use Ca$_{1-x}$La$_x$TaO$_{2-x}$N$_{1+x}$ compounds to substitute currently used harmful Cd-based yellow, orange and red pigments [37]. The perovskite-type materials exhibit appropriate brightness, as well as good thermal and chemical stability. An important advantage of the suggested Ca$_{1-x}$La$_x$TaO$_{2-x}$N$_{1+x}$ pigments is that the band gap (i.e. the color) of these compounds can be continuously tuned within the range of 2.0–2.75 eV by varying the N content (decreasing $x$ from 1 to 0.05) [37]. The color change in the system Ca$_{1-x}$La$_x$Ta$_{1-y}$Ti$_y$O$_{2-z}$N$_{1+z}$ with variations of the N content is shown in Fig. 1.6.

![Color change in Ca$_{1-x}$La$_x$Ta$_{1-y}$Ti$_y$O$_{2-z}$N$_{1+z}$ system](image)

**Fig. 1.6.** The color change in the Ca$_{1-x}$La$_x$Ta$_{1-y}$Ti$_y$O$_{2-z}$N$_{1+z}$ system with different N content. (The powders were synthesized by A. Weidenkaff).

1.4.3 Dielectric properties of perovskite-type oxynitrides

It has been reported that BaTaO$_2$N, BaTa$_{0.95}$Sc$_{0.05}$O$_{2.1}$N$_{0.9}$ and SrTaO$_2$N oxynitrides exhibit very high values of the bulk dielectric permittivities ($k$ about 2500–7500) at temperatures of 180 to 300 K [38,39]. The observed very high $k$ values are explained by the local formation of dipole moments due to the partial ordering of N atoms in the TaO$_4$N$_2$ octahedra caused by the different electronegativity of oxygen and nitrogen. This results in the local Ta displacements in the crystal lattice (~0.1 Å) and breaking of the local centro-symmetric ordering, while the long-range anion arrangement stays disordered, as confirmed
by the XRD data [38].

It has also been reported, that nitrogen incorporation into SrTiO$_3$ films grown by RF sputtering in Ar/O$_2$/N$_2$ atmosphere results in a decrease of the dielectric loss and leakage current (by a factor of ~20), which has been attributed to a decrease of the oxygen vacancies concentration [40]. The dielectric constant of the films of about 60 was not affected by the nitrogen incorporation. Nitridation of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ films in an NH$_3$ inductively coupled plasma also results in a decrease of the leakage current of up to 2 orders of magnitude. However, the dielectric constant was also decreased [23].

1.5. Synthesis of perovskite-type oxynitrides

The most widely used approach to synthesize the perovskite-type oxynitrides powders is thermal ammonolysis, i.e. a reaction of the corresponding oxide precursor with ammonia at high temperatures:

$$ABO_z + NH_3 \Rightarrow AB(O,N)_3 + H_2O \quad (1.12)$$

N$_2$ is inefficient as a nitridizing agent in a similar reaction due to the very high thermodynamic stability of its molecules arising from the very strong triple N≡N bonds ($E_{\text{diss}} = 950$ kJ·mol$^{-1}$). Not only single phase oxides, but also the oxide mixtures, and oxide-carbonate mixtures can be used as precursors for thermal ammonolysis [7,41]:

$$AO_x + BO_y + NH_3 \Rightarrow AB(O,N)_3 + H_2O \quad (1.13)$$

$$ACO_3 + BO_y + NH_3 \Rightarrow AB(O,N)_3 + CO_2 + H_2O \quad (1.14)$$

Thermal ammonolysis is typically carried out at ammonia pressures close to atmospheric pressure and temperatures in a range of 650–1000 °C. The reaction mechanism is still not well studied. It has been suggested that the nitridation most probably involves partial ammonia dissociation at the precursor’s surface with the formation of NH$_2$, NH, atomic N species and hydrogen. Hydrogen acts as a reducing agent that reacts with the lattice oxygen forming water and creating the oxygen vacancies, which act as centers for the surface incorporation of N atoms (Fig. 1.7). Then the incorporated surface N diffuses in the centre of the crystallite. It has been shown, that H$_2$/N$_2$ mixtures are not efficient for nitridation as compared to ammonia under the same reaction conditions [41]. This indicates the importance of atomic N for nitridation.
Fig. 1.7. Possible mechanism of the thermal ammonolysis process (the atom sizes and distances are not to scale):
1. Dissociation of ammonia molecules
2. Surface desorption of the lattice oxygen with formation of water molecules
3. Bulk diffusion of vacancies via the oxygen hopping mechanism
4. Surface incorporation of atomic N
5. Bulk diffusion of the atomic nitrogen

An efficient thermal ammonolysis requires removal of water produced in the reaction (1.12) in order to prevent the reversed hydrolysis reaction and to shift the thermodynamical equilibrium to the production of the oxynitride. Thermodynamical calculations show that at the reaction conditions (temperatures of 650–1000 °C and atmospheric pressure) NH₃ is almost completely dissociated into a mixture of H₂ and N₂, which is rather inefficient for nitridation. The ammonia flow rate has therefore also an important influence on the ammonolysis thermodynamics, as it influences the actual (non-steady state) degree of the dissociation and concentration of NH₃ in the reaction zone. The ammonolysis process can therefore be controlled by thermodynamical parameters (e.g. temperature, pressure) as well as by some kinetic parameters, which have an influence on the reaction’s thermodynamics (e.g. ammonia flow rate, rate of the water removal).

However, thermal ammonolysis has some serious limitations and drawbacks for the synthesis of oxynitrides:

1. There is only a limited control over the reaction path. Side reactions, e.g. formation of the nitrides, are also possible and it is sometimes difficult to avoid them [25,42]. It has been reported that in some cases the formation of nitrides during ammonolysis can be diminished when a mineralizer, such as alkali or alkali earth chloride, is added to the
reaction mixture. The mineralizer melts at the reaction conditions and allows to overcome the diffusion barrier between ions [42].

2. Thermal ammonolysis is a diffusion-limited process. The nitrogen incorporation into the crystal lattice occurs at the surface of the crystallite with subsequent diffusion of the incorporated nitrogen into the crystallite (Fig. 1.8). This may cause a non-homogeneous distribution of nitrogen through the crystallite depth and even different phase composition at the surface, which would result in the formation of grain boundaries.

![Fig. 1.8. Illustration of the disadvantages of thermal ammonolysis: formation of nitrides and non-homogeneous distribution of N through the depth of the crystallite. The color change symbolizes the gradient of the N concentration.](image)

1.6. Plasma-based techniques for synthesis of perovskite-type oxynitrides

The activities of our project were focused on the development of new techniques to synthesize the perovskite-type oxynitrides, which may help to overcome the disadvantages of a thermal ammonolysis reported above. The utilization of nitrogen-containing plasmas can be beneficial for oxide nitridation as they contain active atomic N species, which have a high probability to be incorporated into the crystal lattice.

The project consists of two parts, i.e. deposition of perovskite-type oxynitride thin films by pulsed laser deposition (PLD)-based techniques, which was the topic of the present PhD studies, and nitridation of bulk samples by microwave-induced plasma ammonolysis, which has been carried out in another PhD work performed at Empa, Dübendorf, Switzerland. PLD is a plasma deposition technique, in which the film is deposited from a plasma plume of the ablated target material (Fig. 2.1). More details on this method are given in the experimental part (next chapter).

Microwave-induced plasma ammonolysis has been performed in a pumped ammonia flow reactor consisting of a quartz tube placed in a domestic microwave oven [43] (Fig. 1.9).
A waveguide has been used to concentrate the microwaves in the reactor. The sample has been placed in the active glow discharge region of the ammonia plasma at the end of the quartz tube. Ammonia has been injected with a controlled flow rate close to the sample through an alumina gas pipe. The temperature of the plasma treatment was estimated to be \( \sim 400 \, ^\circ C \).

Fig. 1.9. Scheme of the setup for microwave induced plasma ammonolysis.

1.7. Perovskite-type oxynitride thin films

Until now, the investigations of perovskite-type oxynitrides have been mostly performed on powder samples. More than 50 different perovskite-related N-substituted oxides have been synthesized and characterized [20,21,25,37,38,42,44-69]. Most of them contain Ti, Zr, V, Nb, Ta, Mo or W as a \( B \)-site cation with different alkali earth and rare earth metals in the \( A \)-sublattice.

For many technical applications it is indispensable to use thin films. Oxynitride thin films have been tested in a wide range of electronic, optoelectronic devices and gas sensors. For example, tantalum oxynitride films can be utilized as a diffusion barrier between silver and silicon in p’n diodes [70]; germanium oxynitride films show dielectric properties and can be used in microelectronics [71]; Cd-Ge-O-N films can be utilized in sensors for ammonia and \( H_2S \) detection [72] and In-O-N films can be used as \( NO_2 \) gas sensors [73]; aluminum oxynitride films are studied as water vapor and oxygen barrier in aliment packages [74]. Despite the fact that perovskite-type oxynitrides are promising candidates for dielectric materials and photocatalysts, until now not many investigations have been done in the field of perovskite-type oxynitride thin films preparation and characterization.

There are two different approaches for oxynitride film preparation. The first consists of two main steps:
1. Preparation of an oxide film precursor. For this a variety of techniques can be used including spin coating, slurry coating, molecular beam epitaxy, magnetron sputtering, chemical vapour deposition, pulsed laser deposition, etc...

2. Converting of the oxide precursor film into the perovskite-type oxynitride film. This can be carried out using the same methods as for powders, e.g. thermal or plasma ammonolysis.

This approach was used for the preparation of thin (La,Sr)Ti(O,N)₃ films [75,76]. The precursor oxide films were grown by a soft chemistry process from polymeric solutions deposited by spin coating on SrTiO₃ substrates [75] and by PLD on MgO and SrTiO₃ substrates [76]. The obtained colorless films were afterwards ammonolysed at 950°C in flowing ammonia yielding the colored perovskite-type films. The electrical behaviour of the obtained films varied from insulating LaTiO₂N to semiconducting SrTiO₃:N [75]. It has also been reported, that La₀.25Sr₀.75TiO₂.₇₅N₀.₂₅ films grown on STO reveal metallic-like behavior, whereas the films grown on MgO exhibit semiconducting-like resistivity [76]. As mentioned above, nitridation of the dielectric (Ba,Sr)TiO₃ films in an ammonia inductively coupled plasma results in the surface N incorporation, which allows to decrease the leakage current compared to the initial oxide film [23]. The nitrogen content in the films was not quantified, but the presented XPS spectrum suggests, that it is very low (<0.5 at. %). The main drawback of the two-step approach for deposition of perovskite-type oxynitride thin films is that it adopts the disadvantages of thermal ammonolysis, i.e. potential side reactions and non-homogenous composition across the film thickness.

The second approach is a direct deposition of oxynitride thin films in a one-step process. Until now, the most widely used method within this approach is RF magnetron sputtering with a reactive nitrogen plasma [40,77,78]. Oxides [40], oxynitrides [77], and even pure nitrides [78] can be used as a target for film deposition. LaTiO₃₋ₓNx films (x = 0–0.75) were obtained from a LaTiO₂N target [77]. The N content can be varied as a function of the substrate temperature, gas composition, and RF power. The resulting N-containing films exhibit enhanced conductivity compared to the films without nitrogen, which is probably due to Ti³⁺ formation. The band gap energy decreases with increasing nitrogen content. One of the first studies on the preparation of perovskite-type oxynitrides thin films has been performed for barium niobium and lanthanum niobium oxynitrides [78]. Starting from the multiphase targets made of compressed commercial nitride powders, BaNb(OₓNₙ)ₓ and LaNb(OₓN₂)ₓ films with a wide anionic composition range were prepared using a Ar/N₂ sputtering atmosphere. The obtained films exhibit a high resistivity ~10²–10³ Ohm-cm. As mentioned
above, RF-sputtering of SrTiO$_3$ in an Ar/O$_2$/N$_2$ atmosphere yields N-substituted SrTiO$_3$:N films. Incorporation of nitrogen allows to decrease the leakage current, whereas the dielectric constant was not changed compared to the oxide material [40]. RF magnetron sputtering, however, does not allow deposition of epitaxial perovskite-type oxynitride thin films. Films grown by this technique exhibit often a mixed-oriented growth [77,78].

There is also one report on the one-step deposition of an oriented SrMoO$_{2.3}$N$_{0.6}$ thin film on a LaAlO$_3$ substrate from a SrMoO$_4$ target by pulsed laser deposition in an ammonia background [22]. The obtained film revealed mixed molybdenum oxidation states at the surface (+4, +5, and +6) and a metallic-like resistivity, which has a value of $\sim$0.21 Ohm$\cdot$cm at room temperature.

1.8 Scope of the present work

The main goals of the present work were:

- develop the methodology for a one-step deposition of perovskite-type oxynitride thin films,
- control of the nitrogen content in the films,
- control of the epitaxial quality and film orientation.

To achieve these goals pulsed laser deposition and two of its modifications have been used.

The first system, which has been chosen for our experiments was N-substituted strontium titanate (SrTiO$_3$:N). It has been selected as a model system for a detailed investigation of the influence of the deposition parameters on the film composition, crystallinity and properties. The main motivations to select SrTiO$_3$:N were:

- deposition of high quality epitaxial SrTiO$_3$ films is well described in the literature [79-84]. We can therefore use the previously obtained results as a basis for our studies.
- SrTiO$_3$ exhibits a very high stability of the perovskite-type crystal structure, which allows large variations of the chemical composition and of the lattice mismatch with the substrate [81,85]. This provides a wider range for changing the deposition parameters, while keeping the perovskite-type crystal structure of the films.
- there was only one report on the deposition of amorphous SrTiO$_3$:N thin films, which have been obtained by RF-magnetron sputtering [40]. No detailed characterisation of the composition, crystallinity, and optical properties of these films has been reported.

After the parametric studies on the influence of the deposition parameters on the film composition and crystallinity were performed for the SrTiO$_3$:N model system, the most
promising conditions, which allows the deposition of epitaxial films with the highest nitrogen content have been applied for the deposition of LaTiO$_{3-x}$N$_x$ and SrMoO$_{3-x}$N$_y$ thin films.

It has been shown, that LaTiO$_2$N can oxidize and reduce water under visible light irradiation in the presence of sacrificial reagents [33,34]. The photocatalytic activity of catalysts may depend on the surface orientation [14]. To study this influence oriented thin films can be used as model systems. Until now LaTi(O,N)$_3$ films have been prepared either in a two-step process by thermal ammonolysis of oxide films or by RF sputtering from the oxynitride LaTiO$_2$N target. Both approaches are rather complicated as the first one implies a two-step process, and the second approach requires the fabrication of an oxynitride LaTiO$_2$N target. Our goal was to perform a one-step deposition of epitaxial LaTi(O,N)$_3$ thin films with controlled nitrogen content.

The last system, that we have chosen for our investigations, is SrMo(O,N)$_3$. These compounds belong to the molybdate family. There is therefore a possibility of the anionic charge compensation due to N incorporation by an increase of the transition metal oxidation state, which is not possible for titanate-based materials, such as SrTiO$_3$:N and LaTi(O,N)$_3$. SrMoO$_{3-x}$N$_x$, SrMoO$_{3-x}$N$_y$ powders with a quite broad range of the N content from $x = 0.4$ to $1.2$ were synthesized previously [25,64,65]. The incorporation of nitrogen results in unique properties of these compounds, which are quite different when compared to the parent SrMoO$_3$ oxide. SrMoO$_{3-x}$N$_x$ perovskite-type oxynitrides with $x > 1$ exhibit relatively high Seebeck coefficients of $15–27 \mu V \cdot K^{-1}$ at room temperature [25], which is considerably higher than the $5 \mu V \cdot K^{-1}$ for SrMoO$_3$ [86]. Higher Seebeck coefficients for perovskite-type oxynitrides are most probably due to the mixed molybdenum oxidation states. This may be interesting for the development of new thermoelectric materials [87]. However, the measured resistivity values for SrMoO$_{3-x}$N$_x$ ($x > 1$) powders of $\sim 1–4 \cdot 10^{-2}$ Ohm-cm at room temperature [25] are about 3 orders of magnitude higher than that for the SrMoO$_3$ powder ($\sim 2 \cdot 10^{-5}$ Ohm-cm) [86]. One of the possible reasons for the observed strong decrease of the resistivity of oxynitride powders can be a significant contribution of grain boundaries due to the low relative density of the pressed powder samples [25,64,65]. A strong influence of grain boundaries on the transport properties has been confirmed for compacted SrMoO$_{2.6}$N$_{0.4}$ powders by a comparison of the AC and DC resistivities [64]. The deposition of thin films of SrMo(O,N)$_3$ is therefore important since the films can be used as dense samples for more accurate measurements of the electrical properties.
2. EXPERIMENTAL

2.1 Film deposition

2.1.1 Conventional pulsed laser deposition

Pulsed laser deposition (PLD) is a film growth technique in which the photonic energy is coupled to the bulk target material via electronic processes. The principle of PLD is shown in Fig. 2.1.

![Fig. 2.1. Scheme of a PLD setup.](image)

Conceptually and experimentally PLD is a relatively simple technique. The experimental setup consists of a target and a substrate holder housed in a vacuum chamber. A high-power laser is used as an external energy source to ablate the target material and to deposit thin films. A set of optical components is used to focus and, if necessary, to raster the laser beam over the target surface (Fig. 2.1). The decoupling of the vacuum hardware and the evaporation power source makes this technique flexible and easily adaptable to different operational modes without the constraints caused by the use of internally powered evaporation sources [88-91]. Film growth can be carried out in a reactive environment containing any kind of gas with or without plasma excitation. It can also be operated in conjunction with other types of evaporation sources in a hybrid approach [90,91]. In contrast to the simplicity of the hardware, the laser-target interaction is a very complex phenomenon. Theoretical descriptions are multidisciplinary and combine both equilibrium and nonequilibrium processes [90,91]. The mechanism that leads to material ablation depends on
laser characteristics, as well as the optical, topological, and thermodynamical properties of the target [91,92].

When an intense laser pulse passes through an optical window of a vacuum chamber and is focused onto the surface of the solid state target, it is partially absorbed. The electromagnetic energy of the laser pulse is converted first into electronic excitation and then into thermal, chemical, and even mechanical energy [88-91]. Above a certain laser power density, significant material removal occurs as an ejected plasma plume. The threshold power density needed to produce such a plume depends on the target material, its morphology, and the laser wavelength and pulse duration. It might be of the order of 10–500 MW⋅cm$^{-2}$ for ablation using ultraviolet (UV) excimer laser pulses of 10 ns duration [93]. The evaporated plume consists of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, and in some cases even micro-sized solid and/or liquid particles [90,91]. The collisional mean free path inside the dense plume is very short. As a result, immediately after the laser irradiation, the plume rapidly expands into the vacuum from the target surface to form a nozzle jet with hydrodynamic flow characteristics [90,91]. Material from the plume is then allowed to recondense on a substrate, where film growth occurs. The growth process may be supplemented by a passive or reactive gas or ion source, which may affect the ablation plume in the gas phase or the surface reaction. In this case one talks of reactive PLD. Gases are often used either to thermalize the plasma species through multiple collisions, or to compensate for the loss of an elemental component of the target due to incongruent ablation, larger scattering degree in the plasma plume or lower sticking probability to the growing film [94-96].

Laser ablation for thin film growth has many advantages:

1. Under optimal conditions, PLD allows stoichiometric deposition of thin films even for chemically very complex systems.
2. Almost any condensed matter material can be ablated by proper selection of the laser wavelength, e.g. a 193 nm ArF excimer laser provides a photon energy of ~6.4 eV.
3. The pulsed nature of PLD provides a precise control of the deposition rate and allows to step deposition at the desired film thickness and even desired coverage of the topmost monolayer.
4. The kinetic energies of the ablated species are mainly in the range that promotes surface mobility while avoiding bulk displacement [88] This allows a surface epitaxial reconstruction of the crystal lattice without damage to the film’s deeper layers.
5. The ability to produce species with electronic states far from chemical equilibrium opens up the potential to produce novel or metastable materials that would be unattainable under thermal conditions [91-93]. It is noteworthy to highlight the last advantage of PLD since it can be a very promising technique for deposition of oxynitride thin films. This method should be especially suitable for a one-step deposition of nitrogen-substituted perovskites eliminating the necessity of thermal ammonolysis due to the experimental flexibility of PLD and the plasma involved in this process.

6. The energy source (laser) is outside the vacuum chamber which, in contrast to vacuum-installed devices, provides a much greater degree of flexibility in materials use and geometrical arrangements.

However, PLD also has some technical and fundamental drawbacks, such as:
1. The production of macroscopic particles and globules during the ablation process at some conditions [97].
2. Possible crystallographic defects in the film caused by plasma species with high kinetic energies [91].
3. Inhomogeneous flux and angular distributions of the elements within the ablation plume due to the different mass and scattering probabilities.
4. Possible deficiency of the film with light elements, such as O, N, Li, due to their larger scattering degree in the plasma plume and lower sticking coefficients [88,95,96].

These problems are quite challenging, but most of them can be surmounted by the proper adjustment of the deposition conditions [88,91-93,96,97]. In particular, the anionic content in the films quite often becomes an issue for conventional PLD, since the anionic species, such as O and N, are light and often exhibit deficiencies in the films [88,95,96,98]. A reactive background gas, can be used in conventional PLD to compensate for the loss of anionic species [97]. Another possibility to overcome this problem is to apply modifications of the conventional PLD technique [96].

In our studies we performed the deposition of perovskite-type oxynitride thin films by the conventional PLD using an ammonia reactive background and by two different modified PLD techniques, which are presented below. 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. Sintered cylindrical rods of SrTiO₃, La₂Ti₂O₇ and SrMoO₄ have been used as targets. During the deposition the targets were 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. The substrate holder consisted of a molybdenum body and 10×10 mm Si plate used for the resistive heating. The substrate was fixed tightly on this plate to obtain homogenous heating. The temperature was controlled by adjusting the Si resistance. During deposition the substrate holder was rotated continuously in order to achieve a homogenous film deposition. The target-to-substrate distance was varied in the range of 3–5 cm. The substrate temperature was change in the range of 570–720 °C. The laser beam was focused on the target to an ablation spot of ~1 mm². The laser fluence was varied in the range of 2–6 J·cm⁻². Most of the films were deposited with 20 000–30 000 pulses. The deposition pressure of the ammonia reactive background in the conventional PLD was 1·10⁻¹ mbar.

2.1.2 Pulsed reactive crossed beam laser ablation

Gupta et al. [99] have pointed out that for many systems, the addition of a reactive gas in PLD is only necessary during the time when the ablation plasma is created and propagates to the substrate. The gas needs only to be present for several microseconds, since the target-to-substrate distances are typically about 5.0 cm and the particle velocities are of the order of 10⁴ m·s⁻¹. For a laser repetition rate of 10 Hz, this means that only 0.1 % of the continuous supply of background gas actually takes part in pulsed deposition. The excessive amount of used reactive gas can be efficiently removed by synchronizing a pulsed gas source with the laser.

![Scheme of a pulsed reactive crossed beam laser ablation setup.](image-url)
Pulsed reactive crossed-beam laser ablation (PRCLA), being a modification of PLD, utilizes the ideas of Gupta [100]. The essential difference between PRCLA and the geometry used by Gupta et al. is that the ablation plume is crossed with the gas pulse close to their origins (Fig. 2.2), where the number densities of both the ablation plume and the gas pulse are high. Similar to Gupta’s approach, the particles are allowed to expand freely into the vacuum chamber towards the substrate.

This simple adaptation has been shown to improve PRCLA with some fundamental advantages over conventional PLD. The time difference between the gas pulse and the laser pulse is controlled. The ablation plasma is produced at the moment when the densest portion of the gas pulse emerging from the valve nozzle passes in front of the point on the target where the laser is focused (Fig. 2.2). In our setup the delay time of the laser pulsed with respect to the gas pulse is 30 μs, while the gas pulse duration is 400 μs. As the ablation plasma expands and propagates through the gas pulse, it transfers some of its energy to the gas pulse molecules via collisions. It has been estimated, that the particles number density reaches up to $10^{15}$ cm$^{-3}$ in this relatively high pressure region, where collisions of the gas pulse molecules and plasma species take place [100]. The typical energies of the ablation plasma species are in the range of 1–16 eV [101], which allows to dissociate the gas pulse molecules in collisions, since the chemical bond energies are typically in the range of 3–10 eV. This yields highly reactive atomic species produced from the gas pulse, which can then participate in film growth and/or undergo reactions with the plasma species [100]. Gases, which under conventional PLD conditions would be insufficiently chemically reactive, can be efficiently used in PRCLA [98,100]. GaN, an important optical semiconductor material, can be efficiently produced by PRCLA from the metallic Ga target with the N$_2$ gas pulse; otherwise it can only be produced either using much higher temperatures and nitrogen gas pressures, or by using ammonia instead of N$_2$ [102]. PRCLA with the N$_2$O gas pulse as a source of active oxygen allows to improve significantly the oxygen content in the perovskite-type manganate and cobaltate thin films [88,96].

It is noteworthy that although reactive species are formed by plasma-gas pulse interactions, associative chemistry takes place primarily on the surface of the substrate. In the gas-phase interaction region where the plasma crosses the gas pulse the probability of a three-body collision is very small and there is too much energy for chemical bonds to form permanently without subsequent dissociation [100]. The dominant processes between the ablation and gas pulse species are therefore dissociation, ionization, electron–electron transfer reactions, etc… [100,103]. Only when the species reach the surface of the growing film, the
excess of energy can be removed, which allow bonds to be formed and a film to grow. The kinetic energy, which is delivered to the film by the ablation plasma in PRCLA enhances the surface mobility of ions, which can be beneficial for improving the crystallinity of the growing film. It has been shown, that the presence of the excited state species at the film surface during growth can be essential for good crystallization and formation of the well-oriented film [104].

In our PRCLA experiments the gas pulse was simultaneously used with the same background gas. Ammonia and nitrogen have been tested as potential nitridizing sources. The background gas pressure was kept at $8 \cdot 10^{-4}$ mbar by an adjustable leak valve. The operation conditions for the gas pulse were identical for all experiments. However, using of NH$_3$ and N$_2$ for the gas pulse resulted in the different overall deposition pressures: $\sim 1 \cdot 10^{-3}$ for the N$_2$ gas pulse and $\sim 1.8 \cdot 10^{-3}$ for the NH$_3$ gas pulse. The observed difference can be related to the different pumping efficiency of the used turbo-molecular pump for ammonia and nitrogen. It is noteworthy that the background gas pressure in PCLA experiments ($8 \cdot 10^{-4}$ mbar) is considerably lower compared to conventional PLD with an ammonia reactive gas ($1 \cdot 10^{-1}$ mbar).

