TiN-buffered substrates for photoelectrochemical measurements of oxynitride thin films

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Abstract

Developing novel materials for the conversion of solar to chemical energy is becoming an increasingly important endeavour. Perovskite compounds based on bandgap tunable oxynitrides represent an exciting class of novel photoactive materials. To date, literature mostly focuses on the characterization of oxynitride powder samples which have undeniable technological interest but do not allow the investigation of fundamental properties such as the role of the crystalline quality and/or the surface crystallographic orientation toward photo-catalytic activity. The challenge of growing high quality oxynitride thin films arises from the availability of a suitable substrate, owing to strict material and processing requirements: effective lattice matching,

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sufficiently high conductivities, stability under high temperatures and in strongly reducing environments. Here, we have established the foundations of a model system incorporating a TiN-buffer layer which enables fundamental investigations into crystallographic surface orientation and crystalline quality of the photocatalyst against photo(electro)chemical performance to be effectively performed. Furthermore, we find that TiN as current collector enables control over the nitrogen content of oxynitride thin films produced by a modified pulsed laser deposition method and allows the growth of highly ordered $\text{LaTiO}_{3-x}\text{N}_x$ thin films.

Keywords: Solar Water Splitting, Titanium Nitride, Oxynitride, Pulsed Laser Deposition, Photoelectrochemistry

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1. Introduction

Due to the increasing demand of energy and the urgent need to reduce the amount of emitted greenhouse gases, intense research is carried out in the field of sustainable and renewable energy sources. Solar water splitting, also known as artificial photosynthesis, is among the most investigated routes for environmentally sustainable energy production. Artificial photosynthesis is based on the direct absorption of solar light by semiconductor materials with appropriate band gap matching the solar spectrum. The photo-generated electron-hole pairs drive (electro-)chemical reactions to split water into molecular oxygen and hydrogen. The latter can be used as energy carrier, for example in fuel cells.

Since the first report of TiO_2 as photocatalyst by Fujishima and Honda in 1972[1], a great deal of research effort has been devoted to improving the performance as well as the discovery of new materials for photocatalytic water splitting. A plethora of oxides materials were found to be active for solar water splitting and were subject of further investigations, both experimentally[2, 3, 4, 5, 6] and theoretically[7, 8, 9, 10]. Also non-oxide compounds typically used for photovoltaic application were tested towards their activity for solar water splitting[11, 12, 13].

Oxides have typically a large band gap of more than 3 eV, therefore only absorbing UV radiation (about 5 % of the solar spectrum)[14]. A greater portion of the solar spectrum can be captured by lowering the band gap, thus expanding the absorption window. Anion- and/or cation-doping is typically used to modify the electronic structure and as a consequence the optical properties of materials[15, 16, 17, 18, 19, 20]. For many oxides a reduced band gap can be achieved by substituting nitrogen into the oxygen site to form oxynitride materials[21, 22, 23, 24, 25, 26]. The smaller band gap is the result of the hybridization of the O2p and N2p orbitals which is

most likely to create additional available energy levels above the valence band of the original oxide, while leaving the conduction band unaffected. Density functional theory calculations for BaTaO₂N support this hypothesis[27].

However the size of the band gap of the photocatalyst is just one of the issues
30 to be addressed to make solar water splitting efficient. Beside the chemical and structural stability in operating condition, the semiconductor used as photocatalyst should also offer high mobility of the photo-generated charge carriers to reduce charge recombination. Moreover, for the (electro-)chemical reaction to proceed, the band edges of the valence and conduction bands have to straddle both, the O₂ and H₂
35 evolution potentials. Fulfilling all these requirements remains a challenge.

Photocatalysts are usually characterized using powder samples[28, 29, 30, 20]. However, with powders it is difficult to probe specific material properties, such as the effect on the photocatalytic activity of the crystalline quality and/or surface crystallographic orientation. Moreover, in the specific case of oxynitride powders, the
40 amount of incorporated nitrogen is usually set by the fabrication procedure which hampers the possibility of probing the effect of different nitrogen contents on the performance of the photocatalysts. Highly textured or epitaxial thin films can be used as model system to address these challenges.

