



Pulsed laser deposition and characterization of nitrogen-substituted SrTiO₃ thin films

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ABSTRACT

Nitrogen-substituted cubic perovskite-type SrTiO₃ thin films were deposited in a one-step process using pulsed reactive crossed beam laser ablation (PRCLA) and RF-plasma assisted pulsed laser deposition (RF-PLD). Both techniques yield preferentially oriented films on SrTiO₃(0 0 1), LaAlO₃(0 0 1) and MgO(0 0 1) substrates with the unit cell parameters within $0.390(5) < a < 0.394(9)$ nm. The nitrogen content is higher in films deposited by PRCLA (0.84–2.40 at.%) as compared to films deposited by RF-PLD with nitrogen plasma (0.10–0.66 at.%). PRCLA with an ammonia gas pulse leads to a higher nitrogen content compared to the films grown with a nitrogen gas pulse, while films deposited by RF-PLD with ammonia plasma reveal only minor nitrogen contents (<0.10 at.%). The amount of the incorporated nitrogen can be tuned by adjusting the deposition parameters. Films deposited by PRCLA have a lower roughness of 1–3 nm compared to 12–18 nm for the films grown by RF-PLD. PRCLA yields partially reduced films, which exhibit electronic conductivity, while films deposited by RF-PLD are insulating. There is also a pronounced influence of the substrate material on the resistivity of the films deposited by PRCLA: films grown on SrTiO₃ substrates exhibit a metallic-like behaviour, while the corresponding films grown on MgO and LaAlO₃ substrates reveal a metal-to-semiconductor/insulator transition. Nitrogen incorporation into the SrTiO₃ films results in an increased optical absorption at 370–500 nm which is associated with N(2p) localized states with the energy about 0.7 eV higher than the valence band energy in strontium titanate. The optical band gap energies in the studied N-substituted SrTiO₃ films are 3.35–3.40 eV.

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1. Introduction

Strontium titanate is a band insulator with a cubic perovskite-type structure. This compound attracts a lot of interest as a potential material for different electrical and photochemical applications due to the possibility to tune its properties by modification of the chemical composition. Derivatives of SrTiO₃ are suggested as new high-*k* dielectrics for microelectronics, materials for non-volatile memory devices, field-effect heterostructures and photochemical applications [1,2]. The most common way to change the composition and properties of SrTiO₃ is the substitution of cations in A- and B-sublattices of the perovskite-type structure. Anionic substitutions in strontium titanate are much less explored. However, this type of modification of the chemical composition

offers additional possibilities to tune the electronic structure and properties of oxides [3]. In the present work we investigated the preparation and properties of nitrogen-doped strontium titanate thin films grown by modified pulsed laser deposition (PLD) techniques. PLD is a very flexible and adaptable plasma deposition technique extensively used for the preparation of thin oxide films with complex stoichiometries. A wide range of adjustable deposition parameters provide a versatile control over the crystallinity, composition and microstructure of the grown films [4]. Therefore PLD and its modifications are especially suitable for a one-step deposition of N-doped SrTiO₃ films as different sources of reactive nitrogen can be used in different modifications of PLD. An alternative way is a two-step preparation of N-substituted films, consisting of the deposition of oxide film and its subsequent thermal ammonolysis [5]. It has been shown that partial substitution of nitrogen for oxygen in SrTiO₃ (several at.%) reduces the dielectric leakage current [6] and also induces the formation of localised energy levels inside the SrTiO₃ band gap, thus providing

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Table 1Average composition and energy levels of the N-substituted SrTiO₃ thin films deposited by pulsed reactive crossed beam laser ablation and RF-plasma assisted PLD

Deposition technique	Nitridizing source	Film composition	$E_g \pm 0.05$ eV	$E_N \pm 0.05$ eV
RF-PLD	N ₂ plasma	Sr _{1.0} Ti _{1.0} O _{3.0} N _{0.032}	3.37	2.71
	NH ₃ plasma	Sr _{1.0} Ti _{1.0} O _{3.0} N _{0.005}	3.38	2.74
PRCLA	N ₂ gas pulse	Sr _{0.98} Ti _{1.02} O _{2.9} N _{0.056}	3.38	2.69
	NH ₃ gas pulse	Sr _{0.95} Ti _{1.05} O _{2.7} N _{0.122}	3.38	2.70

the possibility to apply the N-substituted compound as photo-catalyst for water dissociation [2].