2.1.2 Radio frequency plasma assisted PLD

Another possible modification of the conventional PLD technique is RF-plasma assisted PLD (RF-PLD). In this method a continuous plasma beam is directed to the growing film during the deposition process (Fig. 1.3).
The RF-plasma is created in a discharge cavity and expands into the deposition chamber as a directional beam through a nozzle due to the differential pressure between the RF-discharge cavity and the ablation chamber. In this configuration the substrate is simultaneously exposed to the laser plume and RF-plasma beam [105]. The plasma properties are controlled by the gas flow rate and the RF-power applied to the electrodes. Utilization of a RF-plasma allows to dissociate the gas molecules and produce reactive atomic species, which have a higher probability to be incorporated into the growing film. RF-plasma assisted PLD has been successfully utilized for deposition of thin films of oxides (with an O\textsubscript{2} plasma) [106], nitrides (with an N\textsubscript{2} plasma) [107,108] and oxynitrides (with an N\textsubscript{2}/O\textsubscript{2} plasma) [105].

We studied the applicability of the RF-plasma assisted PLD for growing SrTiO\textsubscript{3}:N films. Nitrogen and ammonia RF-plasma beams have been tested. The influence of the RF-power and the gas flow rate on the film composition, crystallinity and properties has been investigated. The RF power was varied in the range of 50–200 W, and the gas flow rate was changed in the range of 50–200 sccm.

2.2 Film characterisation

2.2.1 Profilometry

![Fig. 1.4. Typical surface profile of a film: top – as acquired, bottom – after removal of the waviness contribution.](image)

The film thickness and roughness were 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 high between the uncovered part of the substrate and the deposited film, as illustrated in Fig. 1.4. A typical surface profile of a film is presented in Fig. 1.4, top. The profile reveals the waviness mainly due to the substrate miscut angle, which is typically about 0.3°. For the roughness calculations the waviness contribution has been removed by applying a cut-off filter. Then, the root-mean-square roughness has been calculated for the profile regions, where no particles have been detected (Fig. 1.4, bottom).

### 2.2.2. Film composition

The composition of most of the films has been obtained from a combination of Rutherford backscattering spectroscopy (RBS) and elastic recoils detection analysis (ERDA) [109]. The Sr:Ti:O concentration ratio in the films was determined by RBS, which is more sensitive to heavier elements, compared to ERDA [109]. The measurements were performed using a 2 MeV ⁴He ion beam and a silicon surface barrier detector under 165°. The collected RBS data were simulated with the RUMP software [110]. The experimental uncertainty (accuracy) in cations and oxygen stoichiometries, determined by RBS, are ±3% and ±5%, respectively. Quantification of the N content in the films by RBS was not possible due to the low sensitivity and high uncertainty of this technique to light elements. The nitrogen content in the films was therefore calculated from the combination of RBS results and N:O concentration ratios obtained from ERDA. For the measurements a 12 MeV ¹²⁷I beam was used under 18° incident angle. The scattered recoils were identified by the combination of a time of flight spectrometer with a gas ionization chamber. For the selected films a detailed depth profiling ERDA was performed: the concentration of each element in the film was analyzed as a function of depth in the range of 0–185 nm. The experimental uncertainty in determination of the N:O concentration ratio by ERDA is ±0.001 (which is equivalent to approx. ±0.24 at. % for the N content). The detection limit of ERDA is about 0.24 at. % of N. However, concentrations below approximately 0.5 at. % are quite difficult to quantify. In this case (i.e. for the films deposited by the RF-plasma assisted PLD), the nitrogen content has been determined by X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra were recorded on a PHI Quantum 2000 spectrometer with monochromatic Al Kα X-rays (1486.6 eV). The hemispherical energy analyzer was operated with constant pass energy of 58.7 eV for high-resolution spectra and 117.4 eV for survey scans. The spectra were recorded at room temperature at a photoelectron take off angle of 45° with respect to the surface plane. Electron flood and ion guns were used to neutralize the sample charging during the measurements. The spectra were collected at a depth of 50–100 nm after sputtering the film with an Ar⁺ ion beam.
to avoid contribution from the chemisorbed surface species. All spectra were referenced to the C 1s line at 284.6 eV. The XPS spectra were background subtracted using the Shirley method. The intensity ratios were evaluated using the sensitivity factors supplied by the instrument manufacturer.

2.2.3 Film crystallinity

Grazing incidence X-ray diffraction analysis has been performed to check and confirm the phase composition of the grown films. The measurements were done on a Phillips X’Pert diffractometer using a Cu Kα irradiation at an incident angle of 1–5° (2Θ range of 20–80°, step 0.05°, 0.5 s/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 1–5°. The penetration depth of X-rays at this small incident angles is considerably lower compared to a Θ-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.

Fig. 2.5. Schematic illustration of the X-ray diffraction geometry used for the characterisation of film orientation in the out-of-plane and in-plane directions.

The film texture (i.e. the out-of-plane orientations) and mosaicity (i.e. the in-plane distribution of orientations) have been studied on a Siemens D5000 four-circle X-ray diffractometer that enables to attain arbitrary orientation of the film in three-dimensional space. The scattering geometry used for these studies is schematically illustrated in Fig. 2.5. Θ-2Θ diffraction patterns were obtained by scanning along the c-axis direction of the substrate, which provides information about the growth orientation in the out-of-plane
direction. The pole figure XRD measurements have been performed to obtain the information for the in-plane direction. The azimuthal $\Phi$-circle scans of the SrTiO$_3$ (011) Bragg reflections were recorded at a declination angle ($\chi$) of 45° with respect to the $c$-axis (Fig. 2.5). The in-plane film mosaicities were quantitatively estimated as FWHM of the (011) poles (in logarithmic scale).

### 2.2.4 Optical properties of the films

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 ($E_g$) and energy level positions inside the band gap ($E_N$) were determined by linear extrapolation of $(A \cdot h\nu)^2$ vs. the photon energy in the appropriate linear region using the Tauc equation for direct electron transitions [26]:

\[(A \cdot h\nu)^2 \sim (h\nu - E) \tag{2.1}\]

where $h\nu$ is the photon energy; $E$ is the optical band gap energy or energy levels inside the band gap; $A$ is the film absorbance estimated from the film transmittance as:

\[A = -\lg(T) \tag{2.2}\]

All studied films 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 effect will not affect the position and calculated energy for the absorption bands.

### 2.2.5 Electrical properties of the films

The transport properties of the deposited films were studied on a Quantum Design PPMS instrument. For samples with room temperature resistances above 20 Ohm the temperature dependence of the resistivity was measured from 300 K down to 5–10 K by a 4-probe AC technique at a frequency of 113 Hz. Depending on the film resistance the driven current was varied from 0.01 $\mu$A to 5.0 mA at constant applied voltages of 50±5 mV. The upper measurement limit for the resistance was of the order of $10^6$ Ohm. The film resistivity ($\rho$) was calculated from the measured film resistance ($R$) and the film thickness ($d$) using the following equation for thin films (when the distance between electrodes >> $d$):

\[\rho = \frac{\pi}{\ln 2} \cdot R \cdot d \tag{2.3}\]
For the low resistance films (typical resistance at room temperature of a few Ohm) the Hall effect measurements were performed in the temperature range from 3 to 300 K in order to determine the charge carrier mobility (and the charge carrier concentration, when it was possible). A 4-probe AC technique with two additional Hall-voltage electrodes was applied (Fig. 2.6). The current value of 5 mA at a frequency of 113 Hz was used. The electron mobility ($\mu$) was calculated from the slope of the Hall voltage ($V_H$) vs. magnetic field ($B$) in the range 0–4 T using the following expression:

$$\mu = \frac{V_H}{B \cdot \frac{L}{\omega \cdot V_R}}$$

(2.4),

where $V_R$ (resistance voltage) is the voltage between contacts for resistance measurements at zero magnetic field; $L$ and $\omega$ are the distances between the Hall voltage and resistance voltage contacts, respectively (Fig. 2.6).

Fig. 2.6. Electrode configuration for the Hall measurements on thin films.
3. DEPOSITION OF SrTiO₃:N FILMS: THE EFFECT OF LASER FLUENCE AND TARGET-TO-SUBSTRATE DISTANCE ON THE COMPOSITION AND CRYSTALLINITY

One important aspect for the deposition of the SrTiO₃:N films is the influence of the basic deposition parameters on the film composition and crystallinity. For this purpose, two film series were deposited by PRCLA with the N₂ gas pulse at 650°C on MgO substrates:

- In the first series the laser fluence ($F$) was varied from 2.0 to 6.0 J·cm⁻² keeping the distance between the target and the substrate at 5.0 cm.
- In the second series the target-to-substrate ($d_{T-S}$) distance was varied from 3.0 to 5.0 cm at a constant $F$ of 5.0 J·cm⁻².

For these experiments, a substrate temperature ($T_S$) of 650°C was chosen, which is a typical value for PRCLA [85,96]. MgO was selected as substrate, because it consists of light elements, which allows to perform a more accurate fitting of the RBS data, as compared to LAO or STO substrates. A typical example of the RBS data and the corresponding simulation is shown in Fig. 3.1.

![Fig. 3.1. Typical RBS spectrum of a SrTiO₃:N film deposited by PRCLA on a MgO substrate. The performed simulation yields the Sr:Ti:O ratio in the film. The simulation for the stoichiometric SrTiO₃ is included.](image)

3.1 Film thickness

The film thicknesses ($d$) were measured by a profilometer but were also calculated from the combination of RBS data analysis and the unit cell parameters, using the following equation:
\[ d = \left( \frac{n_M}{S} \right) \cdot a^3 \quad (3.1), \]

where \((n_M/S)\) is the film thickness in molecules per cm\(^2\) obtained from RBS and \(a\) is the unit cell parameter calculated from XRD data. The results of these calculations for a series of films, deposited at different laser fluences at a constant \(d_{T-S} = 5.0\) cm, are shown in Fig. 3.2A together with the measured thicknesses. Both methods give similar values, suggesting a good measurement accuracy. The film thicknesses increase with increasing laser fluence due to the higher target ablation rate for a fixed number of pulses [88].

**Fig. 3.2.** Variation of the film thickness vs. the laser fluence (A) and target-to-substrate distance (B). C) Comparison of the fluence dependence of the ablation rate measured on the polycrystalline SrTiO\(_3\) target vs. the deposition rate of N-doped SrTiO\(_3\) films calculated from the film thickness at a \(d_{T-S}\) of 5.0 cm. The insert shows variations of the transport factor (ratio between the deposition and the ablation rates) with the laser fluence.
Fig. 3.2C shows the comparison of the fluence dependence of the ablation rate (measured on the 93% dense polycrystalline SrTiO₃ target used for PRCLA) vs. the deposition rate (calculated from the film thickness assuming 100% dense films). Both, the ablation and the deposition rates, increase with increasing laser fluences up to 8 J cm⁻². The ratio between the deposition and the ablation rates (transport factor) is ~1% and has a minor fluence dependence (insert in Fig. 3.2C). This suggests that within the studied laser fluence range, the material transport from the target to the substrate is essentially independent on the laser fluence. A small transport factor of ~1% indicates that most of the ablated material is lost during the deposition due to the small size of the substrate compared to the ablation plume volume at the target-to-substrate distance of 5 cm and scattering of the ablated species by collisions in the gas phase during the material transport from the target to the substrate. Fig. 3.2B shows the changes of the film thickness as a function of the target-to-substrate distance. The decrease of the thicknesses with increasing dₜ₋ₛ is due to the higher degree of plasma scattering, which results in a smaller amount of the ablated target material arriving at the substrate [88]. As a result, the deposition rate and therefore the film thickness decrease with increasing target-to-substrate distance.

### 3.2 Film composition

RBS analysis revealed a small barium contamination (~0.5 % vs. Sr concentration) in all samples. This contamination originates from the SrTiO₃ target, which has been confirmed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of the target material*. The physico-chemical properties of Ba²⁺ are very similar to those of Sr²⁺ [111]. Thus, a minor amount of barium acts as an isovalent dopant in the A-site of SrTiO₃ and has most probably a minor influence on the crystal structure and properties of the grown films. The RBS analysis confirms also a stoichiometric transport of the cations from the target to the growing films. The difference between the Sr and Ti content in the films is small and lies within the limit of experimental uncertainty.

The oxygen stoichiometry factor, determined by RBS, lies typically in the range 2.75–2.98 ±0.15. The lowest O content of 2.70 ±0.15 was detected in the samples deposited at the shortest target-to-substrate distance of 3.0 cm, which could be due to an increased probability of resputtering of light elements (such as O and N) at low target-to-substrate distances by

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* performed at the research group of D. Günther (ETH Zurich)
plasma species with high kinetic energies [112]. The observed values of the oxygen content in the studied films are very close to the ideal stoichiometry value of 3 (for 3-dimentional perovskites). This is remarkable, as the only oxygen source used during deposition is the target, and normally an additional source(s) of oxygen must be supplied to achieve an almost ideal oxygen content in oxide films deposited by PLD, or to achieve a pure perovskite phase at all [95,96,106,113]. The oxygen content in the studied films is higher compared to the reported value of 2.50 in the strontium titanate films, deposited by PLD at a base pressure of about $1 \cdot 10^{-7}$ mbar, while deposition with an oxygen background pressure of 0.5 mbar results in less oxygen-deficient films (O content of 2.95) [114]. This is different to the conventional solid state synthesis of titanates in air or oxygen atmosphere, where titanates with ideal stoichiometric oxygen content are usually obtained (i.e. SrTiO$_3$). Previous investigations have shown, that cobaltate and manganese perovskite-type films, prepared by PRCLA using two additional oxygen sources (N$_2$O for the gas pulse and O$_2$ as the background), can exhibit relatively high oxygen deficiencies of up to $\delta=0.6$ [95,96]. Most of the films, studied in this work, were deposited using N$_2$ for the gas pulse and as background gas, i.e. no additional oxidizing source was used at all. The high oxygen content in the studied SrTiO$_3$:N films is therefore prominent and not yet fully understood, as the sticking probability and scattering degree of oxygen should not be influenced too strongly by using N$_2$ as background gas compared to O$_2$. This unambiguously suggests that the oxygen content in films, prepared by PLD, is strongly influenced by the nature of the depositing material in addition to the deposition parameters as reported elsewhere [88,95].

![Graph](image)

**Fig. 3.3.** Variation of the relative N content in the films vs. the laser fluence.
The nitrogen content [N] in the prepared SrTiO$_3$:N films was determined by ERDA. Fig. 3.3 presents the relative N concentration as a function of the laser fluence. The nitrogen content increases with increasing laser fluence, reaching a maximum value of 1.74±0.24 at. % at a fluence of 6.0 J·cm$^{-2}$, which corresponds to the following elemental composition of the film: Sr$_{1.02}$Ti$_{0.98}$O$_{2.95}$N$_{0.089}$. The probability that the N species arriving at the heated surface of the film will be incorporated into the crystal lattice depends mainly on the chemical reactivity of the species and the substrate temperature, although other parameters such as the presence of oxygen species also have an influence. Higher laser fluences result in higher ablation rates, kinetic energies, and plasma excitation degrees, which leads to a higher reactivity of the nitrogen species, e.g. by formation of atomic N by collisions of the energetic plasma species with N$_2$ molecules from the gas pulse and/or background [100]. This results in an increase of the relative N concentration in the films with increasing laser fluence.

![Graph](image)

**Fig. 3.4.** Variation of the relative N content in the films vs. the target-to-substrate distance.

In Fig. 3.4 the relative nitrogen concentration is shown as a function of the target-to-substrate distance. The nitrogen content has a trend to increase with increasing $d_{T-S}$. Most probably this originates from a preferential resputtering of lattice nitrogen by the plasma at lower target-to-substrate distances, where the arriving plasma species have higher kinetic energies [115]. This may be due to the lower sticking probability of N compared to O or due to thermodynamical reasons, e.g. re-sputtering of N atoms from the growing film in the form of very stable N$_2$ molecules.
Depth-profiling analysis of ERDA data was performed for the reference film (deposited at a laser fluence of 5.0 J/cm², and \(d_{TS} = 5.0\) cm). The atomic concentration of each element was analysed as a function of the depth in the range of 0–185 nm. The results of this analysis are presented in Fig. 3.5. No changes in the concentration of cations were detected within the studied depth range. The depth profile of the N content in the film is almost flat, indicating that no essential re-exchange of the incorporated N with O from air occurs at the film surface upon its storage at room temperature. The analysis of the oxygen concentration in the film shows that the O content is just slightly higher at the film surface region and lower in the bulk of the film (the difference is just 3%). This originates most probably from an oxygen uptake by the anion-deficient SrTiO₃:N phase, which occurs at the film surface. The averaged film composition, obtained from the ERDA depth profiling data over the range of 0–185 nm is \(\text{Sr}_{0.94}\text{Ti}_{1.06}\text{O}_{2.91}\text{N}_{0.076}\), which is in good agreement with the RBS data for the same film, i.e. \(\text{Sr}_{0.99}\text{Ti}_{1.01}\text{O}_{2.80}\) over the film thickness of about 440 nm (Fig. 3.1). The slightly higher oxygen content (compared to the RBS results) may originate from the smaller analytical depth of ERDA, where the high O concentration at the film surface results in a higher overall oxygen content. However, the difference in the O content obtained from RBS and ERDA analyses is small and is within the limits of experimental uncertainty.

Two films were also prepared where N₂ was replaced by O₂, either in the gas pulse or in the background to study the influence of the presence of an oxidizing source on the nitrogen content. One film was prepared with N₂ in the gas pulse and in O₂ background while another
one with O\textsubscript{2} in the gas pulse and in N\textsubscript{2} background. For both samples no N could be detected by ERDA in the films. This is in agreement with theoretical estimations, which predict that at high temperatures in oxidizing atmosphere, i.e. in the presence of oxygen, the formation of the oxide phase is thermodynamically much more favourable than the formation of an oxynitride due to the high stability of N\textsubscript{2} [7].

3.3 Structural characterisation. Film crystallinity

Fig. 3.6 shows X-ray diffraction spectra of the N-doped SrTiO\textsubscript{3} films deposited at different laser fluences. The pattern of a MgO(100) substrate is shown for comparison.

![XRD patterns](image.png)

Fig. 3.6. A) XRD patterns of the N-substituted SrTiO\textsubscript{3} films deposited at various laser fluences at constant \(T_S = 650^\circ\text{C}\) and \(d_{T-S} = 5.0\ \text{cm}\). A pattern of a pure MgO substrate is included. B) To enhance visibility of the weak reflections the intensity is plotted on a logarithmic scale.

Due to the small film thickness compared to the analysis depth, the spectra reveal a strong (002) reflection of the MgO single crystalline substrate (2\(\Theta\) ~ 42.9\(^\circ\)). A small peak at 2\(\Theta\) ~ 38.6\(^\circ\) also belongs to the MgO(002) reflection due to the Cu K\(\beta\) X-ray source irradiation line, which was suppressed but not eliminated completely by the diffractometer filter. Analysis of the other reflections shows that all of them belong to the (00\(X\)) peak series of strontium titanate. This suggests an oriented film growth along the \(c\)-axis of the substrate despite the relatively large lattice mismatch \((LM)\) with the substrate, which is defined as:

\[
LM = \frac{a(MgO) - a(SrTiO\textsubscript{3\ bulk})}{a(SrTiO\textsubscript{3\ bulk})} = +7.8\% \tag{3.2}
\]
where $a$(MgO) is the unit cell parameter of the MgO substrate (4.211 Å) and $a$(SrTiO$_3$ bulk) is the unit cell parameter of the bulk SrTiO$_3$ (3.905 Å). The lattice mismatch is compensated by a tensile strain in the growing film. The relative intensity of the (002) film reflection increases with increasing laser fluence (Fig. 3.6) due to an increase of the film thickness.

Fig. 3.7A shows X-ray diffraction spectra of the N-doped SrTiO$_3$ films deposited at different target-to-substrate distances. In general, the spectra look similar to those shown in Fig. 3.6. However, there is a pronounced drop of the intensity of the SrTiO$_3$:N film reflections upon decreasing the target-to-substrate distances from 5.0 to 3.0 cm. The film deposited at the lowest $d_{T-S}$ of 3.0 cm reveals also the presence of an additional (011) reflection (Fig. 3.7B). The observed change of the reflection intensities does not correspond to the variation of the film thicknesses (Fig. 3.2B). The thickness increases with decreasing $d_{T-S}$ due to the smaller degree of plasma scattering, which results in a larger amount of the ablated target material arriving at the substrate [88]. As a result, the deposition rate and therefore the film thickness increase with decreasing the target-to-substrate distance. Increase of the film thickness should in principle result in an increase of the film reflections intensities. However, for the studied film series the opposite trend is observed. The most probable reason for the decrease of the diffraction intensities of the film reflections with decreasing $d_{T-S}$ is degradation of the film crystallinity at low target-to-substrate distances.

![Fig. 3.7. XRD patterns of the N-substituted SrTiO$_3$ films deposited at different target-to-substrate distances at constant $T_S = 650^\circ$C and $F = 5.0$ J·cm$^{-2}$: A) – linear scale, B) – logarithmic scale.](image)

This can happen due to the excessively high kinetic energies of the plasma species arriving at the surface of the growing film, which can cause damage to the crystal structure and partial
amorphisation of the film. As a result, the crystalline quality degrades, which cause a drop of film reflections intensity in the diffraction pattern. Another consequence can be a mixed-oriented growth of the film, which has been observed for the sample deposited at a $d_{T-S}$ of 3.0 cm. Both effects are very undesired for the deposition of the model systems. Therefore, the target-to-substrate distance of 5.0 cm has been chosen for the further experiments.

Fig. 3.8 presents a typical XRD pattern of a SrTiO$_3$:N film recorded in the grazing incidence mode. The PDF card for SrTiO$_3$ from the JCPDF database is included as reference. The XRD pattern reveals a diffraction pattern of polycrystalline strontium titanate due to the small fixed incident angle of the X-rays of $1^\circ$. In this case the penetration depth of X-rays at this small incident angle is considerably lower compared to a $\Theta$-2$\Theta$ scan. Therefore the film roughness (i.e. topographic features at the film surface) is more important in the grazing incidence XRD, resulting in a diffraction pattern of randomly oriented crystallographic planes. The comparison between the diffraction pattern of the film and the PDF card for pure SrTiO$_3$ unambiguously suggests the formation of a single cubic perovskite-type phase. No traces of phase impurities can be detected in the pattern.

![Grazing incidence diffraction pattern of a film. All observed reflections are in agreement with those of SrTiO$_3$, confirming the perovskite-type phase purity.](image)

The unit cell parameters of the studied films, calculated from the XRD data, are presented in Fig. 3.9 as a function of the film thickness ($d$). The lattice constants of all SrTiO$_3$:N films are slightly larger compared to bulk strontium titanate, which can be due to several reasons, such as an anionic deficiency of the resulting films [82,116], N incorporation into the crystal lattice, and a positive lattice mismatch with the substrates. The comparison of
the lattice constants of the oxynitride films to the corresponding oxide films (Fig. 3.9) shows that the oxynitriles have larger unit cell parameters than the corresponding oxides. Therefore, a more precise analysis of the substrate influence on the film lattice constant can be performed by subtracting the increase due to substitution of the smaller oxygen anions in an oxide phase with the larger nitrogen anions in an oxynitride, which can be roughly estimated from the following equation:

\[
\frac{a(\text{oxynitride})}{a'(\text{oxide})} \approx \frac{(1 - \omega) \cdot R(O) + \omega \cdot R(N) + R(Ti)}{R(O) + R(Ti)}
\]  

(3.3),

where \(a(\text{oxynitride})\) and \(a'(\text{oxide})\) are the unit cell parameter of the oxynitride and the corresponding N-subtracted oxide, respectively; \(R(i)\) is the crystallographic radius of the element \(i\) (\(R(\text{Ti}) = 0.745 \, \text{Å}, R(O) = 1.21 \, \text{Å}, R(N) \approx 1.29 \, \text{Å} \, [117]\)); \(\omega\) is the atomic fraction of oxygen substituted with nitrogen in the oxynitride. The resulting subtracted values (\(a'\), shown in Fig. 3.9 as open squares, are in good agreement with those for oxide films. The unit cell parameters of films with thicknesses below 200–250 nm are higher, compared to others with larger thickness due to the influence of the positive lattice mismatch with the MgO substrates, which is compensated by a tensile strain [81-83].

![Fig. 3.9.](image_url)

**Fig. 3.9.** The unit cell parameters of the studied films as a function of the film thickness. *Filled circles* guided by a *solid line* represent lattice constants calculated from XRD data. *Open squares* guided by a *dashed line* represent “N influence subtracted” lattice constants (see more details in the text).
3.4 Conclusions

The influence of the basic deposition parameters, i.e. laser fluence and target-to-substrate distance, on the composition and crystallinity of SrTiO$_3$:N films have been studied. The thin films were prepared by pulsed reactive crossed beam laser ablation using N$_2$ for the background and for the gas pulse. $c$-axis oriented single phase perovskite-type films were deposited on the MgO(001) substrates despite the relatively large lattice mismatch (+7.6%), which is compensated by a tensile strain in the films. RBS analysis reveals stoichiometric cation transport and oxygen content in the range of 2.70–2.98 ±0.15. A control of the composition by the studied deposition parameters allows to adjust the N content within the range of $0.5–1.5$ at.%, which corresponds to film compositions of SrTiO$_{2.70-2.98}$N$_{0.030-0.089}$. The N content in the films increases with increasing laser fluence and decreases with decreasing target-to-substrate distance. The presence of an oxidizing source during deposition results in films without any incorporated nitrogen. The unit cell parameters of the SrTiO$_3$:N films are larger compared to bulk SrTiO$_3$ due to the anionic deficiency of the resulting films, N incorporation into the crystal lattice, and a positive lattice mismatch with the substrates for very thin films (below 200 nm). Deposition at small target-to-substrate distances (about 3.0 cm) results in a considerable degradation of the film crystallinity and mixed-oriented film growth.

For further experiment the largest laser fluences of 5–6 J⋅cm$^{-2}$ and a substrate-to-target distance of 5.0 cm should be used in order to keep the highest N content and good crystallinity and orientation of the deposited films.