Different experimental approaches are used to probe the photocatalytic activity
45 of materials. Using powders one can measure directly the amount of gas produced as a consequence of specific photo-induced chemical reactions[24, 31]. Alternatively, the powders can be dispersed in aqueous solution with an organic dye that decomposes changing its absorbance as a result of the chemical reactions occurring at the photocatalyst under illumination[32, 33]. These techniques generally belong to the
50 family of so-called photocatalytic characterizations. However, for the same illuminated area of the photocatalyst, the active surface area is orders of magnitude smaller

using thin films compared to powders. As a consequence, the yield per unit area is much smaller for thin films than for powders hindering a direct photocatalytic characterization since the effect of the photo-induced reactions could be difficult to follow.

55 Therefore, a photoelectrochemical (PEC) study is the only available technique to investigate thin film photocatalysts towards solar water splitting.

For PEC characterization the photocatalyst in contact with a current collector is immersed into an appropriate electrolyte solution and acts as the working electrode. A Pt wire is typically used as the counter electrode. In the typical 3-electrode
60 configuration, the applied potentials between working and counter electrodes are referred to a reference electrode (Ag/AgCl or hydrogen reference electrode). The photo-generated electrons and holes in the semiconducting photocatalyst reach the current collector and the interface with the electrolyte, respectively. The latter allow oxygen evolution at the photocatalyst surface producing positively charged ions that
65 migrate into the electrolyte toward the working electrode. The electrons flow through an external circuit to the counter electrode where they enable hydrogen evolution. The measurement of the electronic photocurrent density (i.e. per unit of illuminated surface area) is a measure of the photocatalytic activity of the sample under investigation. Since relatively small current densities can be measured with high accuracy,
70 this technique is very well suited for thin films studies if an appropriate conducting substrate or buffer layer for the growth of the photocatalyst is available.

In the literature only a few studies using thin films for PEC measurements have been reported, for example $\text{Bi}_2\text{FeCrO}_6$ to investigate the effect of the ferroelectric polarization on the photoelectrochemical performance[34] and BiFeO_3 to test to-
75 wards photoelectrochemical activity[35]. Concerning oxynitrides, thin films of these materials can be grown using different deposition methods, for example sputtering (TiO_xN_y [15, 36] and $\text{LaTiO}_{3-x}\text{N}_x$ [37]), pulsed laser deposition ($\text{LaTiO}_{3-x}\text{N}_x$ [38],

TiO_xN_y[17], BaTaO₂N[39]) and chemical vapor deposition (TiO_xN_y[40, 41]). However, the reported studies of their photocatalytic activity are quite rare. PEC measurements of polycrystalline titanium oxynitride films were performed using transparent conducting glasses as substrates[36]. The influence of the crystalline quality on the photo-activity of LaTiO_{3-x}N_x was studied using Nb-doped SrTiO₃ as a substrate and IrO₂ as co-catalyst[37]. In both cases, reactive magnetron sputtering was applied to grow the oxynitride films.

For this work, a modified pulsed laser deposition method was selected to further investigate the effect of the nitrogen content and different surface orientations on the PEC performance. Based on our previous studies, highly ordered oxynitride thin films with different nitrogen content can be grown starting from a target of the original oxide, thus making this method potentially applicable to any oxynitride material circumventing the need of an oxynitride target whose preparation is often difficult[38, 42]. Additionally, this technique allows a systematic variation of the nitrogen content in the films, which was quantitatively investigated to minimize the presence of potential anionic vacancies.

However using this method, the strongly reducing environment and the high temperature needed for a sufficient incorporation of nitrogen into the oxynitride thin film[37, 38], preclude the use of several materials as current collector. This study aims to identify a stable and conducting material that allows the epitaxial growth of oxynitride photocatalyst thin films for PEC characterization.

As representative example of oxynitride materials for the photocatalyst, the orthorhombic perovskite LaTiO_{3-x}N_x ($0 < x < 1$) is selected[43].