2. Experimental

Nitrogen-doped SrTiO₃ films were deposited by modified laser ablation techniques from a ceramic SrTiO₃ target: pulsed reactive crossed beam laser ablation (PRCLA) [7,8], and radio frequency plasma assisted PLD (RF-PLD) [9,10]. PRCLA utilizes a gas valve with a nozzle located close to the ablation spot on the target. The injection of the compressed gas is synchronized with the laser pulse by opening the valve 400 μs before and closing 30 μs after. The gas expands in the chamber towards the substrate and crosses the laser plume close to its origin. This geometry leads to an enhanced activation and excitation of the gas pulse molecules by collisions with the highly energetic species in the ablation plume [7]. In our experiments two different gases (N₂ and NH₃) were used to form active nitrogen species to be incorporated into the growing film. In RF-plasma assisted PLD an external source of a continuous plasma beam, generated by an RF discharge is directed to the substrate during film growth [9,10]. Similar to the PRCLA experiments, two different RF-plasmas (N₂ and NH₃) were used. For both techniques a KrF excimer laser was used at a repetition rate of 10 Hz (pulse duration of 20 ns). The laser fluence (F) was in the range 5–6 J cm⁻². Three substrate materials with different unit cell parameters were used for the film deposition: SrTiO₃ (STO, $a = 0.3905$ nm), LaAlO₃ (LAO, $a = 0.3821$ nm), and MgO ($a = 0.4212$ nm). The substrate temperature was fixed at 650 ± 25 °C.

The phase composition and crystallinity of the deposited films were investigated by X-ray diffraction (XRD). The film thickness and the root-mean-square roughness were obtained from profilometry measurements. The chemical composition of the films was determined from a combination of Rutherford backscattering spectroscopy (Sr:Ti:O ratio) and elastic recoil detection analysis (N:O ratio). The experimental accuracy to determine the nitrogen content was ±0.25 at.%. Optical properties of the films were studied by UV-vis-NIR optical spectroscopy in transmittance mode. The electronic properties of the films were characterised by resistivity measurements in the temperature range of 3–300 K.

3. Results and discussion

Rutherford backscattering spectroscopy reveals an almost stoichiometric transfer of cations from the SrTiO₃ target to the deposited films. The Sr:Ti ratio in most films is within 0.95–1.00. Several films deposited by PRCLA with the NH₃ gas pulse exhibit a larger strontium deficiency (Sr:Ti ratio of 0.90–0.95). The observed loss of Sr could be attributed to the formation of volatile Sr-containing phases during the film deposition in reducing media [11]. The oxygen and nitrogen content in the films strongly depends on the deposition technique and nitridizing source (see Table 1). The total anionic content (i.e. oxygen + nitrogen) in films deposited by RF-PLD is close to the ideal perovskite value of 3, whereas films deposited by PRCLA reveal an anionic deficiency (i.e.

O + N content is lower than 3). A deposition with the NH₃ pulse results in a lower anionic content compared to the N₂ gas pulse due to the reducing properties of ammonia. The nitrogen content in the studied films is presented in Fig. 1. RF-PLD yields films with smaller N content compared to films deposited by PRCLA. Our previous parametric studies on N-substituted SrTiO₃ films grown by RF-PLD have shown, that the maximum nitrogen content of 0.66 at.% can be obtained using a N₂ RF-plasma, while a NH₃ RF-plasma results in a negligible amount of the incorporated nitrogen in SrTiO₃ films. The film optimisation was limited by the fixed distance for the RF-plasma in our set-up which could partly explain the unexpected low nitrogen concentration in the prepared films [10]. Similar nitrogen concentrations were achieved in films deposited by classical PLD with an ammonia background (0.65 at.%). Utilisation of the gas pulse in PRCLA has a much more pronounced impact on the N content. Films deposited with the N₂ gas pulse reveal a nitrogen content of up to 1.44 at.%. The ammonia gas pulse has an even bigger influence on the nitrogen content, reaching up to 2.40 at.%. The better performance of the ammonia gas pulse in comparison with N₂ can be explained by the lower dissociation energy of NH₃ molecule compared to N₂, which results in an easier formation of active atomic nitrogen species in the plasma. The amount of the incorporated nitrogen in the films can therefore be tuned by varying the deposition parameters like laser fluence, substrate temperature and RF-power.