Our studies on the influence of the basic deposition conditions suggested that the largest amount of incorporated nitrogen and the best crystallinity of SrTiO$_3$:N films are achieved at a laser fluence of 5–6 J/cm$^2$ and target-to-substrate distance of 5.0 cm. Therefore, these conditions have been taken as standard for further experiments, in which we have studied the influence of the substrate temperature ($T_S$), and the nitridizing source (N$_2$ and NH$_3$) on the film properties. The influence of the lattice mismatch has also been investigated. For these purpose three different substrates were used, which have different lattice mismatches with strontium titanate:

$$LM(MgO) = \frac{a(MgO) - a(SrTiO_3)}{a(SrTiO_3)} = +7.8\%$$

$$LM(LaAlO_3) = \frac{a(LaAlO_3) - a(SrTiO_3)}{a(SrTiO_3)} = -2.9\%$$

$$LM(SrTiO_3) = \frac{a(SrTiO_3) - a(SrTiO_3)}{a(SrTiO_3)} = 0$$

![Fig. 4.1. Temperature dependence of the root-mean-square roughness of the SrTiO$_3$:N films deposited by PRCLA with the N$_2$ gas pulse. The solid line is plotted for visual guidance only.](image)

$$F = 5.0 \text{ J cm}^{-2}$$
$$a_{r-s} = 5.0 \text{ cm}$$
4.1 Film roughness

The roughness of the SrTiO$_3$:N films deposited with the nitrogen gas pulse is shown in Fig. 4.1 as a function of the substrate temperature ($T_S$). The roughness tends to increase with increasing $T_S$. Deposition at higher temperatures results in a higher mobility of atoms, ions and clusters at the substrate surface, which leads to the formation of larger crystallites in the growing films. Films grown at higher substrate temperatures exhibit larger surface topographic features and therefore a higher roughness. The influence of other studied deposition parameters on the film roughness is less pronounced. Films grown at different laser fluences and target-to-substrate distances keeping the same $T_S$ of 650$^\circ$C exhibit a roughness in the range of 0.8–1.4 nm, depending mainly on the homogeneity of the substrate heating. A relatively low roughness of 0.6 nm is achieved for the films grown at the lowest laser fluence of 2 J·cm$^{-2}$, which can be explained by the significantly lower film thickness.

4.2 Chemical composition of SrTiO$_3$:N thin films

Differences in the chemical compositions of the films deposited at the same conditions but on different substrates lies within the statistical deviation range. Thus, no pronounced influence of the used substrate on the chemical composition of the films was detected. The elemental composition depends mainly on the deposition medium, i.e. which gas was used for the gas pulse. To analyze the film composition, all studied samples are grouped in three series: films grown in vacuum, with the N$_2$ gas pulse, and with the NH$_3$ gas pulse. The average compositions for these film series are presented in Table 4.1. The stoichiometry factors for Sr, Ti and O were calculated assuming the following normalization of the film composition: $\text{Sr}_{1-z}\text{Ti}_{1+z}\text{O}_{3-x}N_y$, where $z$ represents the deviation from the ideal cationic stoichiometry Sr:Ti = 1:1, $x$ is the oxygen deficiency with respect to the ideal stoichiometry factor of 3, and $y$ is the stoichiometry factor of nitrogen in the films. The amount of incorporated nitrogen is also often expressed by the relative content of nitrogen atoms, [N] (in atomic %):

$$\text{Sr}_{1-z}\text{Ti}_{1+z}\text{O}_{3-x}N_y : \quad [\text{N}] = \frac{y}{5-x+y} \quad (4.1).$$

It is noteworthy that the Sr content in the films ($l-z$) is consistently lower than the Ti content ($l+z$), which is not yet well understood. This effect is more pronounced for films deposited in vacuum and with the NH$_3$ gas pulse. Similar effects have been encountered during the preparation of SrTiO$_3$ films by PLD [118], as well as during surface treatment of...
SrTiO$_3$ single crystals in ammonia microwave-induced plasma [43] and during ion sputtering of SrTiO$_3$ surfaces [119].

**Table 4.1.** Chemical composition of SrTiO$_3$:N films deposited by conventional PLD and PRCLA in different deposition media at 650 °C.

<table>
<thead>
<tr>
<th>deposition conditions</th>
<th>average film composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLD in vacuum</td>
<td>Sr$<em>{0.97}$Ti$</em>{1.03}$O$_{2.52}$</td>
</tr>
<tr>
<td>PRCLA with N$_2$ gas pulse and background</td>
<td>Sr$<em>{0.98}$Ti$</em>{1.02}$O$<em>{2.89}$N$</em>{0.049}$</td>
</tr>
<tr>
<td>PRCLA with NH$_3$ gas pulse and background</td>
<td>Sr$<em>{0.95}$Ti$</em>{1.05}$O$<em>{2.73}$N$</em>{0.112}$</td>
</tr>
<tr>
<td>conventional PLD in NH$_3$ background</td>
<td>Sr$<em>{0.98}$Ti$</em>{1.02}$O$<em>{2.9}$N$</em>{0.032}$</td>
</tr>
</tbody>
</table>

**Fig. 4.2.** Average oxygen stoichiometry factors in films deposited in vacuum, with ammonia, and with the nitrogen gas pulse. The open symbols are the calculated means within each series of films; the error bars show their confidence intervals.

Fig. 4.2 shows the oxygen content for different deposition conditions. The oxygen content calculated from the RBS data is smaller than the ideal stoichiometric value of 3 for the three-dimensional perovskite-type structure. Oxygen deficiency in films is a typical issue for oxide materials grown by PLD [95,96]. Light elements, such as oxygen, are almost always deficient in a film due to a larger degree of scattering in the plasma plume and a lower sticking coefficient on the heated substrate as compared to heavier metallic species. Different sources of oxygen (e.g. background gas, gas pulse, or RF-induced plasma) are used for the deposition of perovskite-type oxide films by PLD in order to improve the oxygen content in the films [95,96,106,113]. However, in the present study none of these oxygen sources can be used to improve the oxygen content in N-substituted strontium titanate films because a
simultaneous use of oxygen- and nitrogen-containing sources yields films with no incorporated nitrogen, as shown above [98]. This is due to the lower thermodynamic stability of the oxynitride phase with respect to the pure oxide phase, which leads to the lower affinity of the growing film to the nitrogen species compared to oxygen species when both are present in the plasma plume.

The oxygen stoichiometry in the films is different, although all three films series were deposited in oxygen-free media (vacuum, \(N_2\) and \(NH_3\) gas pulse). The lowest oxygen content is observed in the reference films deposited in vacuum at a pressure of \(1 \times 10^{-5}\) mbar. The average oxygen stoichiometry factor of 2.52±0.06 for these films is quite similar to the value of 2.50 reported in the literature [85] for the \(SrTiO_{3.5}\) film grown at a pressure of about \(1 \times 10^{-7}\) mbar. Deposition by PRCLA with \(N_2\) or \(NH_3\) gas pulse yields films with higher oxygen contents (Fig. 4.2). This can be attributed to two effects:

1. During the deposition in vacuum the plasma species have a much higher kinetic energy, which can result in re-sputtering of light elements, such as O, from the surface of the growing films. During the deposition with the gas pulse, the ablated species are slowed down considerably and are not energetic enough to cause significant re-sputtering [104], resulting in a higher oxygen content in the films.

2. A minor impurity of \(O_2\) in the used gases (~0.01%) and a very high affinity of the growing film to oxygen species cause even low concentration of \(O_2\) impurities to be important for the final oxygen content in the films*. The average oxygen stoichiometry factors for films deposited with \(N_2\) and \(NH_3\) gas pulses are 2.89±0.06 and 2.73±0.10, respectively.

Deposition with ammonia results in a smaller oxygen content, probably due to the reducing properties of this gas, i.e. hydrogen-containing species from the \(NH_3\) gas pulse can bind oxygen species in the plasma plume thus reducing the amount of active oxygen. However, the oxygen content in these films is still higher than in the reference films deposited in vacuum.

Elastic recoil detection analysis confirms the absence of nitrogen in the reference films deposited in vacuum, while deposition by conventional PLD or PRCLA yields films with incorporated nitrogen (Table 4.1). A comparison of these two techniques shows that the amount of nitrogen in the films is a factor of 3.5 higher for PRCLA (2.31 at. %) when

* Assuming the concentration of an \(O_2\) impurity in the used gases of 0.01%, the amount of delivered \(O_2\) during the deposition time is about \(1 \times 10^{-5}\) mol, which is considerably larger compared to the amount of oxygen in the films, which is about \((1-2) \times 10^{-6}\) mol (depending on the deposition conditions).
compared to conventional PLD (0.65 at. %) if the same nitridizing source (ammonia) is used. This result shows clearly the importance and advantages of using the synchronized reactive gas expansion in PRCLA. This confirms that an activation of the injected gas pulse molecules via collisions with the highly energetic ablation plasma species in the used experimental configuration leads to the formation of very reactive N-containing species. This is a necessary boundary condition to have N incorporated into the growing film.

![Fig. 4.3](image.png)

**Fig. 4.3.** Average nitrogen content in the films deposited in vacuum, with ammonia and with the nitrogen gas pulse. The *open symbols* are the calculated means within each series of films; the *error bars* show their confidence intervals.

The relative nitrogen content in the films grown by PRCLA with different nitridizing sources is shown in Fig. 4.3. The average nitrogen content in the films deposited with the N₂ gas pulse is 0.99±0.16 at. % while for the NH₃ gas pulse it is 2.31±0.42 at. %. The pronounced difference in the nitrogen content between the samples grown with nitrogen and ammonia gas pulses can be explained by two probable reasons:

1. The different dissociation energy of N₂ and NH₃ molecules. Active atomic nitrogen are probably the most important species for the formation of oxynitrides [120]. 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 energetic ablated species from the target. The N₂ molecule is thermodynamically very stable and has a dissociation energy of 945 kJ·mol⁻¹ (~9.8 eV) [121], which is considerably higher compared to the average dissociation energy for one N-H bond in an NH₃ molecule of 391 kJ·mol⁻¹ (~4.1 eV), [121]. Typical ion energies in PRCLA (close to the target) vary in the
range of 5-15 eV [101]. 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 NH₃ makes this process more likely if compared to N₂. This results in the higher concentration of atomic N species in the plasma, and in a larger nitrogen content in films grown with the NH₃ gas pulse.

2. The second probable reason is the reducing properties of ammonia. As already mentioned, it can capture the oxygen species in the plasma and at the surface of the growing film, therefore reducing the oxygen content in the films. This means that there are more vacant anionic sites in the crystal lattice available for nitrogen incorporation.

![Fig. 4.4. Substrate temperature dependence of the N content in SrTiO₃:N films. The error bars show the confidence intervals for the data points, for which statistics was acquired.](image)

The influence of the substrate temperature (Tₛ) on the nitrogen content in SrTiO₃:N films was also studied in more detail. The variation of the nitrogen content vs. Tₛ in the films grown with the N₂ gas pulse is presented in Fig. 4.4. The N concentration exhibits no obvious dependence on the substrate temperature. It increases slightly with increasing Tₛ in the range from 580–720 °C, probably due to an enhanced kinetics or N incorporation. Deposition with the ammonia gas pulse reveals a completely different influence of the substrate temperature (Fig. 4.4). The nitrogen content increases with increasing Tₛ in the studied temperature range of 570–720 °C. The probable reason for the observed difference in temperature dependence for the N₂ and NH₃ gas pulse is the different thermal stability of these molecules. N₂ is
thermally stable in vacuum at temperatures up to 720 °C, while NH₃ molecules can dissociate at the heated substrate surface, producing different N- and H-containing species, such as N, NH, NH₂, H, N₂, H₂. The presence of an additional atomic nitrogen combined with the reducing properties of H-containing species can result in additional nitrogen incorporation, yielding the larger final N content in the film. The dissociation velocity of ammonia is larger at higher temperatures, resulting in a higher degree of dissociation and therefore a higher nitrogen content in the films which reaches up to 4.06±0.39 at. % at Tₛ of 720°C. This value is considerably larger than the nitrogen content reported elsewhere [122].

4.3 Crystal structure of the films

Fig. 4.5 shows the typical grazing incidence diffraction pattern of the studied SrTiO₃:N films deposited by PRCLA with the ammonia gas pulse. The pattern is similar to that for the films deposited with the nitrogen gas pulse. (see Fig. 3.8) All observed reflections are in good agreement with the SrTiO₃ powder diffraction pattern from the JCPDS database. The absence of any additional reflections on the grazing incidence diffraction pattern confirms the perovskite-type single phase purity of the deposited SrTiO₃:N films.

![Grazing incidence XRD diffraction pattern of a SrTiO₃:N film deposited with the ammonia gas pulse. JCPDS data for SrTiO₃ is included as reference.](image)

Fig. 4.5. Grazing incidence XRD diffraction pattern of a SrTiO₃:N film deposited with the ammonia gas pulse. JCPDS data for SrTiO₃ is included as reference.

Θ-2Θ diffraction patterns measured along the c-axis on films grown on LAO(001) in different deposition media are shown in Fig. 4.6. The patterns reveal only the (00X) series of film reflections (beside those from the substrate) with no other reflections corresponding to
different crystallographic planes. This indicates a textured growth of (001)-oriented SrTiO$_3$N films along the substrate’s $c$-axis on LAO(001).

**Fig 4.6.** $\Theta$-2$\Theta$ XRD diffraction patterns of SrTiO$_3$:N films on LAO substrates measured along the $c$-axis.

A similar behavior is exhibited by films grown on STO(001). $\Theta$-2$\Theta$ diffraction patterns reveal only the (00X) series of film reflections confirming the (001)-texture in the out-of-plane direction (Fig. 4.7). The corresponding SrTiO$_3$:N film reflections appear very close to those of the STO substrate, due to the fact that the unit cell parameters of the films are very close to that of the substrate. The film reflections are shifted to lower 2$\Theta$ angles indicating slightly larger lattice constants compared to the SrTiO$_3$ substrate, which is due to the anionic non-stoichiometry in the films, as discussed below.

**Fig. 4.7.** $\Theta$-2$\Theta$ XRD diffraction patterns of SrTiO$_3$:N films on STO substrates measured along the $c$-axis. Insert shows a detailed region around the STO(002) reflection.
Fig. 4.8. $\Theta$-2$\Theta$ XRD diffraction patterns of SrTiO$_3$:N films on MgO substrates measured along the c-axis. Insert shows a detailed region around the expected STO(011) reflection.

The MgO substrates have a considerably larger lattice mismatch of +7.9 % with SrTiO$_3$:N films compared to LAO (-2.9 %) and STO (-0 %). Therefore, films on MgO(001) show a slightly different behavior. Most of them exhibit also a (001)-oriented growth along the substrate’s c-axis (Fig. 4.8). However, in addition to the (00X) family of reflections some of these films reveal also a weak (011) reflection, with an intensity that typically does not exceed 10 % of the strongest (002) film reflection (insert in Fig. 4.8). This indicates that due to the large lattice mismatch with the substrate not all of these films are purely (001)-textured, but some exhibit mixed oriented growth with a preferential (001) orientation in the out-of-plane direction.

Fig. 4.9. Scheme of tensile (A) and compressive (B) influence of the substrate on the film crystal lattice. (all distances on the figure are not for scaling).
The conducted XRD studies of the film deposited on different substrates show that the lattice mismatch between the film and the substrate plays an important role for the film texture. In the previous chapter we have shown, that at film thicknesses above 200 nm the unit cell parameter of the films is not influenced by the substrate any more. This indicates that above this threshold thickness the crystal lattice of SrTiO$_3$:N films relaxes by the formation of plane dislocations or higher order lattice defect (e.g. grain boundaries). Fig. 4.9 schematically illustrates this process for films with a positive or a negative lattice mismatch to the substrate. For a larger absolute lattice mismatch a higher number of dislocations and grain boundaries are formed, resulting in a low epitaxial quality of the film. The large lattice mismatch between SrTiO$_3$ and MgO suggests that even for oriented films on MgO substrates the number of defects in the film should be larger compared to LAO and STO substrates, where the lattice mismatch is smaller, yielding therefore a higher epitaxial quality of the films.

The formation of crystallites with different crystallographic orientations and defects, such as dislocations and grain boundaries, would affect the film crystallinity and microstructure and consequently the film properties. Therefore, it is important to study the epitaxial quality of the films, which is determined not only by the crystal lattice arrangement in the out-of-plane direction (i.e. along the c-axis of the substrate), but also by the in-plane mosaicity of the film (i.e. orientations distribution in the a-b plane). Pole figure XRD analysis has been performed to examine the in-plane mosaicity of films deposited on different substrates and in different deposition media. Fig. 4.10 shows pole figures of the (011) family of planes for the films grown on STO, LAO and MgO substrates.

The films on STO substrates exhibit four main intense poles at Φ angles of ~0, 90, 180, and 270° with respect to the substrate (100) direction (Fig. 4.10A), which is characteristic for the “cube-on-cube” epitaxial relationship: [001]$_\text{film}$/[001]$_\text{substrate}$ [85]. Very sharp and narrow peaks (FWHM ~0.6° for log(intensity)) confirm a high degree of epitaxy of these films due to the negligible lattice mismatch with the substrate. STO is therefore a perfect substrate for the epitaxial growth of SrTiO$_3$:N films with a minimum amount of defects. The films grown on LAO exhibit also four main poles at 0, 90, 180, and 270° (Fig. 4.10B). However, the peaks are not so intense and broader than for the film on STO (Fig. 4.10D, FWHM ~3.2°), indicating a lower epitaxial quality. The pole figure of the film on MgO substrate (Fig. 4.10C) reveals relatively weak and broad peaks compared to the films on STO and LAO (Fig. 4.10D, FWHM ~5.5°). This indicates a poor epitaxy of the SrTiO$_3$:N films on MgO with an increased number of defects due to the largest mismatch of the crystal lattices between the film and the
substrate. The pole figure XRD analysis reveals that the substrate selection has a strong influence on the film mosaicity. Substrates with larger lattice mismatch (e.g. MgO) reveal a larger mosaicity and lower epitaxial quality of SrTiO$_3$:N films, while substrates with a small lattice mismatch (e.g. STO) allow deposition of high-quality epitaxial films. The in-plane film mosaicity is increasing in the following order of the used substrates: STO < LAO < MgO.

![Fig. 4.10](image)

**Fig. 4.10.** A), B), C) Pole figures of the (011) reflection of SrTiO$_3$:N films deposited on different substrates. D) Comparison of the intensities and widths of the poles at $\Phi$ of 90°.

Fig. 4.11 shows the pole figures of the (011) reflection in films grown on MgO in different deposition media (i.e in vacuum, with the N$_2$ and HH$_3$ gas pulse). The films reveal pronounced differences in the in-plane orientation distribution depending on the deposition medium. The reference films, which have been grown in vacuum, exhibit a higher epitaxial quality (FWHM for the pole at 90° is ~3.8°) whereas films deposited by PRCLA have an
increased mosaicity (FWHM is about 5.5° and 16° for the films grown with the N₂ and the NH₃ gas pulse, respectively). Due to the collisions with gas pulse molecules, the plasma species have a lower kinetic energy when they arrive at the substrate. As a result, the species have a lower mobility at the substrate surface, which impedes a reconstruction of the crystal lattice, leading to a lower epitaxial quality of the films grown with the gas pulse. Another possible explanation could be the different film growth mode during deposition in vacuum and with the gas pulse. In the latter case, the plasma species arriving to the substrate have a larger spread of incident angles due to collisions with the gas pulse molecules. This results in growth of grains with different distributions of orientation and size [104].

Fig. 4.11. A), B), C) Pole figures of the (011) reflection of the films deposited on MgO substrates in different media. D) Comparison of the intensities and widths of the poles at Φ of 90°.
The pole figure of the film deposited with the ammonia gas pulse reveals in addition to the main strong poles at 0, 90, 180 and 270° also weaker poles at \( \Phi \) angles of 45, 135, 225 and 315° (Fig. 4.11C). This indicates that the film exhibit a primary (100) in-plane orientation along the \( a \)- and \( b \)-axes of the MgO substrate (i.e. “cube-on-cube” orientation) and a secondary (110) orientation with a 45° tilt with respect to the substrate crystal lattice. The films grown with the ammonia gas pulse reveal therefore a twin structure consisting of two types of differently in-plane oriented crystallites. This result is quite unexpected, and not yet completely understood. It also suggests that the epitaxial quality in these films is lower and the number of grain boundaries is higher due to the presence of differently-oriented grains, which can have an influence on the electrical conductivity of the films, as discussed in Chapter 6.

**Table 4.2.** Average unit cell parameters of SrTiO\(_3\):N films deposited by PRCLA in different deposition media at 650 °C (the average composition is included).

<table>
<thead>
<tr>
<th>Deposition medium</th>
<th>Average unit cell parameter, Å</th>
<th>Average film composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>3.926±0.004</td>
<td>Sr(<em>{0.97})Ti(</em>{1.03})O(_{2.52})</td>
</tr>
<tr>
<td>N(_2) gas pulse</td>
<td>3.924±0.007</td>
<td>Sr(<em>{0.98})Ti(</em>{1.02})O(<em>{2.89})N(</em>{0.049})</td>
</tr>
<tr>
<td>NH(_3) gas pulse</td>
<td>3.931±0.007</td>
<td>Sr(<em>{0.95})Ti(</em>{1.05})O(<em>{2.73})N(</em>{0.112})</td>
</tr>
</tbody>
</table>

The unit cell parameters of the studied N-substituted SrTiO\(_3\) films vary within 3.91(7)-3.94(5) Å. No pronounced dependence of the films lattice constants on the used substrate was found. This is in agreement with our previous results, which suggest that the influence of the lattice mismatch on the calculated unit cell parameters of the SrTiO\(_3\):N films grown on MgO substrates is present only at film thicknesses below 200 nm and becomes negligible for thicker films [98]. All films discussed in this chapter were 500–1000 nm thick, being considerably thicker than the “critical” thickness of about 200 nm, at which the film crystal lattice constant is still slightly affected by the strain from the substrate lattice mismatch. The average values of the unit cell parameters for films grown in different deposition media are presented in Table 4.2. All values are slightly larger than for bulk SrTiO\(_3\) (\( a = 3.905 \) Å), most probably due to the observed anionic deficiency of the films and/or incorporation of nitrogen. Anionic deficiency in perovskite-type compounds leads to a reduction of the transition metal oxidation state, which is accompanied by an increase of its ionic radius [117]. This results in larger unit cell parameters compared to the fully stoichiometric compound. Substitution of smaller oxygen anions (\( R_O = 1.21 \) Å) with larger nitrogen anions (\( R_N \approx 1.29 \) Å) results also in an increase of the lattice constant of the
oxynitride materials. It is noteworthy that for films on MgO substrates, which exhibit mixed (001) and (011) out-of-plane orientations, the unit cell parameters calculated for these different crystallographic planes are essentially the same. This confirms the cubic symmetry of the unit cell in the films.

4.4 Conclusions

N-substituted SrTiO$_3$ thin films can be deposited in one step by PRCLA with nitrogen or ammonia for the gas pulse. The nitrogen content in the films deposited by PRCLA with ammonia is 3.5 times larger compared to the corresponding films deposited by conventional PLD. Deposition with the NH$_3$ gas pulse yields films with a higher amount of the incorporated N as compared to the N$_2$ gas pulse, which is due to the smaller bond energy in the molecule and reducing behavior of NH$_3$. The N content in the films grown with the ammonia gas pulse increases from 0.8±0.3 to 4.1±0.4 at. % with increasing substrate temperature in the range of 570–720 °C. During deposition with the nitrogen gas pulse only a slight increase of the N content is observed in the substrate temperature range of 580–650 °C. All SrTiO$_3$:N films deposited by PRCLA as well as by conventional PLD are reduced, i.e. they exhibit an anionic deficiency resulting in the formation of Ti$^{3+}$.

The studied films reveal a cubic perovskite-type structure. Deposition on LAO and STO substrates results in perfectly c-axis oriented films, whereas some of the films grown on MgO exhibit small (011) reflections, indicating a not perfect out-of-plane orientation due to the relatively large lattice mismatch. The mosaicity (in-plane orientations distribution) of the studied SrTiO$_3$:N films increases also due to the lattice mismatch in the following order of substrates: STO < LAO < MgO. This indicates that the epitaxial quality, i.e. the absence of non zero-order film defects, such as dislocations and grain boundaries, is the lowest in the films grown on MgO. Films deposited with the NH$_3$ gas pulse reveal a lower epitaxial quality compared to the films grown with the nitrogen gas pulse and in vacuum. The epitaxial quality of the films, i.e. combination of the in-plane and out-of-plane orientations distribution, is an important characteristic, which influences the transport properties, as discussed in Chapter 6.
5. OPTICAL PROPERTIES OF SrTiO$_3$:N THIN FILMS

One of the main motivations for the nitrogen substitution in perovskite-type oxides is to modify the electronic structure in the vicinity of the valence band. N(2$p$) orbitals have a higher energy than O(2$p$) orbitals [36,123]. The introduction of a sufficient amount of N will therefore result in an increase of the band gap in oxynitride materials [8], which suggests potential photochemical and photoelectrical applications [8,36,122]. In this chapter the optical properties of the deposited SrTiO$_3$:N films studied by UV-vis-NIR transmittance spectroscopy are discussed. All films have a typical thickness of 500±50 nm, allowing the direct comparison of their transmittance spectra. The data analysis and discussion is focused on the films deposited on LAO substrates, although exactly the same phenomena were observed for the films grown on MgO.

Fig. 5.1 shows the UV-vis-NIR transmission spectra of SrTiO$_3$:N films deposited on LAO substrates in different deposition media. As-acquired spectra (*thin dashed lines* on the graph) reveal typical interference fringes resulting from the interference of the light reflected from the film surface and film-substrate interface. For better visualization of the spectra the “average” curves were plotted through the half-maxima of the interference fringes (*thick solid lines* in Fig. 5.1).