2. Experimental section

2.1. Oxynitride thin film deposition

LaTiO_{3-x}N_x thin films have been grown on different substrates using a modified pulsed laser deposition (PLD) method called Pulsed Reactive Crossed-beam Laser Ablation (PRCLA). During PRCLA suitable gas jets are injected into the vacuum chamber through a nozzle valve triggered by the laser pulses and crossing the ablation plume near the surface of the target. The specific features of this technique are described in details elsewhere [44], as well as a comparative study of the unique characteristics that distinguish PRCLA from conventional PLD[45]. Briefly, during PRCLA pulsed gas jets synchronized with the laser pulses are injected through a piezoelectric nozzle valve into the deposition chamber near the ablation spot at the target. Here the gas jets cross the ablation plume. By appropriately tuning the delay time (with respect to the laser pulse) and the opening time of the nozzle valve, it is possible to create a temporary strong pressure gradient along the direction of the expansion of the ablated material. The relatively high pressure at the very early stage of the propagation of the ablated species allows efficient physicochemical interaction with the gaseous environment. Moving away from the target toward the substrate the partial pressure rapidly decreases hindering further physicochemical evolution of the plasma species. Using an oxide target of La₂Ti₂O₇ and NH₃ for the pulsed gas jets, nitrogen can effectively be substituted into the oxygen sites allowing the growth of LaTiO_{3-x}N_x thin films[38].

For this work, a La₂Ti₂O₇ target for laser ablation was prepared in our laboratory as a sintered ceramic rod. The vacuum chamber was evacuated to a base pressure of about 10⁻⁶ mbar. For LaTiO_{3-x}N_x deposition a N₂ background partial pressure of 8.0 × 10⁻⁴ mbar was set and NH₃ was used for the pulsed gas jets. A delay time

of 30 μs was set between the opening of the nozzle valve and the laser pulse, while the opening time of the nozzle valve was 400 μs for each laser pulse. The laser (KrF excimer laser with $\lambda = 248 \text{ nm}$ and pulse width of 30 ns) was operated at a repetition rate of 10 Hz. In this condition, the average pressure in the vacuum chamber raises
130 from the N_2 background pressure up to about $1.8 \times 10^{-3} \text{ mbar}$. $\text{LaTiO}_{3-x}\text{N}_x$ thin films were fabricated using different laser fluences from 2 J cm^{-2} to 4 J cm^{-2} on a spot size of about 1 mm^2 with a target-to-substrate distance of 50 mm. Single crystal (100)-oriented SrTiO_3 and LaAlO_3 , and (110) YAlO_3 were used as substrates. The substrates were clamped on a Si plate with the same size, which was then heated
135 resistively up to 870°C . The temperature was measured with a pyrometer using 0.7 as the value of emissivity.

2.2. The current collector

For photoelectrochemical (PEC) characterization an electronic conducting substrate or buffer layer is required for the growth of $\text{LaTiO}_{3-x}\text{N}_x$. Beside the conducting
140 substrate Nb-doped SrTiO_3 used in [37] for the growth of oxynitride films by sputtering, the use of thin SrRuO_3 and TiN buffer layers was investigated.

SrRuO_3 thin films were grown by PLD on (100)-oriented SrTiO_3 . For the deposition, an O_2 partial pressure of 0.1 mbar was set. A SrRuO_3 disc target was ablated using the KrF excimer laser at a repetition rate of 4 Hz and a laser fluence
145 of about 1.8 J cm^{-2} . The target-to-substrate distance was 50 mm and the substrate was heated up to 800°C .

TiN thin films were grown by DC reactive sputtering (Mantis Deposition Ltd, UK, Model: QPrep) of a Ti target in an Ar/N_2 gas mixture. (100)-oriented MgO substrates were used setting a temperature of 700°C of the heating stage. From a
150 base pressure of $2.0 \times 10^{-7} \text{ mbar}$, gas flows of 35 and 15 sccm of Ar and N_2 respec-

tively were let into the vacuum chamber reaching a pressure of 2.9×10^{-3} mbar. The sputtering process was performed by applying an accelerating voltage of 446 V which set a current of about 300 mA.

LaTiO_{3-x}N_x thin films were then grown by PRCLA on the previously mentioned
 155 template platforms using the deposition parameters reported above.

2.3. Photoelectrochemical characterization

PEC measurements were performed using LaTiO_{3-x}N_x thin film grown on TiN-buffered MgO substrates in a three-electrode configuration. The oxynitride film on TiN-buffered MgO was used as the working electrode, while a Pt wire was the
 160 counter electrode. The third electrode was a Ag/AgCl reference electrode in 3 M KCl aqueous solution. The TiN current collector was electrically connected to the electronics using Cu wires and Ag paste.