Grazing incidence XRD measurements were performed in order to verify the phase composition of the films. The obtained diffraction patterns correspond to the perovskite-type SrTiO₃ without any impurity phases, thus confirming single phase N-substituted SrTiO₃ films (inset in Fig. 2). The thickness of the studied films ranged between 500 and 1000 nm. For these relatively large film thicknesses, no influence of the substrate on

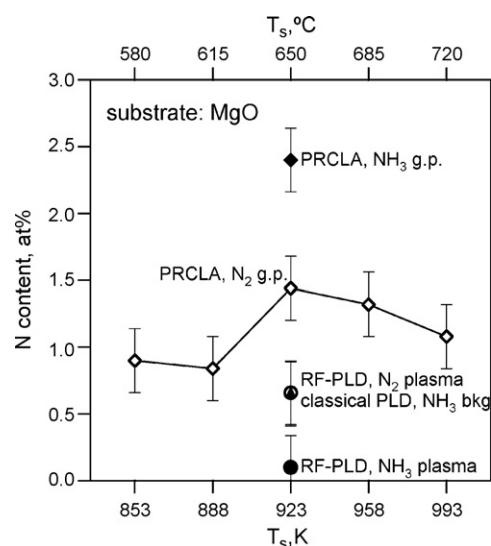


Fig. 1. Nitrogen content in the strontium titanate thin films deposited by different modifications of PLD with different nitridizing sources.

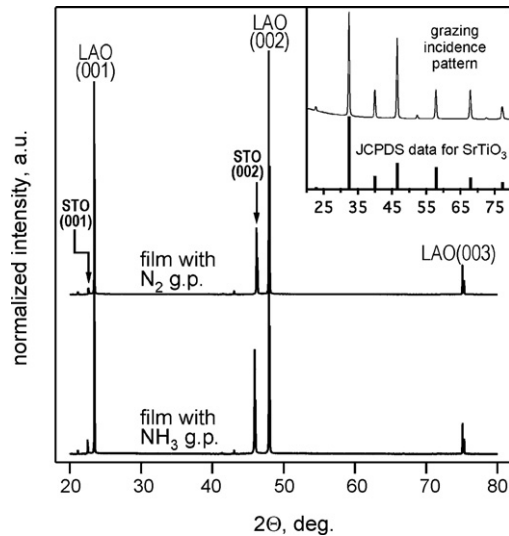


Fig. 2. XRD patterns in θ - 2θ mode of the N-substituted SrTiO₃ films deposited on LaAlO₃(0 0 1) substrate. The films exhibit oriented growth along the (0 0 1) direction. (Inset) Grazing incidence XRD confirms formation of the pure perovskite-type phase.

the unit cell parameters of the film has been observed [8]. The estimated unit cell parameters range within 0.390(5)–0.391(9) and 0.391(2)–0.394(9) nm for films grown by RF-PLD and PRCLA, respectively. The lattice parameters are slightly larger compared to single crystalline SrTiO₃ ($a = 0.3905$ nm). This can be attributed to the larger crystallographic radius of nitrogen ($R_N \approx 0.129$ nm) compared to oxygen ($R_O = 0.121$ nm) and/or to the deviations from the ideal SrTiO₃ stoichiometry. The larger lattice constants of the films deposited by PRCLA compared to RF-PLD can also be attributed to their larger anionic deficiencies. XRD analysis in θ - 2θ mode of the films deposited on STO(0 0 1) and LAO(0 0 1) substrates reveals epitaxial film growth along the (0 0 1) direction (Fig. 2). Some of the films grown on MgO(0 0 1) substrates exhibit also additional (0 1 1) orientation due to the higher lattice mismatch with the substrate. The intensity of these additional (0 1 1) reflections does not exceed 10% of the intensity of the strongest (0 0 2) film reflection. This indicates a preferentially (0 0 1)-oriented N-substituted SrTiO₃ films, but suggests in addition a larger number of grains and grain-boundaries in films grown on MgO when compared to films deposited on LAO and STO. The film surface morphology depends strongly on the deposition technique. PRCLA yields relatively smooth films with a typical root-mean-square roughness of 1–3 nm, while films deposited by RF-PLD exhibit a much higher roughness of up to 18 nm [10].