![Fig. 5.1. Transmittance spectra of the films grown in different media on LAO substrates at $T_S$ of 650°C. Three different regions of light absorption are marked: blue – absorption by free electrons in the conduction band; red – absorption due to incorporated N; grey – absorption through the band gap.](image-url)
The transmittance spectra exhibit three different regions where light absorption occurs through different mechanisms:

1. Absorption of IR and visible light in a wavelength range of 460-2000 nm, which corresponds to photon energies of ~1.2-2.7 eV. Absorption of these low-energetic photons is attributed to the electronic transitions within the conduction band of reduced SrTiO$_3$ [124]. Therefore, films with larger anionic deficiencies (i.e. with higher Ti$^{3+}$ contents) reveal stronger absorption and lower transmittance ($T$) in this wavelength region, i.e. $T$(film in vacuum) $< T$(film with NH$_3$ gas pulse) $< T$(film with N$_2$ gas pulse).

2. Broad absorption band at wavelengths below 367 nm (3.38 eV). Absorption of these high-energetic photons is attributed to the band gap of SrTiO$_3$ and occurs through excitation of the valence band electrons to the conduction band. The large electron density in the valence band results in an almost complete absorption of UV light in this wavelength region.

3. Absorption shoulder between 367 and 460 nm, which is a specific feature of N-substituted SrTiO$_3$, that is not observed in stoichiometric or reduced strontium titanate [122]. This absorption shoulder is attributed to the electron transitions from the localized populated N(2p) states to the conduction band.

![Fig. 5.2. Schematic representation of the energy changes in the electronic structure of 3$d^0$ perovskites.](image-url)
In $3d^0$ perovskites, such as SrTiO$_3$, the top of the conduction band is formed by the O(2$p$) orbitals (Fig. 5.2) [26,125]. The energy diagram is changed when N atoms substitute O in the perovskite-type structure. The energy of the N(2$p$) orbitals is lower compared to oxygen. The N(2$p$) levels are therefore located inside the band gap, close to the top of the valence band in the energy diagram of SrTiO$_3$. It has been shown, that for small nitrogen concentrations (1–2 at % in SrTiO$_3$) the N levels inside the band gap are isolated [122], whereas for higher nitrogen concentrations (e.g. 20 at. % in LaTiO$_2$N) the N orbitals “shift up” the top of the conduction band, therefore decreasing the band gap energy [20,21] (Fig. 5.2).

Fig. 5.3. Tauc plots derived from the transmittance spectra of the studied films deposited in vacuum (A), with the nitrogen gas pulse (B), and with the ammonia gas pulse (C).
The absorption spectra of the studied SrTiO$_3$:N films reveal only an absorption shoulder at 367–460 nm due to the nitrogen incorporation, but not a complete absorption of the light, which is characteristic for the reduction of the band gap. This suggests that nitrogen forms separated N(2$p$) energy levels inside the band gap, which is similar to previously published data [122]. It is noteworthy that SrTiO$_3$:N films with a larger N content (grown with the NH$_3$ gas pulse) reveal stronger absorption associated with the N(2$p$) states when compared to the films grown with the N$_2$ gas pulse, where the nitrogen content is smaller (Fig. 5.1). This confirms also the above suggested assumption of separated N(2$p$) levels.

**Fig. 5.4.** Transmittance spectra of SrTiO$_3$:N films deposited with the ammonia gas pulse at different substrate temperatures. The insert illustrates the increase of the absorption within the “N absorption shoulder” wavelength region with an increase of the nitrogen content.

The band gap energy ($E_g$) and energy of the localized N(2$p$) levels ($E_N$) with respect to the Fermi level are calculated from the Tauc plots (Fig. 5.3). Reduced SrTiO$_{3.5}$ reference films without incorporated nitrogen reveal only one slope corresponding to the band gap energy of 3.36 eV (Fig. 5.3A), whereas N-substituted films exhibit an additional slope, corresponding to the N(2$p$) levels with an energy, $E_N$, of about 2.70 eV (Fig. 5.3B and C). The calculated band gap energy of 3.38±0.05 eV is essentially the same for all studied films. This value is larger than the band gap energy in the stoichiometric bulk SrTiO$_3$ ($E_g = 3.20$ eV). The difference is most probably related to the different composition of the films, i.e. anionic deficiency and/or the small Sr understoichiometry. The energy of the N(2$p$) levels in SrTiO$_3$:N films $E_N = 2.70±0.10$ eV is similar to the 2.8 eV reported in the literature.
for SrTiO$_3$:N powders [122]. The formation of the localized N(2$p$) states inside the band gap of N-substituted SrTiO$_3$ results in absorption of visible light photons and, therefore, suggests a potential application of these materials for photochemical applications. It has been shown previously [122] that a photocatalytic oxidation of gaseous 2-propanol to acetone by SrTiO$_3$:N powders is possible under visible light irradiation. The incorporation of a larger amount of nitrogen and inhibiting the formation of Ti$^{3+}$ in N-substituted SrTiO$_3$ would improve the potential of the oxynitrides for photocatalytic applications [122,126].

As mentioned above, the nitrogen content in SrTiO$_3$:N films deposited with the ammonia gas pulse increases considerably with an increase of the substrate temperature (Fig. 4.4). It is therefore possible to study the influence of a larger N content on the optical properties of the films. The transmission spectra of SrTiO$_3$:N films deposited on LAO substrates with the ammonia gas pulse at different substrate temperatures are shown in Fig. 5.4.

![Figure 5.4](image)

**Fig. 5.4.** Transmission spectra of SrTiO$_3$:N films deposited on LAO substrates with the ammonia gas pulse at different substrate temperatures.

![Figure 5.5](image)

**Fig. 5.5.** Tauc plots for the SrTiO$_3$:N films deposited with NH$_3$ gas pulse. Increase of the nitrogen content to 4.1 at. % does not change the energy of N levels inside the band gap.

The absorption shoulder at $\lambda$ of 367–460 nm increases with an increase of the nitrogen content in the films grown at higher temperatures due to the larger density of the N(2$p$) states inside the band gap. The Tauc plots confirm this observation and reveal no essential change of the energy of the nitrogen levels for different N contents in the films (Fig. 5.5). The films grown at higher substrate temperatures exhibit in addition to the enhanced optical absorption in the range of 367–460 nm also a higher transmittance in the IR region, which can be attributed to the smaller Ti$^{3+}$ content in the films. Both factors (i.e. increased optical
absorption in the visible range and lower Ti$^{3+}$ content) are favorable for possible photocatalytic applications. Hence, the most promising conditions for the deposition of SrTiO$_3$:N films for photocatalytic applications are: PRCLA with ammonia for the gas pulse and substrate temperatures above 700°C.

5.1 Conclusions

Nitrogen incorporation into the crystal lattice of SrTiO$_3$ results in a change of the electronic structure: localized N(2$p$) levels are formed inside the band gap of SrTiO$_3$:N. The energy of these levels is about 2.7 eV lower than the bottom of the conduction band. This results in visible light absorption in the wavelength range of 367–460 nm, which is not observed for pure strontium titanate. The optical absorption in this region increases gradually with increasing the N content from 0.8 to 4.1 at. %. The transmission in the range of 460–2000 nm increases also for the films deposited at the substrate temperatures, which is most probably due the lower Ti$^{3+}$ content in the films. The utilization of an ammonia gas pulse and high substrate temperatures (above 700°C) are therefore the more favorable conditions for the deposition of SrTiO$_3$:N films, which may be tested for photocatalytic applications.
6. TRANSPORT PROPERTIES OF N-SUBSTITUTED SrTiO$_3$ THIN FILMS DEPOSITED BY PRCLA

As already pointed out, the deposition of SrTiO$_3$:N films by PRCLA yields films, which exhibit anionic deficiencies. This is a typical feature for PLD-based techniques, as light species have lower sticking probabilities on the surface of the growing films, are scattered over a large volume in the plasma plume by collisions with heavier species [95,106], and can be preferentially re-sputtered from the growing films [127]. The anionic non-stoichiometry of SrTiO$_3$:N results in electronic conductivity of the films [128], but the chemical composition as well as the crystallinity may also influence the transport properties [22].

6.1 Origin of the electronic conductivity in SrTiO$_3$:N films

The substitution of divalent oxygen anions by trivalent nitrogen anions in SrTiO$_3$ can be expressed in the Kröger-Vink (and classical chemistry) notations as:

$$3O^\circ \rightarrow O^{\circ\rightarrow N} \rightarrow 2N^\circ + V_O^{**}$$

$$3O^{2-} \rightarrow O^{\circ\rightarrow N} \rightarrow 2N^{3+}$$

(6.1),

where $O^\circ$ is a normal oxygen site in the crystal lattice occupied by an oxygen anion; $V_O^{**}$ is a non-occupied oxygen site in the crystal lattice, i.e. oxygen (anionic) vacancy; $N^\circ$ is a nitrogen anion in the oxygen site of the crystal lattice.

The Kröger-Vink notation is a set of conventions used to describe the electrical charge and lattice position for defect species in crystals. Each species is described in the following general format: $M^C_S$, where $M$ corresponds to the species (atoms or vacancies), $S$ indicates the lattice site that the species occupies, and $C$ corresponds to the electric charge of the species relative to the site that it occupies. The Kröger-Vink notation considers an ideal crystal lattice as a reference point and all ions in their normal crystallographic positions as “not charged”. For example, $O^\circ$ is a normal oxygen site in the crystal lattice occupied by an oxygen anion, as it should be in an ideal crystal. This structural element has no charge within the Kröger-Vink notation, which is marked by a symbol $\times$. On the other hand, all possible point defects in the lattice would have their own charges that are equal to the deficiency or excess of the charge with respect to the “not charged” ideally occupied sites in the crystal lattice. For example, $V_O^{**}$ is a non-occupied oxygen site in the crystal lattice, i.e. oxygen vacancy. It is formed by removing a negatively double-charged oxygen anion from its “normal” position. Therefore this crystal site looses two negative charges with respect to its ideal non-charged state. This means that its charge becomes $2^+$, which is marked by two dots. If a nitrogen
anion (having a charge of 3-) substitutes an oxygen anion (with a charge of 2-) in its normal crystallographic position in SrTiO$_3$, then this site gets one “extra” negative charge that is marked by a hyphen: $N'_O$. Electrons and electron holes are considered as separate point defects: $e'$ and $h^*$, respectively. Their site is not specified because often they are delocalized, i.e. belong to the bands but not to discrete atoms. As in the classical chemical equations, all equations in the Kröger-Vink notation must be charge-balanced, i.e. the sum of all charges of the participating crystallographic sites and point defects must be equal to the charge of the reaction products, see Eq. (6.1) and (6.3).

When nitrogen substitutes oxygen in the crystal lattice of SrTiO$_3$, the charge difference is compensated by the formation of anionic vacancies, i.e. three oxygen anions are replaced by two nitrogens, while one site remains vacant (Eq. (6.1)). This reaction by itself does not result in the formation of electronic charge carriers, although the resulting oxynitride is anionic-deficient. This is very different to reduced SrTiO$_3$ without nitrogen, where the oxygen deficiency is directly related to the formation of Ti$^{3+}$ as no other charge compensation mechanisms are allowed.

Pulsed laser deposition of oxide films results almost always in O-deficient films. In the case of the studied SrTiO$_3$:N films, part of the formed oxygen vacancies are involved in the charge compensation for nitrogen substitution and for the Sr deficiency. Please note, that the observed small Sr deficiency in the films cannot be related to the nitrogen charge compensation, because both species (strontium vacancies, $V'_{Sr}$, and nitrogen anions, $N'_O$) are negatively charged. The Sr deficiency should also be charge-compensated by formation of oxygen vacancies:

$$Sr_{Sr}^x+O'_O \rightarrow V'_{Sr}+V'_O$$

However, RBS analysis reveals that the observed loss of oxygen during film deposition is larger than the amount of oxygen vacancies necessary for the nitrogen and Sr charge compensation. The remaining oxygen vacancies are formed due to the reduction process, which results in $3d^0$ perovskites in the formation of free electrons ($e'$), which are the origin for the electronic conductivity in SrTiO$_3$:N films [85,128-130]:
resulting in a decrease of its oxidation state from +4 to +3, as it is reflected in the classical chemistry equation of the process (6.3).

The combination of equations (6.1), (6.2), and (6.3) shows the point defect balance equation for the N-substituted strontium titanate thin films:

\[
[N_o'] + 2[V_{Sr}'] + n = 2[V_{O}']
\]  

(6.4),

where \([N_o']\) is the concentration of nitrogen anions, \([V_{Sr}']\) is the concentration of Sr vacancies, \(n\) is the electron concentration, and \([V_{O}']\) is the concentration of anionic vacancies. This equation illustrates the three above mentioned charge compensation mechanisms. The lack of negative charge in the anionic sublattice caused by the oxygen loss during film deposition (\([V_{O}']\)) is compensated by:

1. excessive charge of nitrogen anions, \([N_o']\) (N\(^{3-}\) instead of O\(^{2-}\));
2. lack of positive charge due to the strontium loss, \([V_{Sr}']\);
3. formation of free electrons (i.e. Ti\(^{3+}\) cations), which are responsible for the observed electronic conductivity in the films.

### 6.2 Parameters determining the electrical conductivity in SrTiO\(_3\):N films

Before starting the analysis of the conductivity results we would like to analyze, which parameters determine the transport properties of SrTiO\(_3\):N films. Electronic conductivity (\(\sigma\)) in any material can be expressed by the fundamental equation [132]:

\[
\sigma = \frac{1}{\rho} = e \cdot n \cdot \mu
\]  

(6.5),

where \(\rho\) is the electrical resistivity, \(e\) is the elemental charge, \(n\) is the electron concentration, and \(\mu\) is the electron mobility. The two main parameters, which determine the electrical conduction in the films, are the charge carrier concentration and their mobility.

The charge carrier concentration is the number of effective charge carriers per unit volume of the sample, which can be estimated from the chemical composition of the films determined by RBS and ERDA [133]. The relative charge carrier concentration per formula unit (i.e. \([Ti^{3+}]/[Ti]_{\text{total}}\) ratio) can be expressed as a function of the film stoichiometry applying the previously used normalization of the film composition (Sr\(_{1-z}\)Ti\(_{1+z}\)O\(_{3-x}\)N\(_y\)):

\[
[Ti^{3+}]/[Ti]_{\text{total}} = \frac{2x - 3y + 2z}{1 + z}
\]  

(6.6).

However, this expression has some serious limitations and drawbacks. It is based on the assumption that all oxygen vacancies are double- but not single-ionized, i.e. \(V_{O}^{**}\) but not \(V_{O}^*\),
and that all formed electrons are capable to participate in the electron transfer. However, it has been suggested that oxygen vacancies in reduced SrTiO$_{3-\delta}$ can be single-ionized for certain conditions [134]. The possibility of all electrons to participate in the conduction is also quite doubtful, as many defects, such as dislocations, grain boundaries, etc., are present in the films. These defects can trap free electrons, resulting in “immobilized” electrons, which do not participate in the conductivity [135]. The anionic vacancies at high concentrations can form clusters, which would also act as traps for free charge carriers. Another important limitation of Equation (6.6) is related to the experimental accuracy of RBS and ERDA [109], which is not high enough for a precise calculation of the [Ti$^{3+}$]. This results in large absolute uncertainties of the [Ti$^{3+}$]/[Ti]$_{total}$ ratio, as shown in Table 6.1. Equation (6.6) can therefore only be used for a rough estimation and comparison of the electron concentrations in SrTiO$_3$:N films.

Table 6.1. Estimations of the Ti$^{3+}$ content from the composition of N-substituted SrTiO$_3$ films grown in different deposition media at 650 °C

<table>
<thead>
<tr>
<th>deposition medium</th>
<th>average film composition</th>
<th>estimated [Ti$^{3+}$]/[Ti]$_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacuum</td>
<td>Sr$<em>{0.97\pm0.03}$Ti$</em>{1.03\pm0.03}$O$_{2.52\pm0.06}$</td>
<td>0.99±0.13</td>
</tr>
<tr>
<td>N$_2$ gas pulse</td>
<td>Sr$<em>{0.98\pm0.03}$Ti$</em>{1.02\pm0.03}$O$<em>{2.89\pm0.06}$N$</em>{0.049\pm0.008}$</td>
<td>0.11±0.13</td>
</tr>
<tr>
<td>NH$_3$ gas pulse</td>
<td>Sr$<em>{0.95\pm0.03}$Ti$</em>{1.05\pm0.03}$O$<em>{2.73\pm0.10}$N$</em>{0.112\pm0.020}$</td>
<td>0.30±0.21</td>
</tr>
</tbody>
</table>

The second main parameter, which determines the electrical conduction in the films, is the charge carrier mobility, which depends on many other parameters and cannot be quantitatively estimated [132]. The electron mobility may also depend on the film composition and concentration of point defects [136]. However, the film microstructure has a much more pronounced influence [22]. The presence of non zero-order film defects, e.g. dislocations and grain boundaries, would reduce the electron mean free path and interrupt the conduction pathways, thus resulting in a lower mobility of the charge carriers [137]. The increased mosaicity of the films and different crystallographic orientations suggest a formation of these higher-order defects, resulting in a decrease of the electron mobilities and therefore an increase of the film resistivity.

6.3 Comparison of transport properties in the films grown on different substrates

The temperature dependencies of the sheet resistance ($R_s$) of films grown on different substrates by PRCLA are shown in Fig. 6.1 (A, B, C). The sheet resistances of SrTiO$_3$:N films...
grown on different substrates reveal a pronounced difference in the thermal behavior: films deposited on MgO and LAO substrates exhibit a semiconductor-like resistivity at temperature below 100 K, whereas all films grown on STO reveal a metallic conductivity and exhibit very similar resistivity values, with only a minor dependence of the film composition. This is most probably due to the reduction of STO substrates during deposition, which will be discussed in detail in Chapter 6.4. Here we will mainly focus on the films grown on MgO and LAO substrates, for which no substrate reduction has been observed.

![Graph A](image1.png)  
**A**  
Temperature dependence of the sheet resistance of SrTiO$_3$:N films grown in vacuum (A), with N$_2$ gas pulse (B), and with NH$_3$ gas pulse (C). The upper limit for the measured resistance is about $10^6$ Ohm.

**Fig. 6.1.** Temperature dependence of the sheet resistance of SrTiO$_3$:N films grown in vacuum (A), with N$_2$ gas pulse (B), and with NH$_3$ gas pulse (C). The upper limit for the measured resistance is about $10^6$ Ohm.

For each deposition medium all films have identical oxygen contents. The observed differences in the nitrogen content are relatively small and have only a minor effect on the estimated Ti$^{3+}$ concentrations, which suggests a similar free electron density in all films.
deposited in the same deposition medium. Therefore, the pronounced difference of the resistance for the films grown on MgO and LAO is most probably related to the different charge carrier mobility in the films caused by their different epitaxial quality. XRD analysis (see Chapter 4) has shown that the highest mosaicity of the films is obtained for MgO substrates, followed by the films on LAO, which correlates to the observed sequence of the resistance curves: $R_S$(on MgO) > $R_S$(on LAO). The strong dependence of the film resistance on the substrate material suggests that scattering of electrons on dislocations and grain boundaries plays a major role in the conduction mechanism of the studied films. This conclusion is also supported by the fact that films on LAO and MgO substrates exhibit a semiconductor-like temperature dependence of the resistivity at low temperatures, as the electron hopping through grain boundaries is a thermally activated process, whereas the epitaxial single-crystalline SrTiO$_3$-$\delta$ films reveal a characteristic metallic-like resistivity [128,129,138].

Some of the SrTiO$_3$:N films grown on LAO substrates exhibit a semiconductor to metal transition at temperatures above 100K (Fig. 6.4). This is observed only for the samples with the best epitaxial quality (i.e. lowest resistances) and can be due to the gradual transition from electron scattering at grain boundaries at lower temperatures to electron scattering at lattice phonons at higher temperatures.

6.4. Transport properties of SrTiO$_3$:N films deposited on SrTiO$_3$ substrates

As already pointed out, all SrTiO$_3$:N and SrTiO$_3$-$\delta$ films grown on STO substrates show a metallic-like resistance between 3 and 300 K, which is different to films grown on MgO and LAO. This can be only partly explained by the best crystalline quality and the lowest number of grain boundaries (Chapter 4). However, the very large differences of the measured resistance values for the films grown on STO compared to other substrates and nearly the same $R_S$ for all films independently on their composition suggest that the crystalline quality is not the most important aspect in this case. The visual inspection of the films revealed a darkening of the STO substrates after deposition, while no color change of the LAO and MgO substrates was detected for the same deposition conditions. No change of the STO substrates has also been observed upon heating of them under the conditions used for the deposition (i.e. at $T_S$ of 650ºC, and pressure of $10^{-5}$–$10^{-3}$ mbar). This indicates that the STO substrates are changed during the growth process. It is known, that reduced SrTiO$_3$-$\delta$ bulk single crystals have a dark-blue color and exhibit metallic conductivity [139-142]. The observed darkening
of STO substrates can therefore be attributed to a partial reduction of the substrates at the film-substrate interface during deposition of SrTiO$_3$:N films at 650°C in vacuum. A series of experiments for the deposition of SrTiO$_3$ films on the $^{18}$O-enriched SrTiO$_3$ substrates has been performed in order to study the possibility of oxygen migration from the stoichiometric substrate into the oxygen-deficient films during deposition. It has been confirmed, that at $T_s \geq 500^\circ$C the migration process occurs, resulting in the formation of an oxygen-deficient surface layer in the SrTiO$_3$ substrate at the interface to the growing SrTiO$_{3-\delta}$ film.

![Temperature dependence of the sheet resistances of SrTiO$_3$:N films grown on STO substrates.](image)

**Fig. 6.2.** Temperature dependence of the sheet resistances of SrTiO$_3$:N films grown on STO substrates.

All films grown on STO exhibit similar resistances independent on the deposition medium and film composition, as shown in Fig. 6.2. The maximum observed differences in the film resistance in the temperature range of 3–300 K is a factor of 2–3, whereas for LAO and MgO substrates the resistivities differ by a factor of 10-10$^4$ depending on the temperature, epitaxial quality, and composition. This suggests that the measured conductivity of the films grown on STO is most probably governed by the properties of the reduced SrTiO$_{3-\delta}$ substrates.

Hall effect measurements have been performed to calculate the electron mobility ($\mu$) for films grown on STO substrates in order to study the conductivity mechanism. The electron mobility has been calculated using equation (2.4). The charge carrier density can be calculated using the following equation:

$$n = \frac{1}{R_s \cdot \mu} \cdot \frac{1}{\ln 2} \cdot \frac{1}{e \cdot \pi \cdot d_{eff}} \quad (6.7),$$

where $R_s$ is the sheet resistance, $\mu$ is the electron mobility, $e$ is the electronic charge, and $d_{eff}$ is the effective thickness.
where \( n \) is the charge carrier concentration, \( R_S \) is the sheet resistance of the sample, \( \mu \) is the electron mobility, \( e \) is the elemental charge, \( d_{\text{eff}} \) is the effective thickness of the conduction layer. However, it is difficult to calculate the absolute charge carrier concentrations in the films grown on STO substrates, because the effective thickness of the conduction layer (\( d_{\text{eff}} \)) is not defined since the depth of the reduced layer of the substrate is unknown. If we assume that \( d_{\text{eff}} \) is similar for all samples deposited on STO, it is possible to compare the relative electron concentrations in the films by comparing the product \((R_S \mu)^{-1}\). The temperature dependence of the electron mobility and \((R_S \mu)^{-1}\) in SrTiO\(_3\):N films grown on STO substrates are shown Fig. 6.3.

![Fig. 6.3](image_url)

**Fig. 6.3.** Temperature dependence of the electron mobility (top) and \((R_S \mu)^{-1}\) as a qualitative estimation for the electron concentration (bottom) in SrTiO\(_3\):N films grown on STO substrates.

The estimated relative electron concentrations \( n \sim (R_S \mu)^{-1} \) exhibit a minor temperature dependence over the entire measured temperature range of 3-300 K (Fig. 6.3 bottom), whereas the electron mobilities reveal three regions with different thermal dependence due to the different electron scattering mechanisms:

1. The electron mobility follows a \( \mu \sim T^{-2.7} \) power-law dependence in the temperature range of 100-300 K (Fig. 6.3 top), which is similar to the value for reduced SrTiO\(_3\)-\(\delta\) single
crystals [143]. It has been suggested that this power-law dependence is due to electron scattering on the longitudinal lattice phonons [143].

2. The vibrations of the crystal lattice become less pronounced at temperatures below 10 K and the electron scattering mechanism changes to scattering from ionized point defects, i.e. mainly by anionic vacancies [143]. The electron mobility becomes almost temperature-independent, as the concentration of point defects in SrTiO$_3$:N does not change significantly with temperature at $T < 10$ K. Films with larger estimated relative electron concentrations $n=-(R_s\mu)^{-1}$ generally exhibit smaller mobilities at $T < 10$ K, due to the higher amount of anionic vacancies, i.e. scattering centers for electron conductivity. The absolute values of the charge carrier mobilities in the studied films at low temperatures are reaching up to $10^4$ cm$^2$·V$^{-1}$·s$^{-1}$, which is a typical value for reduced strontium titanate single crystals and epitaxial films [143-145].

3. At temperatures between 10 and 100 K a mixed mechanism is observed. The vibrations of the crystal lattice decrease gradually upon cooling, and the temperature-independent contribution of the electron scattering at ionized point defects becomes therefore more pronounced.

It is important to mention, that the electron scattering mechanisms in SrTiO$_3$:N films deposited on STO substrates are very different from the scattering on grain boundaries, which is observed for films grown on MgO and LAO substrates.

6.5 Comparison of transport properties in films grown with different gas pulses

In Chapters 6.3 and 6.4 we have discussed the difference in transport properties between films deposited under the same conditions on different substrates. Here we will focus on a comparison of transport properties of films grown with different gas pulses on the same substrates (MgO and LAO). Fig. 6.4A and B show the temperature dependence of the resistivities of SrTiO$_3$:N films grown with different gas pulses on LAO and MgO substrates, respectively. Different to bulk SrTiO$_{3-\delta}$, all these films exhibit a semiconductor-like behavior or a metal-to-semiconductor/insulator transition due to the considerable in-plane mosaicity, which results in an energy-activated charge carrier scattering at dislocations and grain boundaries.
Fig. 6.4. Temperature dependence of the resistivities of SrTiO$_3$:N films deposited on LAO (A) and MgO (B).