The samples were placed in the PEC cell[46] for front-side illumination, since TiN is not transparent. The cell was filled with an aqueous solution of 0.2 M sodium
 165 borate (H₃BO₃ and Na₂B₄O₇ · 10H₂O) buffered at a pH of 9 as electrolyte. An insulating varnish was used to get the electrolyte in contact with the sample under investigation only on a selected area of the LaTiO_{3-x}N_x film surface.

The samples were illuminated with a 300 W Xe lamp (LOT-Oriel) equipped with an UV cutoff filter ($\lambda = 420$ nm). The light intensity was adjusted to 100 mW cm⁻².
 170 A rotating shutter was used to alternately measure the dark current (no light on the sample) and the photocurrent. A Versastat 4 potentiostat was used to measure the photocurrent and a scan rate of 10 mV s⁻¹ was used for linear scan voltammetry measurements.

2.4. Thin film characterizations

175 The chemical composition of the thin films was determined by Rutherford Backscattering measurements using a 2 MeV ^4He beam and a silicon PIN diode detector under an angle of 168° towards the incident beam. The collected data were analyzed using the RUMP program[47]. The nitrogen-to-oxygen ratio was determined by Heavy-Ion Elastic Recoil Detection Analysis (ERDA) using a 13 MeV
180 ^{127}I beam and a combination of a time-of-flight spectrometer with a gas ionization detector[48]. In the composition depth profile a region between 20 nm and 100 nm was chosen for integration of the oxygen and nitrogen signal. The surface and the interface to the conducting substrate or buffer layer were carefully excluded. The crystalline properties were obtained using a Bruker-Siemens D500 X-Ray diffractometer.
185 Transmittance data were collected with a Cary 500 Scan UV-Vis-NIR spectrophotometer in the wavelength range of 200 nm to 1000 nm (6.20 eV to 1.24 eV). For the calibration of the deposition rates, the thicknesses of the samples were measured by surface profilometry (Dektak 8, Veeco Instruments). The surface morphology was investigated using a Zeiss Supra VP55 Scanning Electron Microscope with an in-lens
190 detector.

3. Results and discussion

3.1. The current collector

To collect the photo-generated charge carriers, the photocatalyst has to be in contact with an electronic conducting electrode. The material used for such a current collector has to be chemically stable during the oxynitride film growth, i.e. at temperatures as high as about 800 °C and in NH₃ environment. To enable the investigation of the potential effects of the crystalline properties and surface orientation on the PEC performance, the conducting material has to be lattice matched for an epitaxial growth of the oxynitride thin film with good crystalline quality.

Two different experimental approaches can be followed, either the use of a conductive substrate or the use of a conducting thin film as seed layer for the growth of the oxynitride photocatalyst.

Among the suitable electronic conducting substrates, single crystal Nb-doped SrTiO₃ (STO) show very good lattice matching to LaTiO_{3-x}N_x (the STO lattice parameter is about 3.90 Å (ICSD Coll.Code: 94573), while for LaTiO₂N the lattice constant is in the range of 3.95 Å (ICSD Coll.Code: 168551), which can vary depending on the nitrogen content). These substrates were successfully used in Ref. [37] for the growth and characterization of epitaxial LaTiO_{3-x}N_x films made by sputtering using a target of the cold pressed oxynitride powders. With our experimental conditions, it was not possible to obtain single phase LaTiO_{3-x}N_x thin films on Nb-doped or un-doped STO substrates by PRCLA. The thin films grown on STO were (001) epitaxially oriented with the substrates, but the LaTiO_{3-x}N_x diffraction reflexes appear as the result of the overlapping of multiple reflexes, as can be seen for example in the (400) diffraction reflex of LaTiO_{3-x}N_x in Fig. 1. This may be explained due to the presence of multiple phases of LaTiO_{3-x}N_x layers with different nitrogen content

in the thin film. It has been shown that STO substrates can easily lose oxygen in reducing environment and exchange oxygen with the film growing on its surface[49]. The substrate itself can indeed provide a large part of the oxygen content of the growing film. When an oxynitride film grows on STO, this effect is particularly
220 detrimental since oxygen atoms from the substrate can be incorporated into the film hindering the nitrogen substitution. In addition, the Nb-doped STO substrates showed strongly reduced conductivity after the oxynitride deposition, suggesting a decomposition of this material under the film growth conditions differently to what was observed for sputtering[37].