Before discussing transport properties of the studied films, it is noteworthy to mention the origin of the observed electronic conductivity. Like in many other derivatives of strontium titanate (like e.g. reduced SrTiO_{3- δ}) the electronic conductivity is attributed to Ti³⁺ states (i.e. delocalized free electrons), which are formed in the anion-deficient crystalline structure [12]. This process is called “reduction”, and the anion-deficient phases which exhibit electronic conductivity are called “reduced”. Using PLD and its modifications the reduction of the deposited film occurs due to the losses of oxygen species in the plume during the plasma transfer from the target to the growing film. The oxygen content can be improved by the additional external (i.e. non-target) sources of the oxygen species, e.g. background gas, gas pulse, RF-induced plasma, etc... However, the simultaneous use of any external oxygen source to compensate the anionic deficiency together with a nitridizing source to deposit N-doped non-reduced SrTiO₃ films is

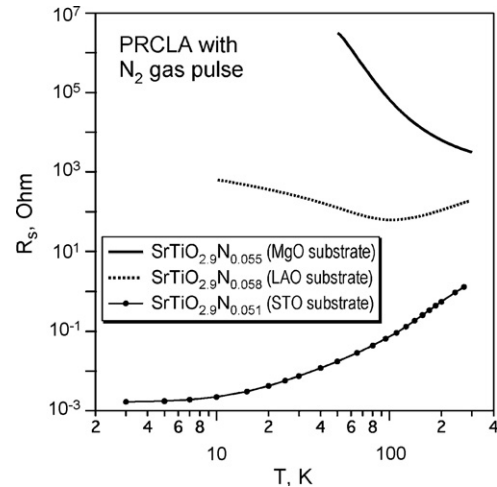


Fig. 3. Temperature dependencies of the sheet resistances of N-substituted SrTiO₃ films deposited by PRCLA. Films grown on SrTiO₃ substrates exhibit a metallic-like behaviour, whereas films grown on LaAlO₃ and MgO substrates reveal a metal-to-semiconductor/insulator transition.

not possible due to the much higher affinity of the growing film to oxygen compared to nitrogen. Hence, the resulting films reveal no nitrogen incorporation [8]. Therefore it is mandatory to only use a nitridizing source to prepare the oxynitride thin films.

As already pointed out, RF-PLD yields non-reduced films, and typical resistivities values are bigger than $2.5 \times 10^3 \Omega \text{ cm}$. Contrary, films grown by PRCLA are anion-deficient (i.e. reduced) and therefore exhibit an electronic conductivity (probably due to scattering of oxygen species in the plume and/or lower sticking coefficient of oxygen species [8]). Typical temperature dependencies of the thin film sheet resistances (R_s) are presented in Figs. 3 and 4. A pronounced influence of the substrate on the resistance of the N-substituted films grown with the nitrogen gas pulse has been found (Fig. 3). Films deposited on the LAO and MgO exhibit considerably larger resistances and reveal a metal-to-semiconductor/insulator transition, while films deposited on STO show a metallic-like behaviour (similar to reduced SrTiO₃ crystals [12]). The observed low metallic-like resistance of these films could be explained by the modification of the substrate stoichiometry during the homoepitaxial growth of the N-substituted reduced

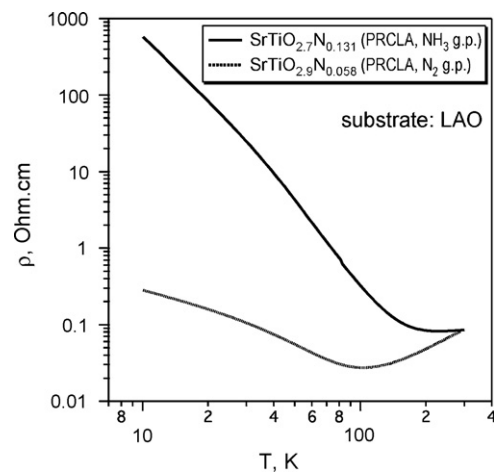


Fig. 4. Temperature dependencies of the resistivities of N-substituted SrTiO₃ films deposited by PRCLA with the ammonia and nitrogen gas pulses. Films grown with the ammonia gas pulse typically exhibit higher resistivities despite the expected higher charge carrier concentrations.

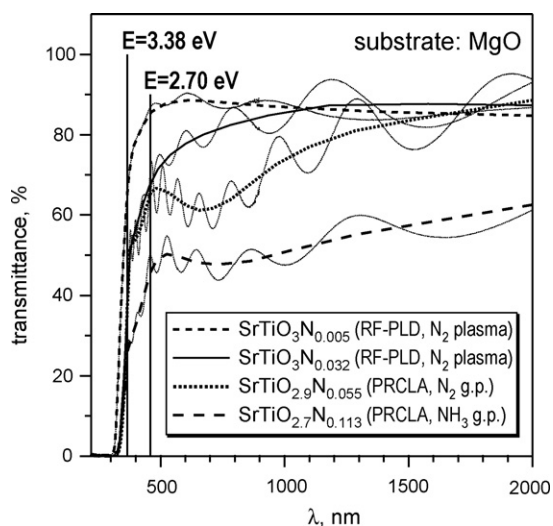


Fig. 5. Transmittance spectra of the N-substituted SrTiO₃ thin films. An absorption shoulder at 370–500 nm is attributed to the N(2p) localized states with the energy about 0.7 eV higher than the valence band energy in strontium titanate.