The estimation of the [Ti$^{3+}$]/[Ti]$_{\text{total}}$ concentration ratio from the film chemical composition according to Equation (6.6) suggests the following order of charge carrier concentration in the films deposited on the same substrate (MgO or LAO): $n$(film in vacuum) > $n$(film with NH$_3$ gas pulse) > $n$(film with N$_2$ gas pulse) (see Table 6.1). However, the observed sequence of resistivities is different for both substrates, i.e. $\rho$(film in vacuum) < $\rho$(film with N$_2$ gas pulse) < $\rho$(film with NH$_3$ gas pulse). The reference films grown in vacuum exhibit the lowest resistivities due to the largest estimated electron concentrations. However, the films grown with the NH$_3$ gas pulse yield typically higher resistivities compared to the films deposited with the N$_2$ gas pulse, which have lower estimated charge carrier concentrations (Fig. 6.4, Table 6.1). This apparent contradiction can be explained by the results of the XRD investigations of the films, which showed mixed (100) and (110) in-plane orientations of the films grown with ammonia. This indicates that the different crystallographic orientations form additional grain boundaries between crystallites, thereby lowering the electron mobility for the films grown with ammonia. This results in higher resistivities of these films compared to the films deposited with nitrogen. The XRD analysis suggests that the charge carrier mobility in the studied SrTiO$_3$:N films should decrease in the following order: $\mu$(film in vacuum) > $\mu$(film with N$_2$) > $\mu$(film with NH$_3$), which correspond to the observed sequence of resistivities. This indicates that the epitaxial quality of the SrTiO$_3$:N films grown by PRCLA is more important for the transport properties than the chemical composition of the films.
6.6 Conclusions

All studied SrTiO$_3$:N films exhibit electronic conductivity due to the presence of Ti$^{3+}$ sites. The electron scattering for the films deposited on MgO and LAO substrates occurs predominantly at grain boundaries. The most important parameter affecting the conductivity of the films is their epitaxial quality, which has a pronounced influence on the electron mobility, whereas the film composition, which determines the electron concentration, is a less important aspect. SrTiO$_3$:N films grown on LAO and MgO substrates exhibit a semiconductor-like behavior or a metal-to-semiconductor/insulator transition. The films deposited on MgO substrates have a larger mosaicity and therefore higher resistivities compared to films grown on LAO under the same conditions. Among the films grown on the same substrate (LAO or MgO) the reference samples deposited in vacuum exhibit the highest epitaxial quality and the lowest resistivity followed by the films grown with nitrogen and ammonia gas pulses.

Homoepitaxial deposition of SrTiO$_3$:N on STO results in a partial reduction of the substrate during the film growth. The thin films reveal similar transport properties as the SrTiO$_{3-\delta}$ single crystals, i.e. a metallic-like resistance, and a very high electron mobility of up to $10^4$ cm$^2$·V$^{-1}$·s$^{-1}$ at temperatures below 10 K. The electron scattering at $T < 10$ K occurs at ionized point defects, e.g. anionic vacancies, while at higher temperatures, in the range of 100–300 K, free electrons are scattered by the lattice phonons.

The transport properties of reduced strontium titanate based materials can be interesting for various applications. Films could be used as electrically conducting layer in epitaxial heterostructures, for example, in ferroelectric devices [85], due to their conducting properties and perovskite-type structure, which has a good matching of the lattice parameter with other functional perovskite-type materials. Another possible application is as a semiconducting layer in metal-insulator-semiconductor heterostructures. This approach has already been investigated [146-148] involving under-stoichiometric semiconducting strontium titanate films. The insulator layer was then directly obtained by anodic oxidation of a semiconducting strontium titanate film, resulting in a field effect device [146].
7. RF-PLASMA ASSISTED PULSED LASER DEPOSITION OF SrTiO₃:N THIN FILMS

Pulsed reactive crossed beam laser ablation (PRCLA), which was discussed in the previous chapters, is one of the possible modifications for conventional PLD, which gives a better control over the anionic composition by using an additional source for anionic species, i.e. the gas pulse [98,100,103,149]. Another possible modification of PLD, which can be used for the same purpose is called RF-plasma assisted PLD (RF-PLD). This technique utilizes a continuous source of a radio frequency induced plasma, which forms a plasma jet directed onto the substrate during thin film deposition (Fig. 1.3) [105,106]. We have tested the applicability of this technique for the deposition of oxynitride thin films using nitrogen and ammonia for the RF-plasma. SrTiO₃:N was used as a model system to perform a comparison between PRCLA and RF-PLD for the deposition of oxynitrides thin films. The influence of the RF-power (\(P_{RF}\)) and the gas flow rate (\(FR\)) on the thin film characteristics, i.e. composition, crystallinity and properties, has been studied in detail.

7.1 Optical appearance of N₂ and NH₃ RF-plasmas

The N₂ and NH₃ RF-plasmas have different optical appearances. The visible part of the nitrogen plasma has a bright orange color and extends more than 6 cm from the RF nozzle, therefore reaching the substrate during the film deposition. The ammonia plasma has a whitish color and its visible part of about 0.5–1 cm is considerably shorter compared to nitrogen. The main origins of these differences are the different plasma composition and the lifetime of the excited state species, which are present in the plasma. Detailed studies of the excited states species in the plasmas will be reported in the next chapter. Here we would like to mention, that the visible length of the RF-plasma plume could be used as a qualitative estimation of the propagation of nitrogen-containing excited species towards the substrate during film deposition.

7.2 Films thickness and roughness

The thickness \((d)\) and root-mean-square roughness \(\left(R_{q}\right)\) of the studied SrTiO₃-based films are included in Table 7.1. In general, two films deposited at the same conditions but with a different gas used for the RF-plasma (i.e. N₂ and NH₃) reveal a similar thickness despite the relatively large (nearly 2 times) difference in the deposition pressure (Fig. 7.1). This indicates that the scattering efficiency of the ablation plasma plume is very different for
these two gases, which is most probably due to the different size and mass of the N$_2$ and NH$_3$ molecules. For a particular gas used in the RF-plasma (N$_2$ or NH$_3$) the films deposited with lower gas flow rates (i.e. at lower deposition pressures) reveal a greater thickness compared to the films deposited at higher flow rates due to the lower scattering at lower deposition pressures. The RF-power has no essential influence on the film thickness deposited at a constant flow rate.

Table 7.1. Properties of N-doped SrTiO$_3$ thin films deposited by RF-plasma assisted PLD using the N$_2$ and NH$_3$ plasmas (where $FR$ is the gas flow rate, $P_{RF}$ is the RF-power applied to create the plasma, $P_{dep}$ is the deposition pressure, $a$ is the unit cell parameter ($\pm 0.005$ Å), $d$ is the film thickness ($\pm 10\%$), $R_q$ is the root-mean-square roughness ($\pm 0.5$ nm), $[N]$ is the nitrogen content at the depth of 50–100 nm determined by XPS ($\pm 0.12$ at. %), and $E_g$ is the optical band gap energy ($\pm 0.1$ eV)).

<table>
<thead>
<tr>
<th>plasma</th>
<th>$FR$, sccm</th>
<th>$P_{RF}$, W</th>
<th>$P_{dep}$, Pa</th>
<th>$a$, Å</th>
<th>$d$, nm</th>
<th>$R_q$, nm</th>
<th>$[N]$, at. %</th>
<th>$E_g$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>50</td>
<td>100</td>
<td>37</td>
<td>3.905</td>
<td>625</td>
<td>18.4</td>
<td>0.67</td>
<td>3.29</td>
</tr>
<tr>
<td>N$_2$</td>
<td>100</td>
<td>100</td>
<td>67</td>
<td>3.918</td>
<td>365</td>
<td>11.3</td>
<td>0.63</td>
<td>3.20</td>
</tr>
<tr>
<td>N$_2$</td>
<td>150</td>
<td>100</td>
<td>95</td>
<td>3.912</td>
<td>331</td>
<td>10.8</td>
<td>0.68</td>
<td>3.20</td>
</tr>
<tr>
<td>N$_2$</td>
<td>200</td>
<td>100</td>
<td>120</td>
<td>-</td>
<td>105</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N$_2$</td>
<td>100</td>
<td>150</td>
<td>66</td>
<td>3.908</td>
<td>391</td>
<td>12.1</td>
<td>0.50</td>
<td>3.22</td>
</tr>
<tr>
<td>N$_2$</td>
<td>100</td>
<td>200</td>
<td>67</td>
<td>3.910</td>
<td>489</td>
<td>11.7</td>
<td>0.23</td>
<td>3.21</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>50</td>
<td>100</td>
<td>75</td>
<td>3.912</td>
<td>595</td>
<td>0.8</td>
<td>&lt;0.1</td>
<td>3.23</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>100</td>
<td>100</td>
<td>140</td>
<td>3.913</td>
<td>398</td>
<td>3.9</td>
<td>&lt;0.1</td>
<td>3.27</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>150</td>
<td>100</td>
<td>200</td>
<td>3.912</td>
<td>345</td>
<td>1.7</td>
<td>&lt;0.1</td>
<td>3.40</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>100</td>
<td>150</td>
<td>150</td>
<td>3.912</td>
<td>400</td>
<td>3.7</td>
<td>&lt;0.1</td>
<td>3.18</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>100</td>
<td>200</td>
<td>167</td>
<td>3.913</td>
<td>380</td>
<td>4.7</td>
<td>&lt;0.1</td>
<td>3.13</td>
</tr>
</tbody>
</table>

The film roughness depends also strongly on the gas used for the RF-plasma. Deposition with NH$_3$ plasma results in a relatively low roughness typically in the range of 1–4 nm, whereas deposition with N$_2$ plasma yields films with much higher roughness of about 12–18 nm (Table 7.1). This difference is not yet understood, but it might be correlated with the lower degree of crystallinity of the films deposited with the NH$_3$ plasma (which will be shown later), i.e. a suppressed construction of the lattice results in a more uniform surface topography. It is also noteworthy, that the roughness of the well-crystallized films grown with N$_2$ RF-plasma is larger than that for the films deposited by PRCLA (typically 1–3 nm).
Fig. 7.1. Thickness of the SrTiO$_3$-based films deposited by RF plasma assisted PLD at different flow rates as a function of the deposition pressure. Solid lines are plotted for visual guidance only.

Fig. 7.2. Typical grazing incidence diffraction pattern of the N-doped SrTiO$_3$ film (deposited using N$_2$ RF-plasma at a FR of 100 sccm and a $P_{RF}$ of 100 W).

7.3 Structural characterisation of the films

A typical XRD pattern of a studied SrTiO$_3$:N film recorded in the grazing incidence mode is shown in Fig. 7.2. The PDF card for SrTiO$_3$ from the JCPDF database is included as reference. The comparison between the diffraction pattern of the film and the PDF card for pure SrTiO$_3$ indicates the formation of a single cubic perovskite-type phase with no detected traces of the phase impurities.
Fig 7.3. Typical XRD patterns of N-doped SrTiO$_3$ films deposited using a N$_2$ RF-plasma as a function of the RF power (A) and nitrogen flow rate (B). The intensity is plotted in logarithmic scale to enhance visibility of the weak reflections.

Fig. 7.3 shows the typical XRD spectra of the films deposited with N$_2$ RF-plasma in comparison with the spectrum of an MgO(100) substrate. Most of the studied films reveal an oriented growth along the $c$-axis of the substrate. However, in addition to the (00X) reflections, some films reveal also a weak (011) reflection, as indicated for example for the film deposited with an N$_2$ plasma at a RF power of 150 W and a gas flow rate of 100 sccm (Fig. 7.3A). The intensity of this additional (011) reflection does not exceed 5% of the most intense (002) reflection. Therefore, it can be considered that these films also exhibit a preferential (001) orientation. The nitrogen flow rate has also a pronounced influence on the film crystallinity. Increasing the flow rate from 50 to 150 sccm results in a gradual decrease of the film’s reflections intensity (Fig. 7.3B), which is probably due to the decrease of the film thickness. However, the XRD pattern of a film grown at a $FR$ of 200 sccm reveals no visible reflections from the film at all. This cannot be attributed only to the decrease of the film thickness, but suggests that the film is not oriented or amorphous. The probable reasons for the formation of non-oriented (or even amorphous) film could be its damage by the highly energetic plasma species [150] or because of the strong temperature drop on the film surface during the growth due to cooling by the flux of a cold gas from the RF power nozzle. For
further experiments and discussion of the results we decided to limit the flow rate range to 150 sccm due to the problems with the crystallinity of the film deposited at a FR of 200 sccm.

The diffraction patterns of the films deposited using the NH₃ plasma reveal no detectable film reflections, which indicates a non-oriented growth or a lower degree of crystallinity (i.e. semi-amorphous structure). Previous studies on the pulsed laser deposition of perovskite-type (La,Ca)CoO₃ films suggest that the presence of excited state species at the substrate surface during deposition can improve the film crystallinity [151]. Therefore, a shorter RF-plasma beam and higher deposition pressure for the NH₃ plasma compared to N₂ indicate that a considerably smaller amount of excited species reach the substrate, which may explain the observed lower degree of crystallinity of the films deposited with the NH₃ plasma.

The unit cell parameters of the studied films were obtained from the position of the most intense (00\(X\)) film reflections. For the films, which exhibit additional minor (011) reflections, no significant difference between the unit cell parameters calculated from the position of the (X00) reflections or (110) reflections is found. This indicates that the crystal structure of the studied films is cubic and that for a film thickness of 330–630 nm no unit cell distortion due to strain effects caused by the lattice mismatch of +7.6% with the MgO(100) substrates is detected, which is also in agreement with our previous findings. The calculated lattice parameters of the studied SrTiO₃-based films are summarised in Table 7.1. They are slightly larger compared to that of pure SrTiO₃ (\(a = 3.905 \, \text{Å}\)), which can be attributed to the larger crystallographic radius of nitrogen (\(R_N \approx 1.29 \, \text{Å}\)) compared to oxygen (\(R_O = 1.21 \, \text{Å}\)) and/or to the minor lattice point defects in the films.

7.4 N content and chemical composition of the films

Analysis of the nitrogen content in the films was performed by two different techniques: ERDA and XPS. XPS was used as a first method to check the presence of incorporated nitrogen. This technique has a typical probing depth of 2–3 nm in oxide materials [152,153], which is considerably smaller than the thickness of the studied films (~350–600 nm). The information obtained by XPS shows therefore only the composition of a thin film layer. The XPS spectra were collected at a depth of 50–100 nm after sputtering with an Ar⁺ ion beam to remove the uppermost layer of the film, which may contain adsorbed gaseous species from the atmosphere. However, the sputtering can also influence the chemical composition and especially the anionic content in SrTiO₃-based films due to possible preferential sputtering of oxygen (and probably nitrogen) [154]. Therefore, ERDA measurements of the N content were
performed in those films, for which nitrogen incorporation was confirmed by XPS. ERDA allows to perform compositional analysis through the film thickness of up to 200 nm [109]. The disadvantage of ERDA is a lower detection limit of the nitrogen content of ~0.3 at. %, compared to ~0.12 at. % for XPS. The studied films reveal N contents close to the detection limit of ERDA (Table 7.1). As a result, the nitrogen concentration determined by this technique has a relatively high uncertainty. Therefore, in this particular case XPS is the preferred method to analyse the N content in the films as a function of the RF-plasma parameters. Generally, the results of the nitrogen content measurements by ERDA and XPS are in agreement within the limits of experimental uncertainties (Fig. 7.5).

Depth-profiling analysis of ERDA data was performed for the film deposited using the N$_2$ RF-plasma at a FR of 100 sccm and a $P_{RF}$ of 100 W. The atomic concentrations of strontium, titanium and oxygen were analysed as a function of depth in the range of 0–140 nm. The results of this analysis are presented in Fig. 7.4. No changes in the concentration of these elements were detected within the studied depth range indicating a homogeneous elemental composition of the film.

![Fig. 7.4. ERDA depth-profile of the chemical composition of the film deposited using the N$_2$ RF-plasma at a flow rate of 100 sccm and a RF power of 100 W.](image)

The nitrogen content ([N]) obtained by XPS analysis is included in Table 7.1. XPS analysis reveals a principal difference between the films deposited with N$_2$ and NH$_3$ RF-plasmas, i.e. deposition using N$_2$ results in N-doped SrTiO$_3$ films, whereas deposition with NH$_3$ yields samples with only traces of incorporated N. This result is in contradiction with the results for PRCLA, where deposition with the ammonia gas pulse resulted in a higher
nitrogen content compared to the N$_2$ gas pulse (Chapter 4). The optical emission spectroscopy investigations of the N$_2$ and NH$_3$ RF-plasmas have been performed in order to study the active nitrogen species in the RF-plasma and understand the possible reasons for the observed difference between RF-PLD and PRCLA (Chapter 8). The N content in the films deposited by RF-plasma assisted PLD using the N$_2$ plasma (~0.2–0.7 at. %) is lower compared to the films deposited by PRCLA under similar conditions using N$_2$ for the gas pulse (~0.9–1.4 at. %) [98]. However, films deposited by PRCLA reveal anionic deficiencies and electronic conductivity, which is a disadvantage for certain applications (e.g. as dielectrics or for photocatalysis) [40,122], while all samples deposited by the RF-plasma assisted PLD are insulating and reveal no anionic deficiency.

Fig. 7.5. Nitrogen content in SrTiO$_3$:N films deposited using N$_2$ RF-plasma as a function of the nitrogen flow rate (A), and RF-power applied to create the plasma (B). Solid lines are plotted for visual guidance only.

For the films deposited at a N$_2$ flow rate of 50 sccm (A) and RF powers of 150 and 200 W (B) ERDA analysis suggests a N content <0.3 atom %.

Fig. 7.5 presents the nitrogen content in N-doped SrTiO$_3$ films as a function of the N$_2$ flow rate and RF power applied to create the plasma. XPS analysis reveals no significant variations of the N content at flow rates of 50–150 sccm (Fig. 7.5A), while ERDA shows no clear trend, probably because the nitrogen content in the studied films is close to the detection limit of this technique. Increasing the N$_2$ flow rate results in a higher amount of excited nitrogen species (molecules, ions and atoms), which reaches the substrate during the film growth. However, a higher flow rate through the RF-discharge cavity results in a reduced plasma excitation, and therefore a smaller amount of reactive nitrogen species in the plasma...
beam. The total deposition pressure increases also with increasing flow rates, which causes a higher degree of interaction of the N\textsubscript{2} plasma with the background gas. This lowers also the reactivity of the nitrogen species in the RF-plasma beam due to collisions with the background gas. The amount of the incorporated N remains almost constant as a result of these two counteracting effects within the studied range of the nitrogen flow rates (Fig. 7.5A).

The N content in the films deposited using the N\textsubscript{2} RF-plasma decreases gradually with an increase of the RF power in the range of 100–200 W (Fig. 7.5B), which is quite unexpected. The plasma excitation degree increases generally with increasing the applied RF power for a fixed nitrogen flow rate. Therefore, more reactive N species should be formed at higher RF-powers. The observed drop of the N content in the films can be due to an increase of the energy delivered by excited state species from the RF-plasma with increasing the RF-power. Large amounts of energy, delivered by the RF-plasma beam to the surface of the growing film may cause a desorption of the light elements. Desorption of the weaker bonded N atoms from the film can therefore be the prevailing process at the used high RF-powers leading to a decrease of the N content in the films.

7.5 Optical properties of the films grown with RF-PLD

Fig. 7.6 shows the typical transmittance spectra of the SrTiO\textsubscript{3}-based films deposited with the N\textsubscript{2} and NH\textsubscript{3} RF-plasma beams. The spectra reveal a broad absorption band at wavelengths below ~370 nm. The optical band gap energies ($E_g$) can be determined from the position of the absorption edge. The results of these calculations are shown in Table 7.1. The optical band gap energies in the studied strontium titanate-based films are close to that of pure SrTiO\textsubscript{3} (~3.2 eV). The transmittance spectra of the N-doped films (deposited using the N\textsubscript{2} plasma beam) contain also an additional absorption shoulder in the visible region around 370–460 nm, which can be attributed to the localized N(2\textit{p}) orbitals located inside the band gap close the bottom of the valence band (similar to SrTiO\textsubscript{3}:N films grown by PRCLA, Chapter 5) [122]. The transmittance spectra of the films with minor N content (deposited with NH\textsubscript{3} RF-plasma beam) reveal no absorption shoulder at 370–460 nm, i.e. they remain transparent in the visible (Fig. 7.6). This confirms that the absorption at 370–460 nm is due to the N incorporation into the crystal lattice of strontium titanate, assuming that the lower crystallinity of the films deposited with the NH\textsubscript{3} RF-plasma is not related to the observed difference of absorption in the visible.
Fig. 7.6. Typical transmittance spectra of the studied SrTiO$_3$-based films. The oscillations above 500 nm are due to the light interference phenomena.

7.6 Conclusions

The applicability of RF-plasma assisted PLD for the deposition of perovskite-type oxynitrides has been tested and the influence of the RF plasma parameters on the film properties was studied. Preferentially (001) oriented N-substituted strontium titanate films were deposited on MgO(001) substrates using a N$_2$ RF-plasma beam, while the deposition with an NH$_3$ plasma results in films with a lower epitaxial quality and a negligible amount of incorporated nitrogen. The N concentration in SrTiO$_3$:N films deposited using the N$_2$ RF plasma varies from 0.2 to 0.7 atom %. These films are insulators and reveal no electronic conductivity as previously observed in anion deficient N-doped SrTiO$_3$ films deposited by PRCLA. This may be an advantage for certain application, such as dielectrics and photocatalysis. N incorporation results also in an increased absorption of the visible light, which suggest a possible application as photocatalytically active materials.
8. OPTICAL EMISSION SPECTROSCOPY OF N₂ AND NH₃ RF-PLASMAS

8.1. Introduction and experimental details

Deposition of N-doped SrTiO₃ thin films by RF-plasma assisted PLD has yielded a quite unexpected result, i.e. a larger nitrogen content in the films grown with the N₂ RF-plasma beam as compared to the films grown with the NH₃ RF-plasma. This result is unexpected, since ammonia molecules are easier to dissociate yielding reactive atomic nitrogen species for incorporation into the growing film, as shown for PRCLA (Chapter 4). Investigations of the nitrogen and ammonia RF-plasmas have been carried out by optical emission spectroscopy (OES) in order to study the active nitrogen species in both plasmas and understand the observed data. The scheme of the experimental setup for OES experiments is presented in the Fig. 8.1.

![Fig. 8.1. Scheme of the optical emission spectroscopy setup for investigation the active species in RF-plasma.](image)

The experiments have been carried out in a vacuum chamber (base pressure of 5·10⁻² mbar) equipped with a RF-plasma tube, similar to the setup used for RF-plasma assisted PLD. The nitrogen and ammonia plasma beams have been studied at RF-powers (P_RF) ranging from 50 to 200 W, and gas flow rates (FR) from 25 to 200 sccm. The RF-power source, matching network and gas flow meters used for the OES experiments were identical to those used for RF-plasma assisted PLD. The emission spectra of the plasma were not spatially-resolved. The integrated optical signal was collected by a small lens placed in front of the fibre optic feedthrough. An Acton Research Corporation “Spectra PRO 500” wide-range 0.5 meter triple grating monochromator-spectrograph equipped with a Princeton Instrument Inc “ICCD-1024 MLDG-E/1” CCD camera was used to record the emission spectra. The spectra were recorded with a grating of the spectrograph, which has a range of
350 nm and a resolution of approximately 0.34 nm per channel. The whole region of interest (200-900 nm) consists of two separately recorded spectra, i.e. the first from 200 to 550 nm and the second from 550 to 900 nm. Each of these spectra was integrated over 10000 cycles with an acquisition time of 0.1 ms per cycle.

Photographs of the plasma plume have been taken simultaneously to the OES measurements through an optical view port on the chamber. The photographs can be used as a simple tool that allows to estimate the length and the shape of the visible part of plasma plume, and to compare for different plasma conditions. Fig. 8.2 shows the typical photographs of the nitrogen and ammonia RF-plasmas taken with different exposure time. The visible prolongation length of the plasma depends on the camera exposure time. For further discussions a value of 10 ms has been chosen as a standard exposure time.

<table>
<thead>
<tr>
<th>nitrogen RF-plasma</th>
<th>ammonia RF-plasma</th>
<th>exposure time</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="nitrogen RF-plasma" /></td>
<td><img src="image2" alt="ammonia RF-plasma" /></td>
<td>10 ms</td>
</tr>
<tr>
<td><img src="image3" alt="nitrogen RF-plasma" /></td>
<td><img src="image4" alt="ammonia RF-plasma" /></td>
<td>50 ms</td>
</tr>
<tr>
<td><img src="image5" alt="nitrogen RF-plasma" /></td>
<td><img src="image6" alt="ammonia RF-plasma" /></td>
<td>200 ms</td>
</tr>
</tbody>
</table>

Fig. 8.2. Photographs of the nitrogen and ammonia RF-plasmas taken for different exposure times. The RF-power is 100 W, and the gas flow rate is 100 sccm.

8.2. Processes and reactions in the N₂ plasma

In the nitrogen plasma collisions of N₂ molecules with highly energetic electrons can cause different plasma reactions, e.g. ionization and dissociation. To initiate these processes the bombarding electron should have certain threshold energies [155]:

<table>
<thead>
<tr>
<th>ionization of the molecule:</th>
<th>N₂ + e ⇒ N₂⁺ + 2e</th>
<th>Eₑ = 15.57 eV</th>
<th>(8.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dissociative ionization:</td>
<td>N₂ + e ⇒ N⁺ + N + 2e</td>
<td>Eₑ = 24.5 eV</td>
<td>(8.2)</td>
</tr>
<tr>
<td>dissociation of the molecule:</td>
<td>N₂ + e ⇒ N + N + e</td>
<td>Eₑ = 9.8 eV</td>
<td>(8.3)</td>
</tr>
<tr>
<td>ionization of the nitrogen atom:</td>
<td>N + e ⇒ N⁺ + 2e</td>
<td>Eₑ = 14.5 eV</td>
<td>(8.4)</td>
</tr>
</tbody>
</table>
In addition to these plasma reactions, collisions of energetic electrons with the plasma species can also result in the formation of excited state species, if the electron energy is high enough. The nitrogen RF-plasma consists therefore of different N-containing species including ground and excited-state nitrogen molecules, atomic N, and atomic/diatomic ions.

The excited state species in the plasma can be de-excited via different mechanisms:

- Collisions of the excited state species with other molecules, ions or atoms in the plasma can result in an energy re-distribution and de-excitation (collisional de-excitation).
- Alternatively, the excited state species can emit photons with characteristic energies (radiative de-excitation). This property allows to determine the presence of different excited state species in the plasma by comparing the acquired emission spectrum of the plasma with reference data for different species.