225 Concerning the use of conducting seed layers, for the conventional characterization of powder samples glass substrates coated with transparent conducting oxides are used to collect the photo-generated charge carriers. Typical coatings are made of aluminum-doped zinc oxide, fluorine-doped tin oxide or indium tin oxide. Polycrystalline TiON films were grown by sputtering at relatively low temperature ($> 250\text{ }^{\circ}\text{C}$)
230 on these kind of conducting glasses[36]. These commercially available substrates are amorphous, thus only polycrystalline films can be obtained. Moreover, at the high temperatures required for the growth of oxynitride films with high crystalline quality ($> 700\text{ }^{\circ}\text{C}$), transparent conducting oxides undergo a thermal decomposition and their conductivity significantly decreases[50]. This makes these materials unsuitable
235 for our purpose even if coatings with high crystalline quality were used.

Thin films of non-transparent electronic conductive oxides could also be used as current collectors. Unfortunately, most of the electronic conducting oxides show suitable electronic conductivity only at relatively high temperatures. But the main problem here is that we could not find any electronic conducting oxide able to provide
240 the required physicochemical stability during the oxynitride growth condition using PRCLA of the native oxide target, i.e. a strongly reducing environment at high

temperatures. Literature reports that SrRuO_3 -buffered substrates were used for the growth of $\text{BaTaO}_{3-x}\text{N}_x$ [39]. This was achieved by conventional PLD using the oxynitride material as the target and an O_2/N_2 gas mixture, i.e. in oxygen-containing
245 environment. For this work we also have attempted the use of SrRuO_3 . Thin films of this material were epitaxially grown on STO substrates at $> 800^\circ\text{C}$ in an oxygen partial pressure of 0.1 mbar. After XRD analysis, the as-grown films were heated up in vacuum at a temperature of about 600°C . Such a thermal treatment in vacuum was enough to decompose the SrRuO_3 film, as revealed by XRD analysis, confirming
250 the poor stability of this material in low oxygen-containing environment at high temperature, as already reported in the literature[51, 52]. In the specific case of $\text{LaTiO}_{3-x}\text{N}_x$, a sufficient nitrogen substitution by PRCLA using the native oxide target requires a gaseous environment with very low oxygen partial pressure (using N_2 and NH_3). This precludes the use of SrRuO_3 as seed layer.

255 Other possible alternative current collectors are thin films of noble metals, such as Pt or Au, which also have the advantage of a cubic crystalline structure with lattice parameter similar to that of $\text{LaTiO}_{3-x}\text{N}_x$ ($3.92\text{ \AA}$ for Pt (ICSD Coll.Code: 180880), $4.08\text{ \AA}$ for Au (ICSD Coll.Code: 52700), and about $3.95\text{ \AA}$ for LaTiO_2N (ICSD Coll.Code: 168551), as an example). However, at the high temperatures
260 required for the oxynitride growth, noble metals show very poor adhesion on the polished surface of single crystal substrates[53] and typically dewet the substrate surface. The use of additional adhesion layers (typically Ti or Cr are used) would be necessary. Beside the additional complication of the growth of a further layer, the typical metals used to aids Pt or Au adhesion show different crystalline structures
265 compare to Pt and Au, thus precluding the growth of current collectors with high crystalline quality which is a fundamental prerequisite for the growth of high quality epitaxial oxynitride films.

In a different approach, the group of metal nitrides comprises electronically conducting compounds that are known to be chemically very stable over a wide range of chemical environments and temperatures. Within these materials TiN was chosen. Besides being a good electronic conductor, this material has a lattice parameter of about 4.24 Å (ICSD Coll.Code: 656836) which is very similar to that of single crystal MgO substrates (about 4.21 Å, ICSD Coll.Code: 52026). Thus in principle it is possible that TiN epitaxial layers could be grown on MgO with very high crystalline quality and may become a suitable seed layer for the growth of highly textured LaTiO_{3-x}N_x films.