SrTiO₃ films on the SrTiO₃ substrates. More work is in progress to study this phenomenon in detail. The resistance of films grown on MgO substrates is higher compared to films grown on LAO. The likely reason is the difference in crystallinity and a larger number of grain boundaries. This interrupts the conduction pathways and reduces the electron mean free path (i.e. mobility), whereas the concentration of charge carriers should be similar in the films deposited on LAO and MgO as the chemical composition of the films is independent on the substrate material. On the contrary, the deposition with different gas pulses results in films with different compositions and electron concentrations (Table 1). Films grown with the ammonia gas pulse exhibit a higher anionic deficiency compared to films grown with the nitrogen gas pulse. Therefore the expected charge carrier concentration in these films should also be higher. However, experimental resistivity curves show the opposite trend: the resistivities of films deposited with the N₂ gas pulse are typically lower (Fig. 4). This suggests that the electron mean free path in these films should be higher compared to films deposited with the NH₃ gas pulse on the same substrate (LAO), which could be due to a different film microstructures and/or the slightly different film compositions (e.g. stronger deviations of the Sr:Ti concentration ratio in the films grown with the ammonia).

Fig. 5 shows the transmittance spectra of the selected films deposited by different techniques with different nitridizing sources on MgO substrates. There are three main features on the transmittance curves. The first feature is a reduced transmittance in the wide wavelength (λ) range of 500–2000 nm. This is attributed to the absorption of low-energetic photons by free electrons in the films. Therefore the absorption is higher in films with larger anionic deficiencies. Hence, the absorption of PRCLA grown films in this wavelength regime is higher compared to RF-PLD grown films (Fig. 5). The second feature on the transmittance curves is an absorption shoulder at around 460 nm. This feature is specific for the N-substituted strontium titanate and is not observed in the stoichiometric or reduced SrTiO₃. It can be attributed to the localized nitrogen 2p-levels located inside the

band gap close the valence band on the energy diagram of SrTiO₃. Simple qualitative estimations show that the shoulder on the transmittance curves is more pronounced in films with a higher nitrogen content due to higher number of N(2p) absorption sites (Fig. 5). The estimated energy for the direct transfer of an electron from this localized N(2p) state to the conduction band (E_N) was estimated to be 2.70 ± 0.05 eV (Table 1), and is independent on the film composition. A similar value of 2.8 eV has been found for N-substituted SrTiO₃ powders [2]. The presence of these additional absorption sites allows to capture the visible light photons. N-doped strontium titanate is therefore of potential interest to be used as a photocatalyst for the visible light driven decomposition of water. The third feature on the transmittance curves is a full absorption of the light below ~ 370 nm. This is attributed to the band gap of SrTiO₃. The estimated direct optical band gap energies (E_g) of the studied films are 3.38 ± 0.05 eV (Table 1), which is slightly larger than for strontium titanate single crystal ($E_g = 3.20$ eV). The observed difference can be due to small deviations from the ideal SrTiO₃ stoichiometry.

4. Conclusions

Nitrogen-substituted SrTiO₃ films have been deposited by pulsed reactive crossed beam laser ablation and RF-plasma assisted PLD. (0 0 1)-oriented single-phase films were obtained on SrTiO₃, LaAlO₃, and MgO substrates. RF-PLD yields insulating films with a minor anion deficiency and a nitrogen content of 0.10–0.66 at.%, whereas films grown by PRCLA reveal a larger anionic deficiency, electronic conductivity, and a higher nitrogen content of up to 2.40 at.%. The conductivity of these films depends on the used substrate and nitridizing source (i.e. gas pulse). N-substituted SrTiO₃ films exhibit enhanced optical absorption of the visible light at the wavelength 370–460 nm which is attributed to localized N(2p) levels in the SrTiO₃ band gap. This makes N-doped strontium titanate an interesting candidate for visible light driven photocatalysis.

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