However, optical emission spectroscopy does not give the complete information about the plasma composition, because it detects only the species that emit light within the studied wavelength range. Other species in the plasma can also be present, which emit at different wavelength or undergo non-radiative de-excitation. Table 8.1 summarizes the excitation energies and radiative de-excitation transitions of some of the most abundant excited state species in a N2 plasma [155]

<table>
<thead>
<tr>
<th>species</th>
<th>excitation energy, eV</th>
<th>de-excitation transition(s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2(A)</td>
<td>6.2</td>
<td>metastable state</td>
</tr>
<tr>
<td>N2(B)</td>
<td>7.6</td>
<td>N2(B) \rightarrow N2(A)</td>
</tr>
<tr>
<td>N2(C)</td>
<td>11.1</td>
<td>N2(C) \rightarrow N2(B)</td>
</tr>
<tr>
<td>N2*</td>
<td>18.7</td>
<td>N2*(C) \rightarrow N2*(X)</td>
</tr>
<tr>
<td>N*</td>
<td>21.51</td>
<td>N*(D) \rightarrow N*(P)</td>
</tr>
<tr>
<td>N</td>
<td>13.19</td>
<td>N(D) \rightarrow N(P)</td>
</tr>
</tbody>
</table>

*) A simplification of the commonly accepted molecular spectroscopy notation is used [156]. X – is the ground state; A, B, and C – are the first, second and third electronically excited states of the molecular species, respectively; P and D – are the first and second electronically excited states of the atomic species, respectively.

8.3. Nitrogen RF-plasma at different conditions

The main species in nitrogen RF plasma are N2 molecules (ground state, metastables, excited state), N2+ ions, N atoms and N+ ions. Usually, N and N+ are present in very small quantities and it is very difficult to detect their excited state species in a N2 plasma by OES.
The concentration of diatomic N$_2^+$ ions is also much lower than the concentration of the neutral molecular species, because the corresponding ionization and excitation energies for N$_2^+$ are higher compared to the excitation energy for N$_2$ (see Eq. 8.1 and Table 8.1). The OES spectra of the nitrogen plasma show therefore mainly the bands attributed to the N$_2$ excited states transitions. A schematic energy diagram of these transitions is presented in Fig. 8.3.

![Schematic diagram of nitrogen transitions](image)

**Fig. 8.3.** Scheme of the transitions between excited states of the N$_2$ molecule.

As already mentioned, there are two main radiative transitions for the N$_2$ excited states (Table 8.1). The transition N$_2$(B) $\Rightarrow$ N$_2$(A) is called the first positive system (FPS). It has several characteristic emission lines in the visible wavelength range at 560–790 nm (Fig. 8.4A). The transition N$_2$(C) $\Rightarrow$ N$_2$(B) is called the second positive system (SPS), and its characteristic emission lines are located in the wavelength range of 290–430 nm (Fig. 8.4A). The excited state N$_2$(A) is a metastable state, which undergoes a radiative transition only with a very low probability (radiative lifetime $\sim$2 s).

Under certain conditions it is possible to detect emission from the N$_2^+$ excited state ions (first negative system, FNS). Most of the emission bands for this transition overlap with the SPS bands, as shown in Fig. 8.4B. The line, which can be unambiguously assigned to the FNS is at 391 nm. It has therefore been used as a main indicator for the presence of molecular N$_2^+$ ions in the plasma.

The radiative lifetimes of the N$_2$(B) and N$_2$(C) states are relatively short, i.e. 9.1·10$^{-6}$ s and 3.7·10$^{-8}$ s, respectively [157,158]. Radiative de-excitation of both species occurs therefore at the place where they are produced, which is also most probably the case for the N$_2^+$ and atomic N excited state species. The N$_2$(C) system is produced in the discharge region, i.e. in the nozzle or at a short distance from it (~0.5–1 cm), where electrons still have a significant energy to excite the N$_2$(C) states. The plasma in this region has a “whitish” color due to the UV-emission of the SPS.
Fig. 8.4. **A)** Emission spectrum of the N\(_2\) plasma at a RF-power of 100 W and gas flow rate of 100 sccm. The emission band corresponding to the vibrational-rotational transitions of the first positive system (FPS) and second positive system (SPS) are marked. **B)** Emission bands of the second positive system of N\(_2\) and of the first negative system of N\(_2^+\) (FNS).

The N\(_2(B)\) states can also be produced by electron excitation in the discharge region (i.e. in the vicinity of the nozzle) or by de-excitation of the N\(_2(C)\) states. However, the N\(_2(B)\) states are also produced by recombination of atomic nitrogen species [159-166]. The ground state atomic nitrogen species have a relatively long life-time in the plasma, because their recombination is a three-body process [166,167]. The recombination may occur at a significant distance from the nozzle, resulting in the formation of N\(_2(B)\) species and their subsequent radiative de-excitation. The FPS emission is therefore observed not only in the vicinity of the nozzle, but also at a significant distance from it (~ 5 cm, see for example the
pictures in Fig. 8.5C). This results in the appearance of the characteristic orange afterglow plasma plume, which can be used as an indicator for the presence of atomic nitrogen. It has been suggested that the recombination of atomic N is the predominant contribution to the FPS emission [166], which is also in agreement with our studies on the N2 and NH3 RF-plasmas. The intensity of the FPS emission was therefore used for the qualitative estimation of the atomic nitrogen concentration in RF-plasma. This is very important, as there is no other direct possibility with OES to perform a quantitative estimation of the concentration of atomic N.

**Fig. 8.5.** A, B) Variation of the emission intensity as a function of the RF-power for the SPS and FPS bands, respectively. C) Evolution of the plasma plume at different RF-powers.

### 8.3.1. Effect of the RF-power

Optical emission spectra and photographs of the nitrogen RF-plasma plumes at different RF-powers are shown in Fig. 8.5. The overall emission intensity increases with increasing the
RF-power due to the larger excitation energy applied to the plasma (Fig. 8.5C). However, the relative increase of the intensity is different for the different emitting systems. For example, the intensity of the FPS emission measured at 659 nm (Fig. 8.5B) increases approximately by a factor of 2.0 when the RF-power is increased from 50 to 200 W, whereas the corresponding ratio for the SPS measured at 337 nm is ~2.9, and ~9.2 for the FNS (spectral line at 391 nm) (Fig. 8.5A). The observed difference in the plasma emission can be attributed to the different formation and excitation energies for the excited state species. The ionization energy to form $N_2^+$ ions is 15.6 eV (Eq. 8.1) and the excitation energy for $N_2^+$ is 18.7 eV (Table 8.1), which is considerably higher compared to the excitation energy of 11.1 eV for $N_2$ molecules (Table 8.1). The increase of the RF-power results in an increase of the average energy of the electron gas in the plasma, resulting in a higher probability for more energetic reactions such as ionization and formation of excited $N_2^+$ ions.

The most important plasma species for N incorporation into the growing films are nitrogen atoms which occupy empty anionic positions in the crystal structure during film growth. Fig. 8.5 shows, that the relative intensity of FPS lines increases with increasing RF-power in the range 50–200 W, which indicates an increase of the atomic N ground state species concentration. Higher atomic nitrogen concentration in the plasma should result in a larger nitrogen content in films grown by RF-plasma assisted PLD. However, the actual nitrogen content in these films, as determined by XPS, decreases with increasing RF-power (Fig. 7.6B). This can be due to an increase of the energy delivered by excited state species from the RF-plasma beam to the surface of the growing film, causing a preferential desorption of the nitrogen atoms. This indicates that at high RF-powers desorption of N from the film can become the prevailing process compared to the advantage of getting more atomic N in the plasma.

8.3.2. Effect of the flow rate

Optical emission spectra and photographs of the nitrogen RF-plasma plumes at different flow rates are shown in Fig. 8.6. The plasma plume becomes more confined with an increase of the nitrogen flow rate. At the same time the extension length of the plasma increases for the flow rates from 50 to 150 sccm, but a further increase of the flow rate to 200 sccm results in a different appearance of the plasma plume. It appears to be more confined and changes its color to more “whitish”. The observed changes in the optical appearance of the plasma can be explained by changes of the concentration of different excited state species at different flow rates.
Fig. 8.6. A, B) Variation of the emission intensity as a function of the N\textsubscript{2} flow rate for the SPS and FPS bands, respectively. C) Evolution of the plasma plume at different N\textsubscript{2} flow rates.

The emission intensity of the SPS does not change significantly within the studied flow rate range (see e.g. the line at 337 nm in Fig. 8.6A). The intensity of the FNS (line at 391 nm in Fig. 8.6A) decreases at the flow rates > 100 sccm. The FPS system exhibits an abrupt drop of the emission intensity at the flow rate of 200 sccm. The observed decrease of the FNS emission can be explained by a decrease of the average energy of the bombarding electrons with an increase of the flow rate, as the gas-plasma mixture spends less time in the discharge cavity before being ejected into the deposition chamber. The concentration of the most energetic electrons is especially decreased. This leads to a significant depletion of the plasma processes that require a high activation energy, i.e. ionization of N\textsubscript{2} molecules and consecutive excitation of the formed N\textsubscript{2}\textsuperscript{+}. The FNS emission intensity decreases therefore.
For processes with smaller activation energies, e.g. excitation of N\(_2\) neutral molecules and formation of atomic N species, the change of the flow rate from 50 to 150–200 sccm has no considerable effect, as the intensity of the corresponding emission systems, i.e. the SPS for the excited N\(_2\) and FPS as indicator for the presence of the atomic N, remains almost constant. As a result, the nitrogen content in the films deposited at a constant RF-power of 100 W does not depend on the flow rate within the range of 50–150 sccm (Fig. 7.6A) due to an almost constant concentration of atomic N ground state species in the plasma. Increasing the flow rate to 200 sccm results in a drastic decrease of the intensity of the FPS emission (Fig. 8.6B and C). This indicates that the concentration of the atomic N in the plume is strongly depleted. Such an abrupt drop is not yet completely understood. One probable reason could be an increased probability of trapping of atomic N early in the plume (i.e. close to the nozzle) via recombination in collisions with N\(_2\) molecules: N + N + N\(_2\) \(\Rightarrow\) N\(_2\) + N\(_2\). The recombination of atomic N species is a three-body process [166,167], which requires the presence of a third species, e.g. N\(_2\), in addition to two N atoms. The probability of N recombination early in the plume therefore increases with increasing the concentration of nitrogen molecules, which is larger at higher flow rates. It would be interesting to confirm this conclusion by measuring the nitrogen content in the corresponding film deposited at 200 sccm. Unfortunately, it was not possible to grow a film of sufficient quality due to the problems with the morphology and crystallinity (see previous chapter).

8.4 Processes and reactions in ammonia RF-plasma

In the ammonia plasma NH\(_3\) molecules are also dissociated and ionized in the RF-discharge cavity via collisions with the high-energetic electrons or plasma species. The primary processes include consecutive de-attachment of two H atoms from the ammonia molecule [168]:

\[
\text{NH}_3 + e \Rightarrow \text{NH}_2 + \text{H} + e \quad (8.5)
\]

\[
\text{NH}_2 + e \Rightarrow \text{NH} + \text{H} + e \quad (8.6)
\]

Then, the formed radicals can undergo further reactions between each other:

\[
\text{NH} + \text{NH} \Rightarrow \text{N}_2 + \text{H}_2 \quad (8.7)
\]

\[
\text{NH} + \text{H} \Rightarrow \text{N} + \text{H}_2 \quad (8.8)
\]

\[
\text{N} + \text{NH} \Rightarrow \text{N}_2 + \text{H} \quad (8.9)
\]

\[
\text{NH}_2 + \text{NH}_2 \Rightarrow \text{N}_2\text{H}_2 + \text{H}_2 \quad (8.10)
\]

\[
\text{NH}_2 + \text{H} \Rightarrow \text{NH} + \text{H}_2 \quad (8.11)
\]
\[ \text{NH}_2 + \text{NH} \Rightarrow \text{N}_2\text{H}_2 + \text{H} \quad (8.12) \]
\[ \text{N}_2\text{H}_2 + \text{H} \Rightarrow \text{N}_2\text{H} + \text{H}_2 \quad (8.13) \]
\[ \text{N}_2\text{H} + \text{H} \Rightarrow \text{N}_2 + \text{H}_2 \quad (8.14) \]

The main result of this sequence of reactions is that NH\textsubscript{3} is mainly converted into a mixture of N\textsubscript{2} and H\textsubscript{2} in the RF-discharge cavity with some intermediate products such as NH\textsubscript{2}, NH, H, N\textsubscript{2}H\textsubscript{2} and N\textsubscript{2}H \[169\].

### 8.5 Ammonia RF-Plasma at different flow rates and RF-powers

A typical spectrum of the ammonia RF-plasma is shown in Fig. 8.7A. The main observed emission lines in the ammonia plasma can be attributed to the bands of the second positive system of N\textsubscript{2} excited-state species: N\textsubscript{2}(C) \Rightarrow N\textsubscript{2}(B), similar to the data reported previously \[168\]. The strongest emission line at about 337 nm overlaps with an emission line at 336 nm for the NH(\(\alpha\)) \Rightarrow NH(\(\lambda\)) transition of the NH radical (Fig. 8.7B), which is one of the most abundant intermediate products in the NH\textsubscript{3} plasma \[170\]. However, a comparison of the relative intensities for the other band of the SPS allows to conclude that the contribution of the NH excited states emission is very small compared to the SPS emission. This suggests that ammonia undergoes an almost complete plasma-induced dissociation in the RF-discharge cavity at the experimental conditions used. The recorded spectra of the NH\textsubscript{3} plasma reveal no atomic H emission (e.g. of the Balmer-\(\alpha\) line at 656 nm), which has been reported elsewhere \[168\].

No significant emission of the N\textsubscript{2} FPS and N\textsubscript{2}\textsuperscript{+} FNS is detected (Fig. 8.7), which is very different to the nitrogen RF-plasma. The absence of the FPS emission and characteristic orange afterglow plasma plume (Fig. 8.8C and Fig. 8.9C) most probably indicates the absence of atomic N in the ammonia RF-plasma \[166, 170\]. The most probable reason for this is quenching of the atomic N species in reactions with H\textsubscript{2} molecules, which are formed in the ammonia dissociation process \[170\]:

\[ \text{N} + \text{H}_2 \Rightarrow \text{NH} + \text{H} \quad (8.15) \]

A similar process can also explain the absence of the FNS emission, i.e. the N\textsubscript{2}\textsuperscript{+} ions may be quenched by H\textsubscript{2} too \[170\]:

\[ \text{N}_2\textsuperscript{+} + \text{H}_2 \Rightarrow \text{HN}_2\textsuperscript{+} + \text{H} \quad (8.16) \]

The absence of atomic N in the ammonia RF-plasma beam is in agreement with the XPS results, which show negligible N content in the films grown with NH\textsubscript{3} RF-plasma, confirming the importance of atomic N species for the nitrogen incorporation into the
growing film. A detailed discussion on the different nitridation possibilities for SrTiO$_3$:N films and comparison between PRCLA and RF-plasma assisted PLD is given at the end of this chapter.

Fig. 8.7. A) Emission spectrum of the NH$_3$ plasma at RF-power of 100 W and gas flow rate of 100 sccm. B) Emission bands of the second positive system of N$_2$ and first negative system of N$_2^+$ (FNS).

The optical emission spectra and photographs of the ammonia RF-plasma plumes at different RF-powers are shown in Fig. 8.8. The main identified emitting system in the plasma is the SPS. The plasma color is therefore “whitish” and the extension length is very small (Fig. 8.8C) compared to the N$_2$ RF-plasma, which has a long orange afterglow plasma plume due to the presence of atomic nitrogen (Fig. 8.5C).
The intensity of the SPS lines increases with increasing RF-power due to a larger amount of electrons with a high energy in the plasma (Fig. 8.8A). At the highest tested RF-power of 200 W very weak lines of the FPS can be detected (Fig. 8.8B). For the N₂ plasma at this RF-power the intensity ratio between the strongest FPS line at 337 nm and the strongest SPS line at 659 nm is about 1/5, whereas for the NH₃ plasma the FPS/SPS intensity ratio is just 1/60, indicating that the presence of the FPS system in the NH₃ plasma even at the largest RF power is negligible.

Optical emission spectra and photographs of the ammonia RF-plasma plumes at different flow rates are shown in Fig. 8.9. The intensity of the observed SPS emission bands decreases gradually with increasing flow rates. This is different to the N₂ RF-plasma, where no decrease of the SPS emission intensity is observed in the flow rate range of 50–200 sccm.
The difference can be attributed to the extensive production of H\textsubscript{2} in the ammonia plasma with increasing flow rate, which quenches the excited states. The general comparison between the N\textsubscript{2} and NH\textsubscript{3} RF-plasmas is performed below. Another possible reason for the rapid decrease of the emission intensity in the ammonia plasma with increasing flow rate is the pressure increase and higher probability of collisional de-excitation.

8.6 Comparison of the performance of the nitrogen and ammonia RF-plasmas in PLD

The analysis of the nitrogen and ammonia RF-plasmas reveals strong differences in their behavior and composition. Fig. 8.2 clearly shows, that the visible part of the nitrogen plasma is much brighter and extends further than for ammonia. The direct comparison of the OES spectra of both plasmas at the same conditions (RF-power of 100 W and gas flow rate of 100 sccm) shows that the intensity of the (SPS) emission bands in the N\textsubscript{2} plasma is a factor of 33 higher than in the NH\textsubscript{3} plasma (Fig. 8.10).

The composition of the N\textsubscript{2} and NH\textsubscript{3} RF-plasmas is also quite different. In the N\textsubscript{2} RF-plasma at least three different excited states can be detected by OES: N\textsubscript{2}(C), N\textsubscript{2}(B) and N\textsubscript{2}\textsuperscript{+}(B) (Fig. 8.4), whereas in NH\textsubscript{3} plasma mainly the N\textsubscript{2}(C) states are detected (Fig. 8.7). Most probably these differences are due to the presence of molecular hydrogen in the ammonia plasma as a result of the plasma-induced dissociation of NH\textsubscript{3}. H\textsubscript{2} molecules can be involved in many processes, acting as a quenching agent for ions, radicals, and excited state species.
The overall emission intensity of the NH₃ plasma is therefore much weaker compared to the N₂ plasma. Another important consequence of the presence of H₂ is that N atoms are also quenched by the formation of NH radicals (Eq. 8.15), which then predominantly recombine into N₂ + H₂ (Eq. 8.7). As a result, the concentration of N atoms in the ammonia plasma is much smaller. This can also be confirmed by the absence of the characteristic long orange afterglow plasma plume and by the absence of the FPS emission in the NH₃ plasma, which is clearly observed in the N₂ RF-plasma.

![Graph](image)

**Fig. 8.10.** Comparison of the intensities of N₂ and NH₃ RF-plasmas at the same conditions (RF-power of 100 W and flow rate of 100 sccm).

The investigations of ammonia and nitrogen RF-plasmas carried out by optical emission spectroscopy helped therefore to understand the difference in the performance of these two plasmas in the RF-plasma assistant PLD better, in particular the fact that a deposition with NH₃ plasma yields films with no incorporated nitrogen. RF-plasma assisted PLD yields generally films with relatively small amounts of incorporated nitrogen compared to PRCLA. To improve the nitrogen content the following optimizations can be applied to RF-PLD with the N₂ plasma:

- Operate at the lowest possible pressure. This would help to decrease the number of collisions in the plasma plume and to preserve the formed N atoms from recombination [170]. Another advantage of using a lower base pressure is a smaller concentration of the residual oxygen in the deposition chamber, which is highly competitive to be incorporated into the growing film.
• The lower RF-power should also be preferable for increasing the nitrogen content in films since there can be a possibility of nitrogen desorption from the surface of the growing film due to a high amount of energy delivered by the RF-plasma beam. In addition, smaller RF-power should improve the crystallinity of the films.

8.7 Nitridation mechanisms of the growing film. Difference between PRCLA and RF-PLD

As mentioned in the previous chapters, PRCLA and RF-plasma assisted PLD yield different anionic composition for the films when they are grown with nitrogen or ammonia as illustrated in Table 8.2. The deposition of SrTiO₃:N thin films by PRCLA with the NH₃ gas pulse yields films with larger nitrogen contents compared to the N₂ gas pulse, whereas deposition by RF-PLD with the NH₃ plasma beam results in a negligible N content in the films. The films deposited by PRCLA are also oxygen deficient, whereas films grown by RF-plasma assisted PLD exhibit no oxygen deficiency.

<table>
<thead>
<tr>
<th>deposition technique</th>
<th>nitridizing source</th>
<th>film composition</th>
<th>N content, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRCLA</td>
<td>N₂ gas pulse</td>
<td>SrTiO₂.89±0.06N₀.05±0.01</td>
<td>0.99±0.16</td>
</tr>
<tr>
<td>PRCLA</td>
<td>NH₃ gas pulse</td>
<td>SrTiO₂.73±0.10N₀.11±0.02</td>
<td>2.31±0.42</td>
</tr>
<tr>
<td>RF-PLD</td>
<td>N₂ RF-plasma beam</td>
<td>SrTiO₃±0.15N₀.03±0.01</td>
<td>0.63±0.12</td>
</tr>
<tr>
<td>RF-PLD</td>
<td>NH₃ RF-plasma beam</td>
<td>SrTiO₃±0.15</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

To understand these differences it is necessary to consider two possible mechanisms of nitridation for the growing films:

1. Plasma-assisted nitrogen incorporation: in N-containing plasmas reactive atomic N species can be formed, which can occupy a vacant anionic position in the crystal lattice of the growing film.

2. Thermal ammonolysis: a film deposition with ammonia sources can result in thermal ammonolysis of the growing films in the time periods between the laser pulses. The efficiency of the thermal ammonolysis during PLD can be much higher compared to the conventional solid-state reaction, because the film lattice is being constructed during the PLD process and each new monolayer of the film is exposed to ammonia. For our deposition conditions about 10-20 pulses are necessary to complete one monolayer of
SrTiO$_3$:N. Thermal ammonolysis during PLD is therefore not diffusion-limited, which is one of the disadvantages of the conventional solid-state reaction. The efficiency of thermal ammonolysis is higher at higher substrate temperatures and lower deposition pressures, at which dissociation of ammonia is facilitated.

The most unexpected difference observed between PRCLA and RF-PLD is that the deposition with the ammonia gas pulse during PRCLA yields films with a higher nitrogen content compared to almost no nitrogen in the films grown with NH$_3$ RF-plasma assisted PLD. To understand this difference we would like to discuss both of the above mentioned nitridation possibilities:

1. For plasma-assisted N incorporation, the presence of the atomic N species at the surface of the growing film is essential. The atomic N species can only be formed in the discharge cavity by RF-induced reactions, while their formation in the RF-plasma beam is not possible. The absence of the characteristic orange plasma plume and FPS emission bands indicates, that there is probably no atomic N species present in the RF-plasma beam. This can be due to quenching of atomic N by H$_2$ molecules or NH$_x$ radicals inside the discharge cavity. The plasma-based nitrogen incorporation is therefore not efficient. The situation is different for PRCLA. In this process, the formation of atomic N species occurs directly in the plasma plume via collisions with highly energetic ablation plume species (Fig. 2.2). Therefore an equilibrium between the formation and quenching of the atomic nitrogen in the whole volume of the plasma plume can be reached. N and NH$_x$ species are most probably present at the surface of the growing film, providing the possibility for the plasma-assisted nitrogen incorporation in PRCLA with the NH$_3$ gas pulse.

2. As it has been shown in this chapter, NH$_3$ is most probably completely dissociated into N$_2$ and H$_2$ in the RF discharge cavity. The ejected RF-plasma beam probably contains no ammonia species and thermal ammonolysis in RF-PLD is therefore also not possible. This can explain the negligible nitrogen content in the films grown with the NH$_3$ RF-plasma beam. The deposition of SrTiO$_3$:N films by PRCLA with the NH$_3$ gas pulse reveals a strong increase of the N content with an increase of the substrate temperature, whereas no significant increase of the N content with increasing substrate temperature was found for the N$_2$ gas pulse (Fig. 4.4). This indicates, that thermal ammonolysis has probably an important contribution to the nitrogen content for the films deposited with the ammonia gas pulse by PRCLA.
The comparison between the \( \text{N}_2 \) and \( \text{NH}_3 \) RF-plasma beams shows, that the deposition with \( \text{N}_2 \) allows to achieve an incorporation of nitrogen into the \( \text{SrTiO}_3: \text{N} \) films. The difference to the \( \text{NH}_3 \) RF-plasma can be explained by the absence of \( \text{H}_2 \) in the nitrogen RF-plasma which quenches the atomic N species. The presence of atomic N in the \( \text{N}_2 \) plasma beam has been confirmed by the characteristic orange afterglow plasma plume and the presence of the FPS emission bands, which are mainly associated to the N recombination process. However, the nitrogen content in the \( \text{SrTiO}_3: \text{N} \) films grown with the \( \text{N}_2 \) RF-plasma beam is smaller compared to the films grown by PRCLA with the \( \text{N}_2 \) gas pulse. This can be attributed to the higher concentration of the atomic N species at the substrate surface in PRCLA, as they are formed in the whole plasma volume, and not only in the RF-discharge cavity, as in the case of RF-PLD. A contribution of thermal nitridation is not possible in both cases.

It is also noteworthy, that all films grown by RF-PLD (with \( \text{N}_2 \) and \( \text{NH}_3 \) plasma beams) exhibit no oxygen deficiency and are insulating, whereas all films grown by PRCLA are oxygen-deficient and conductive. As discussed in Chapter 4, this can be partly attributed to the presence of oxygen impurities in the applied gases and the very high affinity of the growing film to oxygen species. The gas consumption in RF-PLD (about 5 litres at standard conditions) is higher compared to PRCLA (about 2 litres), and the gas purity for RF-PLD may also be lower due to higher probability of gas leaks in the setup. A larger amount of oxygen is therefore delivered as impurity with the gas for RF-PLD, which results in a higher oxygen content compared to PRCLA. This may also have an influence on the decrease of the nitrogen content in RF-PLD due to a competition between oxygen and nitrogen species in the growing films.