The most important issue is the lattice mismatch between LaTiO_{3-x}N_x and TiN which is $(a_{\text{LaTiO}_2\text{N}} - a_{\text{TiN}}) / a_{\text{TiN}} \approx -6.8\%$. This is a very large value that cannot be elastically accommodated at the interface between the two materials. However, the literature reports examples of high quality STO films (which have similar crystal structure and lattice parameter to LaTiO₂N) grown on MgO substrates showing cube-on-cube epitaxial relation and small degree of misalignment between adjacent crystallites[54, 55]. Even examples of multilayered epitaxial heterostructures of TiN + MgO + STO grown on (100)-oriented Si wafers are reported [56, 57, 58], showing that materials like MgO and TiN on one side and STO, thus potentially also LaTiO_{3-x}N_x, on the other side can indeed be coupled in highly ordered epitaxial heterostructures.

The large interfacial lattice mismatch can in fact be accommodated at the interfaces in some cases by introducing misfit dislocations that fully relax the excess stress still preserving the epitaxial relation. Examples of such a mechanism can be found in [59, 60] where highly textured epitaxial films of ceria-based materials were grown on MgO substrates via an almost continuous line of interfacial misfit dislocations capable of adjusting a lattice mismatch as large as 29%.

3.2. The growth of the oxynitride photocatalyst on the selected current collector

295 On the basis of these considerations, we attempted the growth of $\text{LaTiO}_{3-x}\text{N}_x$ on TiN-buffered MgO substrates. Fig. 2a shows the $2\theta/\theta$ scan of one samples. As expected the TiN layer grew epitaxially oriented with the substrate. On the contrary, under the selected growth parameters, the oxynitride film clearly shows multiple crystallographic orientations. Further, small shifts toward smaller 2θ angles of the
300 $\text{LaTiO}_{3-x}\text{N}_x$ peak positions can be measured in Fig. 2a compared to the literature values of the stoichiometric LaTiO_2N composition (ICSD Coll.Code: 168551). This difference indicates slightly larger out-of-plane lattice parameter which could be explained by a lower nitrogen content ($x < 1$).

The cross sectional Scanning Electron Microscopy (SEM) micrograph in Fig. 2b
305 shows a well-defined interface between $\text{LaTiO}_{3-x}\text{N}_x$ and TiN. At the applied magnification the morphology of the TiN layer looks uniform without evidence of clear grain separation, while the oxynitride film shows the typical features of polycrystalline morphology with columnar grains of about 50 nm in diameter elongated along the substrate surface normal. This columnar micro-morphology is often observed
310 for thin films grown by PLD. The thicknesses measured by SEM for the two layers (about 230 nm for $\text{LaTiO}_{3-x}\text{N}_x$ and 65 nm for TiN) are in good agreement with the values expected from the calibration of the deposition rates.

Before addressing the issue of improving the crystallographic properties of the oxynitride film, we focused on the analysis of its chemical composition performed by
315 Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA).

Fig. 2c shows an RBS spectrum of a $\text{LaTiO}_{3-x}\text{N}_x$ film. At high energies, the first peak corresponds to La, the heavy element, present in the oxynitride film. At intermediate energies, signals from Ti were detected and since Ti is in both layers, a

320 double peak is formed, where the right part at higher energies belongs to the outer $\text{LaTiO}_{3-x}\text{N}_x$ layer and the left part at lower energies belongs to the buried TiN current collector. The different yields reflect the different Ti content of the two materials.

The thicknesses of the two layers of $\text{LaTiO}_{3-x}\text{N}_x$ and TiN as evaluated by the La and Ti peaks shown in Fig. 2c are in good agreement with the SEM cross section
325 measurement of Fig. 2b. Finally, at low energies the lighter elements are detected; Mg and O from the substrate, but also O and N from the current collector and the oxynitride photocatalyst.

For a precise investigation of the composition of the oxynitride, ERDA measurements are required to determine the nitrogen-to-oxygen ratio (N/O) which turned
330 out to be about 0.36. This value compared to $N/O = 0.5$ of the fully nitrated compound ($x=1$) and indicates an under-stoichiometric nitrogen content in this film, in agreement with the result of the XRD analysis of Fig. 2a.

For the specific sample described in Fig. 2, using the combination of both techniques, RBS and ERDA, a chemical composition of $\text{La}_{1.01}\text{Ti}_{0.99}\text{O}_{2.2}\text{N}_{0.8}$ could be
335 determined very precisely with an error of $< 3\%$ to 5% . Other phases originating from the oxide LaTiO_{3+x} ($0 < x < 0.5$) were not detected by XRD (Fig. 2a). Moreover, RBS and ERDA measurements show a uniform compositional depth profile (Fig. 2c).

3.3. *Tuning the nitrogen content*

340 The reason for the under-stoichiometric nitrogen content was investigated to understand up to which extent the nitrogen content could be tuned in our films. Previous studies on $\text{LaTiO}_{3-x}\text{N}_x$ film growth by PRCLA showed that high laser fluence and high deposition temperatures are required to achieve high nitrogen substitution[38]. For this work we systematically investigated the effect of the laser fluence and sub-

strate material on the N/O ratio as determined by ERDA for several $\text{LaTiO}_{3-x}\text{N}_x$ films. For this investigation the laser fluence was varied from 2 J cm^{-2} to 4 J cm^{-2} and (100)-oriented SrTiO_3 (STO) and LaAlO_3 (LAO), (110)-oriented YAlO_3 (YAO), as well as (100)-oriented TiN-coated MgO substrates were used. Following this approach, the typical composition of the oxynitride thin films determined by RBS and ERDA can be written as $\text{La}_{1+y}\text{Ti}_{1-y}\text{O}_{3-x}\text{N}_z$ where $0 < y < 0.03$ and $0.5 < x < 0.85$, depending on deposition parameters. Further, the sum of the oxygen and nitrogen content is close to 3 ($x \approx z$), thus forming the $\text{LaTiO}_{3-x}\text{N}_x$ perovskite with a very small amount of anionic vacancies.

In particular, Fig. 3 shows the measured N/O ratio as a function of laser fluence for the different substrates. As a first observation, it appears clearly that a TiN-buffered substrate allows a more reliable control of the nitrogen content by only changing the laser fluence. The points corresponding to TiN-buffered MgO show a linear increase of the N/O ratio with increasing fluence (from 2.5 J cm^{-2} to 4.1 J cm^{-2}). The points corresponding to the oxide substrates are more scattered. As mentioned previously, STO substrates do not preserve their oxygen content at high temperatures and in reducing environment. Oxygen atoms from the substrate can even migrate into the growing film hindering the nitrogen substitution. In fact, a clear dependence of the N/O ratio on the laser fluence using STO substrates is not visible, neither at low nor at high fluence.

Using the other oxide substrates, YAO and LAO, we observed a trend similar to that observed for TiN-buffered MgO at lower fluences (2.0 J cm^{-2} to 3.0 J cm^{-2}), but with increasing fluence the values of N/O ratio measured for the $\text{LaTiO}_{3-x}\text{N}_x$ films are much more scattered. More importantly, the maximum achievable nitrogen content is lower when the oxynitride films grow directly on the oxide surfaces than on the TiN-coated substrates. The effect of oxygen diffusion into the film as described

before for STO, is also known for LAO substrates[49]. This suggests that with YAO substrates such a mechanism may also apply, but it is less significant when using YAO or LAO instead of STO. However, the possible presence of a gradient in the nitrogen content of the film along the growth direction should be taken into account.

375 Fig. 3 shows that to achieve a better control of the nitrogen content and a larger amount of nitrogen substitution in the oxynitride film a nitride-coated substrate like TiN-buffered MgO is preferable and underlines the advantage of the sample design proposed here for the PEC characterization of oxynitride photocatalysts.

Fig. 4 shows the effect of different nitrogen contents on the optical properties of the $\text{LaTiO}_{3-x}\text{N}_x$ films. For this measurement double-side polished LAO substrates were used to acquire UV-Vis spectra in transmission mode. The transmittance is plotted as a function of the incident wavelength showing a shift of the band gap towards longer wavelengths with increasing nitrogen content, as expected. Out of the UV-Vis spectra a band gap of about 2.35 eV to 2.85 eV can be estimated for the
 385 oxynitride thin films[38]. For comparison, the UV-Vis spectrum of a thin film of $\text{La}_2\text{Ti}_2\text{O}_7$ grown on LAO by conventional PLD is also shown.

3.4. *Tuning the crystallographic properties*

Concerning the crystalline quality and crystallographic orientation of the oxynitride films grown on (100)-oriented TiN-buffered MgO we observed a remarkable effect of the laser fluence. The polycrystalline film discussed in Fig. 2 were grown
 390 using a laser fluence of about 3.7 J cm^{-2} . By keeping all other deposition parameters constant but lowering the fluence to 3.0 J cm^{-2} , the $\text{LaTiO}_{3-x}\text{N}_x$ thin films grew epitaxially oriented with the substrate, as shown in Fig. 5. In this case, it comes at the cost of a lower nitrogen content. As shown in Fig. 3, for a laser fluence of about
 395 3.0 J cm^{-2} the N/O ratio is about 0.30, while 0.36 was the value measured for a laser

fluence of about 3.7 J cm^{-2} , though in the second case only polycrystalline samples could be grown.

This experimental observation could be explained in analogy with the equivalent effect often encountered during conventional PLD; by increasing the laser fluence both the kinetic energy of the ablated species and the deposition rate increase. Above a certain threshold this may hinder the ordered growth of the film. Literature on PRCLA is scarce and we cannot refer to any specific examples to support this speculation but it is likely to assume the same mechanism to apply also for PRCLA.

While higher laser fluence favors the growth of polycrystalline thin films with higher nitrogen content, reduced laser fluence leads to an epitaxial film growth with lower nitrogen content. A similar effect was observed for $\text{LaTiO}_{3-x}\text{N}_x$ films grown by reactive radio-frequency sputtering[37]. The N/O ratio was estimated by coupled energy-dispersive spectroscopy. Films with higher nitrogen content were polycrystalline while those with lower nitrogen content were epitaxially grown.

A comparative investigation of the effect of the surface orientation and crystalline quality on PEC performance should be performed using films with similar nitrogen content. This could be achieved by keeping the laser fluence within a range that promotes the epitaxial highly ordered growth on TiN-buffered MgO but changing the substrate material and/or deposition parameters, such as substrate temperature, in order to grow TiN layers with different orientations or as polycrystalline seed layers for the growth of the oxynitride films. The oxynitride films will thus show different crystallographic and morphological properties but their nitrogen content will be comparable with that of the highly ordered epitaxial film.

3.5. Proof of concept of the model system using photoelectrochemical characterization

420 As a preliminary test experiment to validate our sample design, the polycrystalline $\text{La}_{1.01}\text{Ti}_{0.99}\text{O}_{2.2}\text{N}_{0.8}$ sample grown on TiN-buffered MgO substrate was characterized in a PEC setup. The photocurrent generated under the effect of Xenon lamp front-illumination was measured while sweeping the applied voltage from 0.2 V to 1.4 V versus the reversible hydrogen electrode (RHE). A rotating shutter
425 was used to chop the light allowing the simultaneous measurement of the so-called dark current (no illumination of the sample). ERDA analysis showed that a small but measurable amount of oxygen is present in the TiN current collector (N/O ratio > 6.5). In order to exclude any contribution to the photocurrent from the buried TiN layer, a PEC measurement was performed using a bare TiN-buffered MgO sample.
430 As expected no photoresponse was detected.

For an unoptimized system the result of our preliminary PEC measurements for $\text{La}_{1.01}\text{Ti}_{0.99}\text{O}_{2.2}\text{N}_{0.8}$ is promising, as per the linear voltammetry measurements shown in Fig. 6. We note that the measured photocurrents are lower than what has been reported for powder based oxynitrides, this is to be expected due to the
435 difference in surface-to-volume ratio (or the extent of the electrochemically active area). Furthermore, the specific morphology of this sample characterized by extended grain boundary regions where untimely recombination of the photo-generated charge carriers is strongly favored likely represents a possible loss channel. We anticipate that by employing sacrificial reagents acting as hole scavengers or co-catalysts instead
440 of just the semiconductor in direct contact with the electrolyte, will improve the performance[37]. Finally, the very broad absorption edge of this sample as shown in Fig. 4 may negatively influence the values of the photocurrent.

4. Conclusion

In summary we report a new experimental approach which, starting from the
445 pristine oxide material, enables the growth and the photo(electro)chemical characterization of oxynitride thin films with tunable crystallographic, morphological and optical (nitrogen content) properties, a goal that cannot be achieved with conventional powder samples. As a proof of concept we have demonstrated photocatalytic response of oxynitride thin films integrated into our model system. This work es-
450 tablishes the foundation an effective experimental approach for future investigations into the oxynitride thin film class of photocatalyst. Gaining insight into the relationship between crystallographic properties and electrochemical response is expected to aid the development and design of better performing materials for solar-driven water splitting.

⁴⁵⁵ **Acknowledgment**

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