Another important factor that may have an influence on the film nitridation is the presence of excited state species at the film surface, which may deliver a significant amount of energy and facilitate the oxygen-nitrogen exchange, e.g. by producing the active N species directly at the film surface or by formation of anionic vacancies, i.e. sites for potential nitrogen incorporation. The growing film in PRCLA is exposed to the plasma during the laser pulse and for some time after it. In RF-PLD with the \( \text{N}_2 \) plasma the films is continuously exposed to the afterglow plasma plume, whereas the \( \text{NH}_3 \) RF-plasma beam is much shorter and does not reach the growing film (Fig. 8.2). This may be another possible explanation for the observed negligible N content in films grown by RF-PLD with an ammonia plasma.
9. DEPOSITION AND CHARACTERISATION OF LaTiO$_{3.5}$N$_x$ THIN FILMS

Substitution of 3 oxygen ions with 2 nitrogen ions in a layered perovskite, e.g. La$_2$Ti$_2$O$_7$, yields a three-dimensional perovskite-type LaTiO$_2$N oxynitride [20,21]. The incorporation of nitrogen results in a reduction of the optical band gap energy, which allows to absorb visible light [21,33]. This has been used to demonstrate the photocatalytic activity of the lanthanum titanium oxynitride powders for water decomposition under visible light irradiation [33,34]. We study the deposition of LaTiO$_{3.5}$N$_x$ thin films by PRCLA and perform their basic characterization. Our previous studies on the SrTiO$_3$:N model system have shown that the most promising conditions for the one-step growth of oxynitrides films with a good crystallinity and high nitrogen content are PRCLA with ammonia for the gas pulse, high substrate temperatures, and high laser fluences. For the present experiments, we have therefore chosen the following experimental conditions:

- Laser fluences in the range of 5–5.5 J·cm$^{-2}$;
- Target-to-substrate distances of ~5.0 cm;
- NH$_3$ and N$_2$ for the gas pulse;
- Substrate temperatures ($T_S$) of 600–700 °C for the deposition with the NH$_3$ gas pulse and 650°C for the N$_2$ gas pulse, respectively;
- MgO(001) and LAO(001) substrates.

All films were deposited from a sintered LaTiO$_{3.5}$ ceramic target. First, the LaTiO$_{3.5}$ powder has been synthesised by a conventional solid-state technique from La$_2$O$_3$ and TiO$_2$ oxides. Then, the formation of the phase-pure LaTiO$_{3.5}$ was confirmed by XRD analysis, and the powder was isostatically pressed and sintered in air at 1500°C for 10 hours. The XRD analysis of the ceramic target revealed the formation of a pure single-phase LaTiO$_{3.5}$ (Fig. 9.1).

The nominal metal-to-anion ratio in LaTiO$_{3.5}$ 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 a selection of the anion over-stoichiometric target was to avoid a large loss of oxygen during the PLD process. As mentioned before, PRCLA yields films with considerable oxygen deficiency [95,96,98]. Therefore, an over-stoichiometric initial oxygen content in the target can help to maintain the desired anionic stoichiometry in the perovskite-type films (i.e. 1:1:3).
Fig. 9.1. XRD analysis of the La$_2$Ti$_2$O$_7$ target confirms formation of a layered perovskite-type structure.

9.1 Phase composition of the LaTiO$_{3-x}$N$_x$ films

The first experiment with the new films was to check their phase composition. For this purpose a series of films deposited on MgO substrates was analysed by grazing incidence XRD. Fig. 9.2 shows the diffraction patterns for this film series.

Fig. 9.2. Grazing incidence diffraction patterns for a series of films grown on MgO substrates in different deposition conditions. The intensity is plotted on a logarithmic scale to enhance the visibility of weak reflections.
The diffraction patterns for all studied films reveal a series of reflections, which corresponds to the orthorhombic perovskite-type structure reported for LaTiO$_2$N [48]. The reflections at $2\Theta$ of 26–29° are due to the substrate holder of the grazing incidence setup. Additionally, some patterns reveal also 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 appropriateness of the target selection with exceeding oxygen content. The perovskite-type films were successfully grown from the La$_2$Ti$_2$O$_7$ target due to the loss of oxygen during the deposition (Fig. 9.3).

![La$_2$Ti$_2$O$_7$ and LaTi(O,N)$_3$](image)

**Fig. 9.3.** Formation of the three-dimensional perovskite-type LaTiO$_{3-x}$N$_x$ from the layered perovskite-type LaTiO$_{3.5}$.

### 9.2 Chemical composition of LaTiO$_{3-x}$N$_x$ films

The chemical composition of the films shown in Table 9.1 was determined by the combination of RBS and ERDA. All films exhibit a significant Ti deficiency, typically about 10 at. % vs. the La content. This is most probably due to the larger atomic mass of La compared to Ti, which probably results in a stronger scattering of Ti species in the plasma plume during deposition. Similar effects have also been observed during pulsed laser deposition of (La,Ca)MnO$_3$ and (La,Ca)CoO$_3$ thin films [95,96], where the concentration of
La in the films was enhanced, whereas the concentration of Ca was depleted (vs. the Mn or Co content). Therefore, RBS analysis of the studied films suggests the formation of Ti vacancies in the $B$-sublattice of the perovskite-type structure $ABO_3$. However, this does not change the film structure, as confirmed by grazing incidence XRD.

<table>
<thead>
<tr>
<th>Table 9.1. Composition and properties of LaTiO$_{3-x}$N$_x$ films deposited by PRCLA.</th>
</tr>
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<tbody>
<tr>
<td>gas pulse</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>NH$_3$</td>
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<tr>
<td>NH$_3$</td>
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<tr>
<td>N$_2$</td>
</tr>
</tbody>
</table>

*(Small font used for crystallographic orientations indicates that this orientation is minor compared to the main orientation).*

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 is lower than in films grown with the ammonia gas pulse at the same substrate temperature, as described in Chapter 4 for SrTiO$_3$:N. However, in the case of LaTiO$_{3-x}$N$_x$ films, the difference ([N]$_{NH_3}$/[N]$_{N_2}$ ≈ 1.2) is not so pronounced, as for SrTiO$_3$:N ([N]$_{NH_3}$/[N]$_{N_2}$ ≈ 2.3), see Table 9.1 and Table 4.1. This is probably related to the higher thermodynamic stability of the perovskite-type LaTiO$_{3-x}$N$_x$ compared to SrTiO$_3$:N, with respect to possible re-oxidation processes. This results in a higher affinity of lanthanum titanate to nitrogen species compared to strontium titanate. It is also noteworthy that the re-oxidation of LaTiO$_{3-x}$N$_x$ can yield two different oxides:

$$\text{LaTiO}_{3-x}\text{N}_x \Rightarrow \text{LaTiO}_{3.5}$$  \hspace{1cm} (9.1);

perovskite $\Rightarrow$ layered perovskite

$$\text{LaTiO}_{3-x}\text{N}_x \Rightarrow \text{LaTiO}_{3.0}$$  \hspace{1cm} (9.2);

perovskite $\Rightarrow$ perovskite
The first reaction requires a larger amount of additional oxygen for the re-oxidation, and it also results in a structural change, which makes it less probable for PLD conditions (due to small amount of available oxygen). The second reaction does not require a structural change. However, the product, LaTiO$_{3.0}$, is thermodynamically not much more preferable compared to the nitrogen-substituted LaTiO$_{3-x}N_x$ since titanium exhibits an oxidation state of $+3$ in LaTiO$_3$, whereas in the oxynitride a mixture of Ti$^{+3}$ and Ti$^{+4}$ is present. Ti$^{+4}$ forms stronger bonds with the anions compared to Ti$^{+3}$, although nitrogen is weaker bonded in the lattice compared to oxygen. The stabilities of the nitrogen-substituted compound and pure LaTiO$_3$ are therefore comparable, resulting in a higher affinity of the growing LaTiO$_{3-x}N_x$ films to nitrogen species, compared to SrTiO$_3$:N.

![Fig. 9.4](image)

**Fig. 9.4.** Substrate temperature dependence of the N stoichiometry factor in the films deposited by PRCLA with the ammonia gas pulse.

The variation of the N content in the films grown with the NH$_3$ gas pulse at different substrate temperatures is shown in Fig. 9.4. 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 [20,21]. Another possibility is the previously discussed additional reaction of thermal ammonolysis of the growing films between laser pulses by NH$_3$ molecules from the background. This results is also similar to SrTiO$_3$:N system, where the same trend has been observed. The largest nitrogen content of $x \sim 0.8$ 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 RF sputtering in N$_2$ [77].
The oxygen content is decreasing with increasing $T_S$ for the same reasons, i.e. it is inversely linked to the N content, as shown in Fig. 9.5. 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 noteworthy, that the overall anionic content in the films is quite close to the ideal value for perovskites of 3 (Fig. 9.5, Table 9.1). This confirms that the loss of oxygen in LaTiO$_{3-x}$N$_x$ films during PLD is balanced by selecting a LaTiO$_{3.5}$ target with a higher oxygen content, and by the nitrogen incorporation, yielding a good overall anionic stoichiometry. The studied LaTiO$_{3-x}$N$_x$ films ($x \sim 0.4–0.8$) reveal mixed titanium oxidation states of +3 and +4. This indicates the presence of free electrons in the conduction band, which consequently results in an electronic conductivity of these films and other characteristic properties, e.g. the dark grayish color due to visible and IR light absorption by the free electrons. This is different to LaTiO$_2$N powder, which remains insulating if the composition is exactly achieved [7].

![Figure 9.5](image.png)

**Fig. 9.5.** Variations of the oxygen, nitrogen and overall anionic stoichiometry as a function of the substrate temperature.

### 9.3 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 [33,34]. It can be interesting to study the influence of the surface orientation, since it can affect photocatalytic properties [14]. 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 mismatch (MgO, LaO, STO). The same approach was tested for LaTiO$_{3-x}$N$_x$. The chosen substrates were cubic MgO(001) with $a = 4.212$ Å and pseudo-cubic LaAlO$_3$(001) with $a = 3.79$ Å. SrTiO$_3$ was not used as a substrate due to its possible reduction during the deposition (see Chapter 6).

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 $c = 7.888$ [48]. 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, as illustrated in Fig. 9.6. In this case the $c$-axis of the film points in the out-plane direction, indicating a (001)-orientation.

![Fig. 9.6. Schematic representation of the epitaxial relationship between the substrates (MgO or LAO) and LaTiO$_2$N. The unit cell of LaTiO$_2$N is tilted by 45° with respect to the substrate $a$-$b$ plane. (The distances are not to scale).](image)

The Θ-2Θ diffraction patterns of the studied LaTiO$_{3-x}$N$_x$ films grown on MgO substrates are shown in Fig. 9.7. 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 (00$X$) series and (112) reflections, indicating that there are two predominant out-of-plane orientations: (001) and (112). 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:

$$LM(MgO) = \frac{\sqrt{2}a(MgO) - a(LaTiO_2N)}{a(LaTiO_2N)} = +6.8\%$$
LaAlO$_3$ substrates have a better lattice matching. Its negative lattice mismatch is about -3.9%, suggesting that this substrate may be potentially better for the deposition of single (001)-oriented films:

$$LM(\text{LaAlO}_3) = \frac{\sqrt{2}a(\text{LaAlO}_3) - a(\text{LaTiO}_2N)}{a(\text{LaTiO}_2N)} \approx -3.9\%$$

![Graph showing XRD diffraction patterns](image)

**Fig. 9.7.** $\Theta$-2$\Theta$ XRD diffraction patterns of LaTiO$_{3-x}$N$_x$ films deposited on MgO substrates. The intensity is plotted on a logarithmic scale to enhance the visibility of weak reflections.

Diffraction patterns of the LaTiO$_{3-x}$N$_x$ films deposited on LAO substrates are shown in Fig. 9.8. These films reveal a series of relatively intense (00X) reflections. However, an addition weak (022) reflections can 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). A good candidate would be SrTiO$_3$ (a = 3.905 Å), which can, as mentioned above, be modified during deposition making it impossible to study the optical properties. Another possibility is the spinel-type MgAl$_2$O$_4$ with an a/2 of 4.04 Å.
Fig. 9.8. Θ-2Θ XRD diffraction patterns of LaTiO$_{3-x}$N$_x$ films deposited on LAO substrates. The intensity is plotted on a logarithmic scale to enhance the visibility of weak reflections.

The out-of-plain unit cell parameters were calculated from the positions of the film reflections. The (00X) series has been used for calculating the $c$ parameter. For the films where additional reflections are observed, i.e. most of the samples, the $a$ and $b$ parameters were estimated from the position of the corresponding reflections using the calculated value of $c$ (assuming $a=b$). All results are summarized in Table 9.1. The $c$ lattice parameter in the studied LaTiO$_{3-x}$N$_x$ (x ~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). There are two parameters, which influence the lattice constants in the studied films:

- The N content, since nitrogen has a larger crystallographic radius compared to oxygen, i.e. $R$(N) ≈ 1.29 Å, $R$(O) = 1.21 Å [117]. A decrease of 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 of the unit cell parameters.

- The Ti oxidation states, since Ti$^{3+}$ and Ti$^{4+}$ have different crystallographic radii, i.e. $R$(Ti$^{3+}$) = 0.81 Å, $R$(Ti$^{4+}$) = 0.745 Å [117]. 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 mixed oxidation state of Ti should therefore exhibit larger unit cell parameters.
The actual unit cell 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. an increase of the cell constants with decreasing N content and an increase due to the mixed Ti oxidation states. This conclusion is valid for the out-of-plane $c$ parameters in all films as well as for $a$ and $b$ parameters in the films deposited on MgO (Table 9.1). The $a$ and $b$ parameters of the films grown on LAO substrates, however, do not follow this trend: they are considerably smaller than in the LaTiO$_2$N reference and other films deposited on MgO (Table 9.1). This result is quite unexpected and may be related to the strong lattice distortion of the film crystallites, which have (011) out-of-plain orientation. This may be due to a bad in-plane matching of the crystal structures between the LAO substrates and the (011)-oriented crystallites of the films. Grazing incidence XRD analysis of these films revealed no detectable phase impurities, therefore excluding the possibility that the observed (022) reflection on the $\Theta$-2$\Theta$ patterns belong to another phase.

### 9.4 Optical properties of LaTiO$_{3-x}$N$_x$ films

In the previous chapters we have discussed 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. 5.2). In this case, the transmittance spectra of the corresponding SrTiO$_3$N films with 1–4 at. % of N reveal an absorption shoulder near the band gap absorption edge (Fig. 5.1). For the LaTiO$_{3-x}$N$_x$ system the situation changes, as the amount of incorporated nitrogen is considerably larger, i.e. 8–16 at. %. The N(2$p$) 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. 5.2). The transmittance spectra of the studied LaTiO$_{3-x}$N$_x$ films are shown in Fig. 9.9. 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, which is due to the presence of Ti$^{3+}$ in the films, as discussed previously. The LaTiO$_{3.5}$ oxide film grown in oxidizing conditions on MgO (orange curve in Fig. 9.9A) exhibits almost a 100% transmittance in this wavelength range, indicating a minor amount of Ti$^{3+}$.

The spectra of the LaTiO$_{3-x}$N$_x$ films clearly reveal a shift of the absorption edge towards longer wavelengths compared to the parent oxide film (Fig. 9.9A). An increase of the nitrogen content results in a stronger shift, indicating 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(2$p$) states was found.

Fig. 9.9. Transmittance spectra of LaTiO$_{3-x}$N$_x$ films deposited on MgO (A) and LAO (B) substrates.

The band gap energies were calculated from the Tauc plots for direct electronic transitions. The results of these calculations are summarized in Table 9.1 and plotted in Fig. 9.10A. 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 considerable 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. On the other hand, 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) [21] due to the smaller nitrogen content in the films. The increase of the nitrogen content in the films results in a gradual decrease of the $E_g$
Similar results have been previously found for Ca$_{1-x}$La$_x$TiO$_{3-x}$N$_x$ powders synthesized by thermal ammonolysis [21]. 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 9.1), which is not yet understood. One possible reason may be the different texture and strain in films grown on MgO and LAO, which may affect the band gap, as discussed in Chapter 1. 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. 9.10B) [21]. This is a quite interesting result, which shows that the composition of the $A$-sublattice in the $A$TiO$_{3-x}$N$_x$ family of perovskite-type titanates has no significant 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. 5.2), 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.

![Fig. 9.10. A) Variation of the optical band gap energies as a function of N content in LaTiO$_{3-x}$N$_x$ films. B) Comparison of the $E_g$ for LaTiO$_{3-x}$N$_x$ films and Ca$_{1-x}$La$_x$TiO$_{3-x}$N$_x$ powders as a function of the N content.](image)

9.5 Conclusions

LaTiO$_{3-x}$N$_x$ films with high nitrogen contents ($x \sim 0.4–0.8$) 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. The deposition with the NH$_3$ gas pulse yields films with larger nitrogen contents compared to the films deposited with the 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, which are predominantly (001)-oriented with a minor (011) orientation. The nitrogen incorporation leads to a considerable decrease of the band gap energy from ~4.0 eV for LaTiO$_{3.5}$ to ~2.4–2.9 eV for LaTiO$_{3-x}$N$_x$ ($x \sim$0.4–0.8) films. This results in a strong visible light absorption at wavelengths below ~500 nm, which can be promising for possible photocatalytic applications as suggested for LaTiO$_2$N powders [33,34]. The band gap energy in LaTiO$_{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 [21].
In this chapter the deposition and properties of another perovskite-type oxynitride with a composition of SrMoO$_{3-x}N_x$ are discussed. These compounds belong to the molybdate family, where an anionic charge compensation due to N incorporation by an increase of the transition metal oxidation state is possible. This is a charge compensation mechanism, which is not realized in the titanate-based materials discussed in this thesis. SrMoO$_{3-x}N_x$ powders with a quite broad range of N contents, ranging from $x = 0.4$ to $1.2$, have been synthesized [25,64,65]. The incorporation of nitrogen results in quite unique properties of these materials, such as a relatively high Seebeck coefficient attributed to the mixed $+4$, $+5$ (and $+6$) oxidation states of Mo [25]. Most studies on SrMoO$_{3-x}N_x$ up to now have been performed on porous compacted powders, suggesting that thin films as dense samples would allow a more accurate measurement of their properties.

Fig. 10.1. XRD diffraction pattern of the sintered SrMoO$_4$ ceramic target in comparison with the reference data from the JCPDS database.

The thin films of SrMoO$_{3-x}N_x$ were deposited from a SrMoO$_4$ ceramic target, which has an over-stoichiometric oxygen content with respect to the perovskite-type structure. The idea of using the over-stoichiometric target was the same as for the previous LaTiO$_{3-x}N_x$ system, i.e. to avoid pronounced losses of oxygen during film deposition and to achieve a final anionic content as close as possible to the ideal value of 3. The SrMoO$_4$ powder was synthesized by co-precipitation from the solutions containing equimolar quantities of Sr(NO$_3$)$_2$ and Na$_2$MoO$_4$. Then the precipitated powder was washed several times with
distilled water (to avoid contamination with Na$^+$ ions) and calcined at 600°C. The calcined powder was then isostatically pressed and sintered in air at 1000°C for 10 hours to achieve a target for PLD. The XRD analysis of the ceramic target revealed the formation of the pure single-phase SrMoO$_4$ (Fig. 10.1).

For the deposition of SrMoO$_{3-x}$N$_y$ thin films the following conditions have been chosen, which yield films with the highest N content, as shown for SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$:

- A laser fluence of 5–5.5 J⋅cm$^{-2}$;
- A target-to-substrate distance of 5.0 cm;
- NH$_3$ and N$_2$ for the gas pulse;
- Substrate temperatures ($T_S$) of 600–700°C for NH$_3$ and 650°C for N$_2$, respectively

SrMoO$_{3-x}$N$_y$ thin films were deposited on MgO(001) and LAO(001) substrates in order to check and optimize the film orientation.

![Grazing incidence diffraction patterns of SrMoO$_{3-x}$N$_y$ thin films deposited on MgO substrates reveal the formation of a cubic perovskite-type phase similar to SrMoO$_3$ (shown as a reference). The intensity is plotted on a logarithmic scale to enhance the visibility of weak reflections.](image)

**Fig. 10.2.** Grazing incidence diffraction patterns of SrMoO$_{3-x}$N$_y$ thin films deposited on MgO substrates reveal the formation of a cubic perovskite-type phase similar to SrMoO$_3$ (shown as a reference). The intensity is plotted on a logarithmic scale to enhance the visibility of weak reflections.

**10.1 Phase composition of SrMoO$_{3-x}$N$_y$ thin films**

Grazing incidence XRD diffraction patterns of the SrMoO$_{3-x}$N$_y$ films grown on MgO substrates are shown in Fig 10.2. The XRD analysis suggests the formation of a perovskite-type phase for all samples with no detectable phase impurities. All reflections are in good
agreement with those reported for the cubic perovskite-type SrMoO$_3$. This result indicates that a significant amount of oxygen is lost during the PRCLA process, which leads to the formation of the perovskite-type SrMoO$_{3-x}N_y$ films from a scheelite-type SrMoO$_4$ target as shown in Fig. 10.3.

![Crystal structures of the SrMoO$_4$ target and SrMoO$_{3-x}N_y$ films.](image)

**Fig. 10.3.** Crystal structures of the SrMoO$_4$ target and SrMoO$_{3-x}N_y$ films.

### 10.2 Chemical composition of SrMoO$_{3-x}N_y$ thin films. Influence of the deposited materials on the anionic composition

The chemical composition of the studied SrMoO$_{3-x}N_y$ films is presented in Table 1. RBS analysis reveals a small molybdenum deficiency in these films, typically ~5–10 % vs. the strontium content. This can be due to the formation of highly volatile MoO$_3$ in the plasma or due to the sublimation of MoO$_3$ from the surface of the growing films. However, once Mo atoms participate in the formation of the SrMoO$_{3-x}N_y$ film, they are “quenched” in the perovskite-type structure. The thermal stability of the SrMoO$_{3-x}N_y$ films at substrate temperatures of 600–650 °C is confirmed by grazing incidence XRD analysis (Fig. 10.2). A further increase of the substrate temperature to 700°C results in the thermal decomposition of the perovskite and an almost complete loss of Mo. The atomic ratio between Sr and Mo in these films is ~0.9/0.1 (Table 10.1), while quantification of the oxygen content was not possible due to the poor quality of the RBS spectra. The grazing incidence XRD pattern of the films reveals no film reflections at all, indicating the formation of an amorphous film.
Table 10.1. Composition, out-of-plain crystallographic orientations and unit cell parameters of SrMoO$_{3-x}$Ny thin films deposited at different conditions.

<table>
<thead>
<tr>
<th>gas pulse</th>
<th>$T_s$, °C</th>
<th>substrate</th>
<th>composition, ±5 at. %</th>
<th>orientations*</th>
<th>$a$±0.01, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>600</td>
<td>MgO(001)</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{1.8}$N$</em>{0.86}$ mixed</td>
<td>4.05</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>650</td>
<td>MgO(001)</td>
<td>Sr$<em>{1.08}$Mo$</em>{0.95}$O$<em>{1.5}$N$</em>{1.07}$ mixed</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>700</td>
<td>MgO(001)</td>
<td>Sr$<em>{1.09}$/Mo$</em>{0.9}$ = 0.9/0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>650</td>
<td>MgO(001)</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{2.3}$N$</em>{0.54}$ mixed</td>
<td>3.99</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>600</td>
<td>LAO(001)</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{1.48}$N$</em>{1.06}$ (001), (111)</td>
<td>4.09</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>650</td>
<td>LAO(001)</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{1.34}$N$</em>{1.19}$ (001), (111)</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>650</td>
<td>LAO(001)</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{2.13}$N$</em>{0.67}$ (001), (111)</td>
<td>4.01</td>
<td></td>
</tr>
</tbody>
</table>

*(Small font used for crystallographic orientations indicates that this orientation is a minor compared to the preferential).

The SrMoO$_{3-x}$Ny films grown on MgO and LAO substrates at the same conditions reveal different anionic compositions. The observed difference is not large and comparable to that for the SrTiO$_3$:N and LaTiO$_{3-x}$Nx films (Fig. 4.3, Table 9.1). However, the SrMoO$_{3-x}$Ny films deposited on MgO exhibit consistently a lower N content and a higher O content compared to the corresponding films grown on LAO (Table 10.1, Fig. 10.4A), whereas for the titanium-based oxynitrides no preference was achieved. The observed consistently higher N content in the SrMoO$_{3-x}$Ny films deposited on LAO substrates compared to MgO can be a statistical feature due to the small number of films grown on each substrate (3 samples). However, it can also be due to a not careful handling of the films deposited on MgO, which were stored in air after the deposition. It has been reported, that SrMoO$_{3-x}$Nx powders ($x>$1) are very sensitive to moisture and loose nitrogen due to red-ox hydrolysis if they are kept not in a dessicator [25]:

$$\text{SrMoO}_{3-x}N_x + \text{H}_2\text{O} \Rightarrow \text{SrMoO}_{3-y}N_y + \text{NH}_3 + \text{N}_2 (x>y)$$  (10.1)

The films grown on LAO were kept in a dessicator, which may explain the observed higher N and lower O content of these films compared to the corresponding films deposited on MgO. The deposition of a larger number of samples is planned for a more accurate estimation of the average N content.

PRCLA allows the deposition of SrMoO$_{3-x}$Ny films with nitrogen contents of up to $x=1.19\pm0.06$. This is considerably higher compared to that in SrMoO$_{2.3}$N$_{0.6}$ films, deposited by conventional PLD with an ammonia background gas [22], and comparable to the highest reported N content of $x=1.19(5)$ in SrMoO$_{3-x}$Nx powders [25]. Fig. 10.4B shows variations of the average anionic content in SrMoO$_{3-x}$Ny films grown at different conditions. For films
grown using NH$_3$ for the gas pulse, the N content increases with an increase of the substrates temperature from 600 to 650°C. The deposition with ammonia yields films with larger N content compared to the N$_2$ gas pulse. The oxygen content follows the opposite trend, i.e. it is lower in films grown with ammonia and decreases with an increase of the substrate temperature. These results are in full agreement with observations for titanium-based oxynitrides.

**Fig. 10.4.** Variation of the nitrogen, oxygen and total anionic content in SrMoO$_{3-x}$N$_y$ films deposited at different conditions.

The overall anionic content in SrMoO$_{3-x}$N$_y$ films ranges from 2.53 to 2.66 for samples grown with the NH$_3$ gas pulse and from 2.80 to 2.84 for films grown with the N$_2$ gas pulse. Thus, a considerable anionic deficiency is observed in these films despite the fact that an oxygen over-stoichiometric SrMoO$_4$ target was used. A lower anionic content in the films grown with the ammonia gas pulse compared to the films deposited with the nitrogen gas pulse is due to the reducing properties of ammonia. This result is similar to SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$ thin films.

The loss of oxygen during the deposition of SrMoO$_{3-x}$N$_y$ is much higher compared to SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$ titanium-based systems (Table 10.2). This indicates that not only the deposition conditions, but also the nature of the depositing material affects the oxygen transport from the target to the growing film. The observed difference between molybdate and titanate systems can be related to the different red-ox stability of these compounds. The titanates are much more stable and have a lower equilibrium coefficient for the oxygen loss reaction ($K_{red}$) than the molybdates:
\[ O_0^* \rightarrow V_0^{\bullet\bullet} + 2e + \frac{1}{2}O_2 \]

\[ K_{red} = \frac{p^{0.5}(O_2) \cdot n^2 \cdot [V_0^{\bullet\bullet}]}{[O_0^*]} \] (10.2)

This results in a larger affinity of the titanate-based growing films to any oxygen species present in the plasma and therefore larger oxygen content in these films as compared to molybdates. The same argumentation and conclusions can be applied to other systems. For example, it is known that the deposition of cobaltate or manganate-based materials by PRCLA yields oxygen-deficient films even when an oxidizing gas pulse and background are used [95,96], whereas similar or even smaller oxygen deficiencies were observed in SrTiO₃:N films grown with the N₂ gas pulse, when no additional oxidizing source is used at all. This can also be explained by the higher stability of titanates against reduction compared to cobaltates or manganates, which results in a higher affinity of SrTiO₃-based film for oxygen. A larger amount of oxygen from the target is therefore incorporated to the growing SrTiO₃:N film. In addition, oxygen may be captured from oxygen impurities in the N₂ used for the gas pulse, as discussed above.

<table>
<thead>
<tr>
<th>target</th>
<th>film composition</th>
<th>transported relative fraction of O, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO₃</td>
<td>Sr₀.⁹₈±₀.₀₃Ti₁.₀₂±₀.₀₃O₂.₈₂±₀.₀₆N₀.₀₅±₀.₀₁</td>
<td>96.3</td>
</tr>
<tr>
<td>LaTiO₃.₅</td>
<td>La₁.₁₅±₀.₀₃Ti₀.₹₅±₀.₀₅O₂.₅₉±₀.₀₉N₀.₅₁±₀.₀₃</td>
<td>74.0</td>
</tr>
<tr>
<td>SrMoO₄</td>
<td>Sr₁.₀₃±₀.₀₃Mo₀.₉₇±₀.₀₃O₂.₂₁±₀.₁₇N₀.₆₁±₀.₁₃</td>
<td>55.2</td>
</tr>
</tbody>
</table>

The difference between the oxygen transport factors for the two studied titanate systems (SrTiO₃:N and LaTiO₃.₅-xNx) can be explained as follows:

1. Losses of a certain amount of oxygen during its partial substitution with a smaller amount of nitrogen results in the formation of a stable perovskite-type LaTiO₃-xNx from the LaTiO₃.₅ target.

2. The LaTiO₃-xNx incorporates a larger amount of nitrogen compared to SrTiO₃:N, since this is favorable for the stabilization of the perovskite-type structure. Therefore, a stronger competition between oxygen and nitrogen species for the vacant anionic sites in the crystal lattice exists, whereas for SrTiO₃:N the growing films have a much higher affinity for oxygen species compared to nitrogen. However, a similar argumentation cannot be used for SrMoO₃-xNy, since the resulting films still contain a large number of anionic vacancies which could have been occupied by O or N (Table 10.2).
10.3 Texture of the SrMoO$_{3-x}$N$_y$ thin films and their unit cell parameters

The parent SrMoO$_3$ oxide has a cubic perovskite-type structure with a unit cell parameter $a = 3.975$ Å. We expected to have a “cube-on-cube” [001]$_\text{film}$/[001]$_\text{substrate}$ growth of N-substituted SrMoO$_3$ films on MgO(001) ($a = 4.212$ Å) and LaAlO$_3$(001) ($a = 3.79$ Å) substrates, similar to SrTiO$_3$:N thin films.

The $\Theta$-2$\Theta$ XRD diffraction patterns of SrMoO$_{3-x}$N$_y$ films grown on MgO and LAO substrates are shown in Fig. 10.5. The deposition on MgO substrates yields films with no predominant out-of-plain orientation. The diffraction pattern reveals several weak reflections, including (011) and (002) (Fig. 10.5A), whereas the deposition on LAO substrates yields films with predominant (001) out-of-plain orientation. The diffraction patterns reveal a series of intense (00$\lambda$) reflections (Fig. 10.5B). There are also weak (111) reflection detected, but their relative intensity is less than 5% compared to the main (002) reflections. The results on the texture analysis of SrMoO$_{3-x}$N$_y$ films grown on different substrates are quite unexpected because the lattice mismatch of the films is smaller for MgO substrates (+4.0 – +5.6 %) compared to LAO (-5.5 – -7.3 %). This indicates, that the negative lattice mismatch in the
case of LAO substrates is more favorable for epitaxial film growth of SrMoO$_{3-x}$N$_y$ films compared to the smaller positive lattice mismatch in the case of MgO substrates.

The out-of-plain unit cell parameters of the studied films are presented in Table 10.1. The lattice constants vary from 3.99 to 4.09 Å, which is larger than in the parent SrMoO$_3$ oxide ($a = 3.975$). The increase of the unit cell parameters in SrMoO$_{3-x}$N$_y$ films compared to SrMoO$_3$ is most probably due to the nitrogen incorporation, as its effective crystallographic radius is larger than for O, i.e. $R$(N$^3$)$=1.29$ Å, and $R$(O$^2$)$=1.21$ Å [117]. Another factor, which strongly influences the cell parameters in perovskites, is the oxidation state of the $B$-cation in $ABO_3$. The chemical composition suggests that the average oxidation state of Mo in the studied SrMoO$_{3-x}$N$_y$ films ranges from +4.1 to +4.3, whereas in SrMoO$_3$ molybdenum exhibits an oxidation state of +4. This indicates the presence of a mixture Mo$^{+4}$ and Mo$^{+5}$ in the films, which should result in a decrease of the lattice constant as Mo$^{+5}$ has a smaller effective crystallographic radius than Mo$^{+4}$, i.e. $R$(Mo$^{+5}$)$=0.75$ Å, and $R$(Mo$^{+4}$)$=0.79$ Å [117]. The increase of the unit cell parameters in SrMoO$_{3-x}$N$_y$ films compared to SrMoO$_3$ suggests that the lattice expansion due to nitrogen incorporation has a stronger effect than the contraction due to the increase of the Mo oxidation state. Similar results have been found for SrMoO$_{3-x}$N$_x$ powders with $x>1$, where the average Mo oxidation state is larger than +5, which show an increase of the unit cell parameter from 3.978 Å to 3.984 Å when the nitrogen content is increased from 1.05 to 1.19 [25].

Pole figure XRD analysis of the films deposited on LAO substrates has been performed to examine the in-plain orientation of these films, which exhibit a preferentially (001)-oriented growth in the out-of-plane direction. Fig. 10.6 shows the Φ-scans for the (011) reflection of the films grown with different conditions. All films reveal four poles at Φ values of 90°, 180°, 270°, and 360° (Fig. 10.6), which confirms the “cube-on-cube” [001]$_{film}$/[001]$_{substrate}$ epitaxial growth. Similar intensities and FWHM for the films grown with the ammonia gas pulse at different substrate temperatures suggests their similar epitaxial quality (Fig. 10.6D). The film grown with the N$_2$ gas pulse reveal slightly broader (FWHM ~6.6°) and less intense poles compared to films grown with the NH$_3$ gas pulse (FWHM ~4.8°). This indicates a slightly lower epitaxial quality of these films deposited with the N$_2$ gas pulse. However, the difference in the pole figures for the SrMoO$_{3-x}$N$_y$ films grown with different gas pulse is not as pronounced as for the SrTiO$_3$:N thin films, for which the deposition with the NH$_3$ gas pulse yields films with high mosaicity and two in-plain orientations (Chapter 4).
Fig. 10.6. A), B), C) Pole figures of the (011) reflection of SrMoO$_{3-x}N_y$ films deposited under different conditions. D) Comparison of poles at $\Phi$ of 90$^\circ$.

10.4 Transport properties of the SrMoO$_{3-x}N_y$ thin films

Three preferentially $c$-axis oriented SrMoO$_{3-x}N_y$ films grown on LAO(001) substrates have been chosen for resistivity measurements in order to minimize the grain boundary effects caused by the mixed out-of-plane orientations which have been observed for samples grown on MgO. The films grown with different gas pulses reveal a large difference of the resistivity values and thermal dependence of the resistivities (Fig. 10.7). Films deposited with ammonia reveal semiconductor-like resistivities, which exhibit a power law temperature dependence in the range of 8–300 K with $\rho \sim T^m$ with $m=1.57$ for a Sr$_{1.03}$Mo$_{0.97}$O$_{1.48}$N$_{1.06}$ film grown at $T_S$ of 600$^\circ$C and $m=1.69$ for a Sr$_{1.03}$Mo$_{0.97}$O$_{1.34}$N$_{1.19}$ film grown at 650$^\circ$C (Table 10.3). The room temperature resistivities for these films are 0.020 Ohm-cm and 0.017 Ohm-cm, respectively. The film deposited with the N$_2$ gas pulse reveals a much lower
resistivity which has a weak dependence on the temperature, i.e. $\rho(300 \text{ K})=6.1 \cdot 10^{-4} \text{ Ohm-cm}$, and $\rho(3\text{K})=5.4 \cdot 10^{-4} \text{ Ohm-cm}$. The large difference in conductivity of the films deposited with the NH$_3$ and N$_2$ gas pulses is quite unexpected and not yet understood. The estimated average Mo oxidation state is nearly the same for all samples (Table 10.3), which may indicate that the charge carrier density should be similar for all films. XRD analysis revealed also no significant differences in the film orientations and mosaicity. This suggests that the epitaxial quality is not responsible for the large difference in conductivity. The observed difference could be due to the different N content in the films, which may change the electronic structure of SrMoO$_{3-x}$N$_y$ (Table 10.3). More investigations have to be carried out in order to explain the transport properties of the SrMoO$_{3-x}$N$_y$ films deposited by PRCLA.

### Table 10.3. Composition, estimated average oxidation state of molybdenum and temperature dependence of the resistivities of SrMoO$_{3-x}$N$_y$ films grown on LAO substrates.

<table>
<thead>
<tr>
<th>gas pulse</th>
<th>$T_s$, °C</th>
<th>composition, ±5 at. %</th>
<th>Mo oxidation state</th>
<th>$\rho$ vs $T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ 600</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{1.48}$N$</em>{1.06}$</td>
<td>4.3±0.3</td>
<td>$\rho \sim T^{-1.57}$</td>
<td></td>
</tr>
<tr>
<td>NH$_3$ 650</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{1.34}$N$</em>{1.19}$</td>
<td>4.2±0.3</td>
<td>$\rho \sim T^{-1.69}$</td>
<td></td>
</tr>
<tr>
<td>N$_2$ 650</td>
<td>Sr$<em>{1.03}$Mo$</em>{0.97}$O$<em>{2.13}$N$</em>{0.67}$</td>
<td>4.3±0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 10.7.** Temperature dependence of the resistivities of SrMoO$_{3-x}$N$_y$ films grown on LAO substrates at different deposition conditions. The reference data for the SrMoO$_{1.95}$N$_{0.05}$ powder [66] and the SrMoO$_{2.3}$N$_{0.6}$ film on LAO substrate [22] are included.
The resistivity of the SrMoO$_{2.13}$N$_{0.67}$ film deposited with the N$_2$ gas pulse is relatively similar to that for the SrMoO$_{2.3}$N$_{0.6}$ film on LAO substrate [22], and much lower than for the SrMoO$_{1.95}$N$_{1.05}$ powder [66] (Fig. 10.7). The films grown with the NH$_3$ gas pulse reveal resistivities comparable to the SrMoO$_{1.95}$N$_{1.05}$ powder at room temperature and significantly higher at low temperatures. A large difference in the resistivity values for SrMo(O,N)$_3$ samples is attributed to the grain boundary effects by many authors [25,64-66].

10.5 Conclusions

SrMoO$_{3-x}$N$_y$ thin films have been deposited by PRCLA. The nitrogen stoichiometry in these films can be varied in the range of ~0.6–1.2 by changing the deposition conditions. The deposition with the NH$_3$ gas pulse yields films with higher nitrogen contents compared to the N$_2$ gas pulse. The N content for the films grown with ammonia increases with an increase of the substrate temperature from 600$^\circ$C to 650$^\circ$C, while further heating to 700$^\circ$C results in a phase decomposition due to a loss of Mo. The total anionic content in all studied films is lower than 3 (e.g. Sr$_{1.03}$Mo$_{0.97}$O$_{1.34}$N$_{1.19}$), which is due to a large loss of oxygen during the deposition process although an oxygen-overstoichiometric SrMoO$_4$ target has been used for the film deposition.

Films grown at the substrate temperatures below 700$^\circ$C exhibit a perovskite-type structure, similar to cubic SrMoO$_3$. The cubic unit cell parameters of the SrMoO$_{3-x}$N$_y$ films (3.99–4.09 Å) are larger compared to SrMoO$_3$ ($a = 3.975$ Å). Films deposited on MgO substrates reveal a mixed oriented growth, whereas deposition on LAO yields films which are predominantly (001)-oriented. The in-plane epitaxial quality of the films grown with the NH$_3$ gas pulse is slightly higher compared to the film deposited with the N$_2$ gas pulse.

Films grown with the ammonia gas pulse reveal semiconductor-like resistivities with resistivity values at room temperature of ~0.02 Ohm-cm. The resistivity of the film deposited with the N$_2$ gas pulse is much lower and has a weak dependence on temperature, i.e. $\rho(300$ K$)=6.1\cdot10^{-4}$ Ohm-cm, and $\rho(3$ K$)=5.4\cdot10^{-4}$ Ohm-cm. The origin of the observed difference is not yet understood.
SUMMARY

Perovskite-type oxynitride thin films have been successfully deposited in a one-step process by pulsed laser deposition and two modifications of PLD, i.e. pulsed reactive crossed beam laser ablation and radio frequency plasma assisted PLD. Materials successfully prepared have been SrTiO$_3$:N, LaTiO$_{3-x}$N$_x$ and SrMoO$_{3-x}$N$_y$. SrTiO$_3$:N has been used as a model system to compare the differently prepared films with the available modifications of PLD. Here, the influence of the different deposition parameters has been investigated with respect to film composition, crystallinity, optical and electrical properties.

PLD equipped with a synchronized gas pulse allows to achieve a higher N content in films compared to conventional PLD. Applying NH$_3$ for the gas pulse in PRCLA yields SrTiO$_3$:N films with an average N content of 2.3±0.4 at.%, which is a factor of ~3.5 higher compared to the N content of 0.6±0.2 at. % in films grown by conventional PLD with an ammonia background. Utilization of N$_2$ for the gas pulse in PRCLA yields films with a lower average nitrogen concentration of ~1.0±0.1 at. % compared to NH$_3$. The amount of incorporated N increases with increasing laser fluence for N$_2$ and NH$_3$ for the gas pulse. The N content in films grown with the ammonia gas pulse increases from 0.8±0.3 to 4.1±0.4 at. % with increasing substrate temperature in the range of 570–720 °C. During the deposition with the nitrogen gas pulse only a small increase of the N content is observed in the substrate temperature range of 580–650 °C. All SrTiO$_3$:N films deposited by PRCLA as well as by conventional PLD are oxygen reduced, i.e. they exhibit an anionic deficiency resulting in the formation of Ti$^{3+}$.

The studied SrTiO$_3$:N films have a cubic perovskite-type structure. Deposition on LaAlO$_3$ and SrTiO$_3$ substrates results in perfectly c-axis oriented films, whereas some of the films grown on MgO reveal a non-perfect out-of-plane orientation due to the relatively large lattice mismatch. The mosaicity of the SrTiO$_3$:N films increases also due to the lattice mismatch in the following order of substrates: SrTiO$_3$ < LaAlO$_3$ < MgO. The films deposited with the NH$_3$ gas pulse reveal a lower epitaxial quality compared to films grown with the nitrogen gas pulse and in vacuum. The unit cell parameters of the SrTiO$_3$:N films are larger compared to bulk SrTiO$_3$ most probably due to the anionic deficiency of these films and N incorporation into the crystal lattice.

Nitrogen incorporation into the crystal lattice of SrTiO$_3$ results in a change of the electronic structure: localized N(2p) levels are formed inside the band gap of SrTiO$_3$:N. The
energy of these levels is about 2.7 eV lower than the bottom of the conduction band. This results in visible light absorption in the range of 367–460 nm, which is not observed for pure strontium titanate. The optical absorption in this region increases gradually with increasing the N content from 0.8 to 4.1 at. %.

All studied SrTiO₃:N films deposited by PRCLA and conventional PLD exhibit an electronic conductivity due to the presence of Ti³⁺ sites. The electron scattering for films deposited on MgO and LaAlO₃ substrates occurs predominantly at grain boundaries. The most important parameter affecting the conductivity of the films is their epitaxial quality, which has a pronounced influence on the electron mobility. However, the film composition that determines the electron concentration is a less important aspect. Homoeptaxial deposition of SrTiO₃:N on SrTiO₃ results in a partial reduction of the substrate during the film growth. As a result, these films reveal transport properties similar to the SrTiO₃₋δ single crystals. The transport properties of reduced strontium titanate based materials can be interesting for various applications. Films could be used as electrically conducting layer in epitaxial heterostructures, for example, in ferroelectric devices, due to their conducting properties and perovskite-type structure, which has a good matching of the lattice parameter with other functional perovskite-type materials. Another possible application is as a semiconducting layer in metal-insulator-semiconductor heterostructures.

The applicability of radio frequency plasma assisted PLD for the deposition of perovskite-type oxynitrides has been tested and the influence of the RF-plasma parameters on the film properties was studied. Preferentially (001) oriented N-substituted strontium titanate films were deposited on MgO(001) substrates using a N₂ RF-plasma beam, while the deposition with an NH₃ plasma results in films with a lower epitaxial quality and a negligible amount of incorporated nitrogen. The N concentration in SrTiO₃:N films deposited using the N₂ RF-plasma varies from 0.2 to 0.7 at. %. These films are insulators and reveal no electronic conductivity as observed in anion deficient N-doped SrTiO₃ films deposited by PRCLA. This may be an advantage for certain application, such as dielectrics and in photocatalysis. Analysis of the NH₃ and N₂ RF-plasma beams has been performed by optical emission spectroscopy, and a possible nitridation mechanism of SrTiO₃ films in radio frequency plasma assisted PLD and PRCLA has been proposed.

The best deposition condition, which allow to achieve epitaxial SrTiO₃:N thin films with the highest possible N content have been applied for deposition of LaTiO₃₋ₓNₓ and SrMoO₃₋ₓNy thin films.
Textured LaTiO$_{3-x}$N$_x$ films with high nitrogen contents ($x \sim 0.4–0.8$) have been grown on LAO substrates by PRCLA from an oxygen over-stoichiometric La$_2$Ti$_2$O$_7$ target used to compensate for the strong oxygen loss during PLD. The films exhibit a perovskite-type structure, similar to orthorhombic LaTiO$_2$N. The nitrogen incorporation results in a considerable decrease of the band gap energy from ~4.0 eV for LaTiO$_{3.5}$ to ~2.4–2.9 eV for LaTiO$_{3-x}$N$_x$ ($x \sim 0.4–0.8$) films. This results in a strong visible light absorption at wavelengths below ~500 nm, which can be promising for possible photocatalytic applications as suggested for LaTiO$_2$N powders.

SrMoO$_{3-x}$N$_y$ thin films have been deposited in a one-step process by PRCLA from a SrMoO$_4$ target. The nitrogen stoichiometry in the films can be varied in the range of $x = 0.6–1.2$ by changing the deposition conditions. Films deposited on MgO substrates reveal a mixed oriented growth, whereas deposition on LaAlO$_3$ yields predominantly oriented thin films. SrMoO$_{3-x}$N$_y$ thin films exhibit an electronic conductivity due to the mixed Mo$^{+4}$ and Mo$^{+5}$ oxidation states. Films grown with the ammonia gas pulse reveal a semiconductor-like resistance with resistivity values at room temperature of ~0.02 Ohm-cm. The resistivity of the film deposited with the N$_2$ gas pulse is much lower and has a weak dependence on temperature, i.e. $\rho(300 \text{ K})=6.1 \cdot 10^{-4}$ Ohm-cm, and $\rho(3 \text{ K})=5.4 \cdot 10^{-4}$ Ohm-cm.

The detailed parametric study on the one-step deposition of perovskite-type oxynitride thin films by PLD and its modifications has allowed to determine the best deposition conditions, which yields epitaxial films with high nitrogen concentrations. These results can be used as basis for the deposition of other perovskite-type oxynitride thin films.
OUTLOOK

The next possible step within this project could be to control the oxidation state of the transition metal. As we have shown, the B-site cation in the perovskite-type oxynitride films as deposited by PLD exhibits always a lower oxidation state than in the parent compound. The decrease of the average titanium oxidation state below +4 in SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$ films results in a pronounced modification of the properties, i.e. appearance of the electronic conductivity and optical absorption of the low-energetic photons due to the electronic transitions within the conduction band. This influences the comparison of the perovskite-type oxynitrides with the parent oxides. To perform correct studies of the influence of nitrogen for oxygen substitution on the properties of perovskite-type oxynitrides it is indispensable to keep the transition metal oxidation state constant unless this kind of substitution is not specifically used to change the oxidation state of the transition metal, like in SrMoO$_{3-x}$N$_x$ oxynitrides. The reduction of the average titanium oxidation state in SrTiO$_3$:N and LaTiO$_{3-x}$N$_x$ films is undesirable for photocatalytic and dielectrical applications, since Ti$^{3+}$ acts as a recombination center for photo-generated electron-hole pairs, which is detrimental for photocatalysis. Ti$^{3+}$ is also responsible for the leakage current in titanate-based dielectrics.

To overcome this problem for SrTiO$_3$:N we propose to use RF-plasma assisted PLD with improved conditions. Although this technique in its present state has yielded a lower N content and a worth epitaxial quality of the films compared to those deposited by PRCLA, the films grown by RF-PLD were insulating indicating the absence of Ti$^{3+}$. To improve RF-PLD a nozzle with a smaller diameter can be used, which would enable a lower flow rate and the utilization of the turbo-molecular pump during deposition instead of the rotary pump. This would also allow to decrease the deposition pressure significantly, which should reduce the recombination rate of N atoms in the RF-plasma beam. As a result, the concentration of the atomic nitrogen species at the surface of the growing film would be higher. A lower deposition pressure would also be an advantage to improve the epitaxial quality of the films.

RF-plasma assisted PLD under improved conditions can be tested for the deposition of the LaTiO$_{3-x}$N$_x$ films in order to avoid a reduction of Ti during the deposition. An alternative approach could be PRCLA with an ammonia gas pulse at higher substrate temperatures, e.s. above 700°C. The substrate temperature has a pronounced influence on the N content (see Fig. 9.4), whereas the overall anionic content is not affected significantly (shown in Fig. 9.5), i.e. the average Ti oxidation state in the films, grown at higher substrate temperatures increases. It is therefore likely that a further increase of the substrate temperature would allow to deposit LaTiO$_2$N films, in which Ti exhibits an oxidation state of +4.
More detailed analysis of the properties of already prepared thin films is required for deeper understanding of the effect of the nitrogen for oxygen substitution in perovskites. The influence of the nitrogen incorporation on the transition metal oxidation state can be studied in more detail by X-ray absorption spectroscopy (XAS). This information can then be used for better explanation of the transport properties of the SrTiO₃:N and SrMoO₃ₓNᵧ thin films. For electrical measurements it is advantageous to grow film on the substrates with a minimal lattice mismatch with the films in order to improve their epitaxial quality and eliminate the grain boundary effects. SrMoO₃ₓNᵧ thin films deposited on MgO and LaAlO₃ substrates have shown strong differences in their electrical properties, probably due to a major contribution of the electron scattering on the grain boundaries. It is therefore necessary to deposit additional films on substrates with a better lattice matching, e.g. SrTiO₃, and study their transport properties.

Films of Ti-based oxynitrides, i.e. SrTiO₃:N and LaTiO₃ₓNₓ, can be tested as model electrodes for water splitting under visible light irradiation. Although thin film exhibit much smaller surface area, compared to powders, epitaxial oriented films can be utilized to evaluate catalytic activity of different crystallographic planes, which is not possible with powders. For this purpose, thin films should be grown on the substrates, which are compatible with the experimental conditions for photocatalytic activity tests, i.e. aqueous media. LaAlO₃ is an appropriate choice, whereas MgO can not be used due to its hydroscopicity.

Detailed parametric study of the influence of the deposition conditions on the composition and crystallinity of the oxynitride thin films grown by PLD has allowed to evaluate the best deposition conditions, under which epitaxial films with high nitrogen concentrations can be obtained. These conditions can be used for deposition of other oxynitride films. One of the potentially interesting systems can be Li₂LaTaNO₆. This material is capable to reversibly intercalate Li ions, which can be utilized in electrodes for Li-ion batteries [171]. N-doped MgO was suggested as a possible insulating ferromagnetic compound for spintronics [172,173]. ZnO doped with nitrogen exhibits p-type electronic conductivity and can be utilized for electrodes in solar cells [174]. For all these applications it is indispensable to deposit and study thin films of the corresponding oxynitrides. Pulsed laser deposition and its modifications can be used for deposition of these complex compounds with partial nitrogen for oxygen substitution. Furthermore, PLD can also be utilized for growth of thin films of other novel materials with anionic substitutions, i.e. oxyfluorides and oxysulphides. This can be achieved by application of NF₃ and H₂S for the reactive gas pulse, respectively.
REFERENCES

Curriculum Vitae

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List of publications related to the thesis:


Publications in preparation:

1. Composition and optical properties of N-substituted SrTiO$_3$ thin films grown by pulsed laser deposition (submitted for publication).

2. Influence of epitaxial quality on electrical conductivity of N-substituted SrTiO$_3$ thin films grown by pulsed laser deposition.

3. One-step deposition and optical properties of LaTiO$_{3-x}$N$_x$ thin films.

Attended conferences:


