Plasma-Assisted Atomic Layer Deposition of SrTiO3: Stoichiometry and Crystallinity Studied by Spectroscopic Ellipsometry

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Strontium titanate (SrTiO3, STO) films were deposited by plasma-assisted ALD using cyclopentadienyl-based Sr- and Ti-precursors with O2 plasma as the oxidizing agent. Spectroscopic ellipsometry (SE) was employed to determine the thickness and the optical properties of the layers. As determined from Rutherford backscattering spectrometry (RBS), [Sr]/[Sr]+[Ti] ratios ranging from 0.42 to 0.68 were achieved for 30–40 nm thick films by tuning the [SrO]/[TiO2] ALD cycle ratio. Films deposited at 250 °C were amorphous and required post-deposition annealing to crystallize into the ultrahigh-k perovskite structure. The crystallinity of the films after rapid thermal annealing strongly depended on the film composition as observed by X-ray diffraction measurements. Using RBS data for a set of as-deposited samples, an optical constant library was built to determine the film stoichiometry from SE directly for the amorphous as-deposited films. After rapid thermal annealing the crystalline phase could be determined from the position of critical points of the measured dielectric function and the estimation of the stoichiometry was also possible for crystallized layers. These results open up a new way to use SE as a real-time characterization method to monitor and tune the STO film composition and crystallinity.

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Strontium titanate (SrTiO3, STO) is a perovskite material which has attracted considerable attention in recent years due to its various properties. Stoichiometric SrTiO3 is a dielectric material, however oxygen vacancies and doping can be used to obtain semiconductive and conductive STO.1–4 Furthermore, STO shows other interesting properties such as paraelectricity and ferroelectricity, also when deposited as a thin film.5–6 Resistive switching behavior has been reported for metal-insulator-metal (MIM) structures where STO was employed as the dielectric material.6 However, among all STO properties, its ultrahigh permittivity value (theoretically k > 100) need to be deposited conformally over high aspect-ratio critical points of the measured dielectric function and the estimation of the stoichiometry was also possible for crystallized layers. These results open up a new way to use SE as a real-time characterization method to monitor and tune the STO film composition and crystallinity.

To achieve the required ultrahigh-k values, STO films must be crystallized into the perovskite structure by post-deposition thermal annealing or they have to be deposited at relatively high temperatures. To deposit STO thin films over high aspect ratio structures, atomic layer deposition (ALD) is the method of choice since its characteristic layer-by-layer growth results into high-quality layers and excellent step coverage. A common approach to deposit ternary oxides by ALD consists in alternating ALD cycles of the binary oxides, with a certain ratio, to obtain the desired material.5,6,7 In this way, not only the thickness, but also the film composition can be precisely controlled by ALD.

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In this work, we report on the plasma-assisted ALD of STO films from cyclopentadienyl-based precursors for both, TiO2 and SrO. The oxidizing agent was an O2 plasma generated in a remote inductively coupled plasma (ICP) source. In our previous work, STO films were deposited with the same precursors in a home-built reactor.25 In this paper the process was scaled-up in a commercial Oxford Instruments FlexAL tool which can accommodate wafers up to 200 mm in diameter. It was demonstrated that the film stoichiometry is related to the [SrO]/[TiO2] ALD cycle ratio. Using X-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) data as a cross-reference it was shown that it is possible to probe directly the stoichiometry and crystallinity of thin STO films by spectroscopic ellipsometry (SE). In addition, we present a pragmatic approach to determine the stoichiometry of amorphous STO films by means of an optical constant library that was built with the CompleteEASE software (J.A. Woollam). Since SE measurements can also be taken in-situ this could provide a means for monitoring the film properties during processing.

**Experimental**

The STO thin films were deposited in an Oxford Instruments’ FlexAL reactor on 100 and 200 mm Si (100) wafers with native oxide. This reactor was upgraded during this experimental work, leading to slightly different results before and after the upgrade. Hereafter, we will indicate the system before the upgrade as FlexAL-A and after the upgrade as FlexAL-B. The precursors employed were Ti-Star, (pentamethycyclopentadienyl)trimethoxy-titanium, CpMe5Ti(OMe)3 and Hyper-Sr, bis(tri-isopropylcyclopentadienyl)strontium with the 1,2-dimethoxyethane adduct, Sr(Pr3Cp)2DME, both from Air Liquide. Since the Ti-Star precursor is not reactive toward H2O in an ALD process, an O2 (>99.999% purity) plasma generated by an inductively coupled plasma (ICP) source was used as the oxidizing agent. The precursors were stored in stainless steel canisters heated to 70 °C and 120 °C for Ti-Star and Hyper-Sr, respectively. For both precursors, the delivery to the deposition chamber was achieved with a 100 sccm Ar (>99.999% purity) bubbling flow. The delivery lines were kept at a temperature 30 °C higher than the precursor canisters to avoid condensation and clogging. As confirmed by calibration measurements, the actual sample temperature is lower than the set value (by 20–25% in °C). We will hereafter report this set value and refer to it as “set temperature.” Rapid thermal annealing (RTA) for 10 minutes in flowing N2 was employed to crystallize the STO layers into the perovskite structure using an AST SHS100 system. The crystalline phase of the films was determined by grazing incidence X-ray diffraction (GI-XRD) at an incidence angle of 0.5° with respect to the substrate plane. X-ray
Rutherford backscattering spectroscopy (RBS) was used to determine the elemental composition and atomic areal densities of the films using 2 MeV $^4$He$^+$ ions (AccTec BV, The Netherlands). X-ray photoelectron spectroscopy (XPS) measurements were also performed on a Thermo Scientific K-Alpha KA1066 spectrometer using monochromatic Al $K\alpha$ X-ray radiation ($hv = 1486.6$ eV). Photoelectrons were collected at a take-off angle of $60^\circ$. A $400 \mu$m diameter X-ray spot was used in the analysis and the samples were neutralized using an electron flood gun to correct for differential or non-uniform charging. For cross-referencing the atomic composition from XPS measurements, a stoichiometric SrTiO$_3$ substrate (20 mm diameter, Crystal GmbH) was measured and the sensitivity factors for the Sr3d, Ti2p and O1s peaks were tuned accordingly to obtain stoichiometric SrTiO$_3$ from the detected relative amounts of the single elements. This procedure was executed after surface contamination removal by Ar$^+$ ion (500 eV) sputtering. Ar$^+$ ion sputtering was also employed for depth profiling of the stoichiometric STO sample to exclude the possibility of preferential sputtering. The analysis confirmed that the sensitivity factors were accurate throughout the depth profile.

**Results and Discussion**

**Plasma-assisted ALD of TiO$_2$ and SrO.**— The deposition processes of the individual binary oxides, TiO$_2$ and SrO, were first developed to determine the growth-per-cycle, the appropriate purge times and the saturation behavior for both the precursor doses and the O$_2$ plasma exposure in the FlexAL-A reactor. For the TiO$_2$ process a dosing time of 2 s for the Ti-Star precursor and an exposure time of 8 s for the O$_2$ plasma were required to achieve saturation. For the SrO process the Hyper-Sr precursor dosing time and the exposure time of O$_2$ plasma were 15 s and 8 s, respectively. Purge times required to avoid any CVD-like growth, were 2 s and 10 s after the Ti- and Sr-precursor step, respectively. After the O$_2$ plasma, the purge step times were 2 s and 15 s for TiO$_2$ and SrO process, respectively. With these settings saturation was reached for both processes at a set temperature of 250°C. The growth-per-cycle (GPC), as determined by SE, was 0.036 and 0.11 nm/cycle for TiO$_2$ and SrO, respectively. These values deviate from those reported previously by Langereis et al. for the home-built ALD-I reactor, in which the GPC for TiO$_2$ and SrO were 0.054 and 0.051 nm/cycle, respectively. Differences in GPC between these two setups have previously been reported for plasma-assisted ALD process of Ta$_2$O$_5$, and were ascribed to the differences in the reactor design. Differences in precursor delivery and plasma source design can result in different radical and ion fluxes in the two reactors.

The GPC of SrO is, however, in good agreement with a GPC of $\sim$0.1 nm/cycle reported for Hyper-Sr and O$_2$, and 0.11 nm/cycle for Hyper-Sr and H$_2$O.$^{26}$ In one of the first reports on ALD of STO, the GPC for the SrO process using Sr(C$_5$iPrH$_2$)$_2$ (Hyper-Sr without the DME adduct) and H$_2$O was also 0.11 nm/cycle. The GPC of TiO$_2$ is comparable to those reported in the literature, with values ranging from 0.022 nm/cycle$^{27}$ to $\sim$0.03 nm/cycle$^{26}$ for the combination of Ti-Star and O$_2$. These values show the variation in GPC reported in the literature for ALD processes employing the same precursors but developed in different equipment, showing the sensitivity of ALD processes to the varying reactor design and experimental conditions.

**Plasma-assisted ALD of STO.**— ALD of STO was achieved by combining ALD cycles of the two binary oxides to obtain one STO supercycle. In this way an STO supercycle is composed of x SrO cycles and y TiO$_2$ cycles and the [SrO]/[TiO$_2$] ALD cycle ratio is defined as x/y. The STO films were deposited with various ALD [SrO]/[TiO$_2$] cycle ratios in the FlexAL-A reactor at a set temperature of 250°C. Two different approaches to combine the binary oxides were employed. The first consisted in executing the SrO cycles followed by the TiO$_2$ cycles (indicated hereafter as “consecutive” or simply by “2:5”), e.g. a supercycle with cycle ratio [SrO]/[TiO$_2$] = 2:5 corresponds to 2 cycles SrO followed by 5 TiO$_2$ cycles. The other approach consisted of intermixing the TiO$_2$ and SrO cycles (indicated hereafter with the notation “2:5 mixed”), e.g. a supercycle with cycle ratio [SrO]/[TiO$_2$] = 2:5 corresponding to the sequence 1 SrO, 2 TiO$_2$, 1 SrO and 3 TiO$_2$ cycles.

The ALD temperature window of the STO process was also investigated. For this purpose films were deposited in the FlexAL-B reactor with a [SrO]/[TiO$_2$] cycle ratio 1:3. The growth per supercycle, obtained by dividing the total thickness of the film by the number of STO supercycles, (Figure 1) was nearly constant from 150°C to 350°C. A slight decrease in growth with increased temperature is most likely due to desorption of surface groups and/or to densification of the film at higher temperatures. At a set temperature of 375°C a higher growth per supercycle was observed as well as an enhanced non-uniformity and higher Sr-concentration in the layers, suggesting the decomposition of the Hyper-Sr precursor. The difference between the decomposition temperature of the Hyper-Sr precursor (300°C) reported by Katarmreddy et al.$^{26}$ and our data is most likely due to the difference between the set and the actual wafer temperature.

**Film composition and cation incorporation.**— RBS measurements were performed to determine the composition of the STO films and to establish a relation between the stoichiometry of the film and the [SrO]/[TiO$_2$] cycle ratio. XPS measurements were performed on the same set of samples after surface contamination removal by Ar$^+$ ions.

![Figure 1](image-url)  
**Figure 1.** Temperature dependence of the growth per supercycle of STO films deposited with a [SrO]/[TiO$_2$] ALD cycle ratio of 1:3 in the FlexAL-B reactor.
Table 1. Influence of the [SrO]/[TiO₂] ALD cycle ratio on the elemental composition of STO films determined by RBS. The relative errors in the atomic density are ±3% for Sr, Ti, and O. Also the [Sr]/([Sr]+[Ti]) content ratios obtained from XPS measurements are listed. The relative errors in the [Sr]/([Sr]+[Ti]) ratios from RBS and XPS are 6% and 5% respectively. The thickness of the films was determined by ex-situ SE. The error in thickness is ±0.5 nm.

<table>
<thead>
<tr>
<th>ALD cycle ratio</th>
<th>Thickness (nm)</th>
<th>Sr atomic density (10²² atom/cm²)</th>
<th>Ti atomic density (10²² atom/cm²)</th>
<th>O atomic density (10²² atom/cm²)</th>
<th>[Sr]/([Sr]+[Ti]) content ratio from RBS</th>
<th>[Sr]/([Sr]+[Ti]) content ratio from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:10</td>
<td>31.4</td>
<td>1.06</td>
<td>1.46</td>
<td>4.36</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>2:9</td>
<td>32.6</td>
<td>1.16</td>
<td>1.24</td>
<td>4.39</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>2:8</td>
<td>29.4</td>
<td>1.21</td>
<td>1.16</td>
<td>4.41</td>
<td>0.51</td>
<td>0.52</td>
</tr>
<tr>
<td>1:4</td>
<td>30.5</td>
<td>1.31</td>
<td>1.06</td>
<td>4.10</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>1:3</td>
<td>35.1</td>
<td>1.33</td>
<td>0.78</td>
<td>4.27</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>2:4</td>
<td>40.5</td>
<td>1.42</td>
<td>0.67</td>
<td>4.35</td>
<td>0.68</td>
<td>0.68</td>
</tr>
<tr>
<td>2.5 mixed*</td>
<td>30.1</td>
<td>1.18</td>
<td>1.12</td>
<td>4.22</td>
<td>0.51</td>
<td>0.51</td>
</tr>
</tbody>
</table>

*Film deposited in the FlexAL-B reactor. In the “mixed” approach TiO₂ and SrO ALD cycles were intermixed (i.e. the [SrO]/[TiO₂] ALD cycle ratio = 2.5 mixed corresponds to the sequence 1 SrO, 2 TiO₂, 1 SrO and 3 TiO₂ cycles).

The relation between the film growth and the cation incorporation was investigated. Figure 2 shows the [Sr]/([Sr]+[Ti]) content ratio calculated from the RBS data reported in Table I. The horizontal axis was weighted taking into account the two different GPC values for the single processes. In this way the expected Sr-content is represented by a straight line connecting the two extremes corresponding to the binary processes. The Sr-content resulting from RBS analysis was higher than expected, thus suggesting an enhanced incorporation of Sr cations into the film. Furthermore, when films were deposited with the same [SrO]/[TiO₂] cycle ratio but with different cycle sequences, the Sr-content was higher when single SrO cycles were intercalated between TiO₂ cycles, i.e. in the mixed approach. This is evident for cycle ratios 1:4 and 2:8, where the [Sr]/([Sr]+[Ti]) content ratio was 0.55 and 0.51, respectively. This implies that SrO growth is slightly enhanced by the underlying TiO₂ surface. Earlier, we already reported that the deposition of SrO could be enhanced after TiO₂ ALD cycles, resulting also in a higher Sr-content than simply expected from the cycle ratio. A strong dependency of the metal cation on the ligand removal and on the hydroxylation of the surface during the precursor and oxidizing steps was found for different ternary oxide compounds deposited by ALD from β-diketone precursors. The concentration of –OH groups on the surface is therefore dependent on the previous reactant step and thus influences the number of precursor molecules that react with the surface in the following dosing step.

Taking into account that not only the [SrO]/[TiO₂] ALD cycle ratio but also the sequence in which the precursors are dosed influences the cation incorporation, it is possible to precisely tune the film composition both by adjusting the cycle ratio as well as by choosing the cycle sequence in an STO supercycle.

Optical properties of STO.— The optical properties of crystalline bulk STO have been investigated by various techniques such as valence electron energy-loss spectroscopy, vacuum ultraviolet spectroscopy, reflectivity and spectroscopic ellipsometry measurements. Studies have been also reported on the optical properties of thin crystalline STO films. Zollner et al. extracted the dielectric function of bulk STO from spectroscopic ellipsometry measurements in the spectral range 0.74–8.7 eV. In this work we performed SE measurements on an STO (100) bulk sample. Figure 3 shows the dielectric function of the STO from our measurement and it is compared to the results from

![Figure 2](image2.png)  
**Figure 2.** [Sr]/([Sr]+[Ti]) content ratio as extracted from the RBS measurements. The [SrO]/([SrO]+[TiO₂]) ALD cycle ratio (horizontal axis) was weighted by the GPC values of the individual SrO and TiO₂ processes. The straight line represents the expected Sr-content, based on the GPC of the binary oxides and the ALD cycle ratio.

![Figure 3](image3.png)  
**Figure 3.** Dielectric function of bulk stoichiometric SrTiO₃ (100) measured by spectroscopic ellipsometry in this work (solid line) and from Zollner et al. (dashed line).
Zollner et al. showing an excellent agreement. In their work, the so-called critical points related to interband optical transitions were identified from the dielectric function and assigned to the electronic band structure of crystalline STO. For this purpose the electronic structure was calculated within the local-density approximation (LDA). Other works can be found in the literature on the calculation of the electronic structure and density of states (DOS) of STO using different approximations. Independently of the approximation used for the ab initio calculation, all authors reported that the top valence bands are related to O2p orbitals and that the lowest conduction bands consist of Ti3d orbitals. Sr-related bands were found at higher energies. Calculations also predicted that crystalline STO has an indirect and direct bandgap. The calculated bandgap values can vary depending on the approximation used and can be corrected to reproduce the experimental bandgap. These calculation results are in agreement with optical measurements where the indirect and direct bandgap values were reported to be 3.2 eV and 3.4 eV respectively. The critical points in the dielectric function at 3.8, 4.3, 4.8 and 6.2 eV reported by Zollner et al. were then assigned to transitions from the O2p valence bands to Ti3d conduction bands. Features in the dielectric function in the spectral range 7–9 eV were assigned to Sr5d orbitals and sp-antibonding orbitals. As a result of its critical point structure, STO, as evident in Figure 3, has its maximum in the real part of the dielectric function, $\varepsilon_1$, at 3.9 eV. This feature is a fingerprint of the crystallinity of STO and, as will be shown below, can be used to discriminate between amorphous and crystalline thin films. Regarding the optical properties of amorphous STO, calculations of the band structure and its relation to the dielectric function, cannot be found in literature to our knowledge. In the next sections we will show how the dielectric function of both amorphous and crystalline layers is affected by the film stoichiometry. Also the influence of the film thickness on the dielectric function will be discussed.

**Spectroscopic ellipsometry measurements of amorphous STO films.** The dielectric functions, $\varepsilon_1$ (real part) and $\varepsilon_2$ (imaginary part), of the TiO$_2$ and SrO films, as well as those of STO films deposited in the FlexAL-A reactor with different [SrO]/[TiO$_2$] cycle ratios were measured by spectroscopic ellipsometry. Figure 4 shows the dielectric functions of the as-deposited STO films for which RBS was performed. The dielectric functions of TiO$_2$ and SrO films are given for comparison. The optical band gaps of the two binary oxides, ~3.3 eV for TiO$_2$ and >5 eV for SrO, were in good agreement with the values reported in the literature. Figure 4 shows that the dielectric functions of the as-deposited STO films are all distributed in a logical compositional order, and lie between the dielectric functions of TiO$_2$ and SrO indicating that mixtures of the two binary oxides were deposited in the amorphous phase. The values for the refractive index $n$ (at 1.96 eV) of all STO films deposited in the FlexAL-A reactor with different [SrO]/[TiO$_2$] cycle ratios are shown in Figure 5a and were obtained from the dielectric function values through the relations:

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

where k is the extinction coefficient. Values are distributed between those of the two binary oxides (also shown) and $n$ increases when the relative number of TiO$_2$ cycles increases. Values of $n$ for the

![Figure 4](image-url) Real and imaginary part of the dielectric functions $\varepsilon_1$ (a) and $\varepsilon_2$ (b), respectively, of as-deposited TiO$_2$, SrO and of STO films. The corresponding [Sr]/([Sr]+[Ti]) content ratio from RBS and [SrO]/[TiO$_2$] cycle ratio are indicated for the STO films.

![Figure 5](image-url) Refractive index, $n$, at 1.96 eV (a) and bandgap, $E_g$, (b) for STO films deposited with different [SrO]/[TiO$_2$] cycle ratios. The results are plotted versus [SrO]/([SrO]+[TiO$_2$]) cycle ratio. Both consecutive (SrO cycles followed by TiO$_2$ cycles in an STO supercycle) (circles), and mixed (SrO and TiO$_2$ cycles intermixed in an STO supercycle) (squares) approaches were employed for the depositions. Refractive index values are also shown for TiO$_2$ and SrO. The inset shows how the bandgap $E_g$ is obtained by plotting $(\alpha h\nu)^{1/2}$ as a function of the photon energy and by extrapolation of the linear part of the curve.
SrO cycles were always intercalated in between TiO2 cycles while in mixed and consecutive approach in Figure 5. For the mixed approach film. A distinction can be made between samples deposited with the by probing the refractive index and/or the bandgap of the deposited figure clearly shows that the film composition can also be estimated

\[ \frac{[\text{Sr}]}{([\text{Sr}]+[\text{Ti}])} \]

values are plotted in Figure 6a and 6b, respectively, as a function of the refractive index and a higher bandgap. This confirms our observation that SrO deposition is slightly enhanced in the mixed growth mode.

The results confirm that the dielectric function of STO is strongly related to the film stoichiometry. Optically determined parameters, such as refractive index and bandgap, can be used to determine the \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio of amorphous STO films. For this purpose, RBS results were used to determine the relation between the optical properties and the elemental composition of a set of samples with different stoichiometries. Once this was done the \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio can be directly derived from the SE data.

For the determination of the film composition directly from the ellipsometry data, the CompleteEASE software (J.A. Woollam) offers the possibility to build composition- or temperature-dependent B-spline-based optical constant libraries. A set of dielectric constants parameterized by B-splines corresponding to samples of known compositions (or temperatures), are loaded into the software by the user. The library is then built by interpolating these dielectric functions. The interpolation is based on the critical point shifting algorithm described by Snyder et al. for AlxGa1-xAs optical constants,39 where the dielectric function of a film with unknown composition is estimated by shifting the closest two dielectric functions of known compositions in energy to align their critical points. The unknown composition is then determined by taking a weighted average of the two dielectric functions of known composition. For this purpose, CompleteEASE makes use of polynomials to shift the reference dielectric functions in energy accordingly to their known composition. In contrast to the approach by Snyder et al., who calculated the wavelength shifts to accurately align the critical points of the reference dielectric functions, the CompleteEASE software calculates polynomials using a non-linear regression fit to minimize the error between two adjacent reference spectra when shifted in energy to the average of the two known compositions called hereafter “mid-point composition”. Snyder et al. used a linear interpolation for the wavelength shift algorithm (i.e. the B-spline node spacing) and the maximum degree of the polynomials should be optimized accordingly to the case to obtain the best results. In our case, the library was built using the B-spline parameterization of the dielectric functions of the films for which RBS was performed \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) from 0.42 to 0.68. Here, we used a resolution of 0.05 eV, and for the calculation of the polynomials the reference spectra were shifted by a constant (polynomial degree of 0 for the wavelength) and linearly interpolated for the calculation of the composition (polynomial degree of 1 for the component). The absence of sharp features in the dielectric function of amorphous STO makes it possible to keep the degree of the polynomials low. Higher polynomial degrees can result in interpolation artifacts due to non-linear continuum fitting. In our case, constant fitting of the degree of the polynomials resulted in higher values of the shifts. Since the dielectric function of the mid-point composition is calculated as a weighted average of the two shifted adjacent dielectric functions of known compositions, high values of shifts resulted in misalignment of the transparent region of the two shifted spectra. This led to small non-zero values absorption below the bandgap for the interpolated spectra. Figure 7 displays the B-spline parameterized dielectric functions of STO of known compositions (solid lines) and of the mid-point compositions calculated by the CompleteEASE library (dashed lines), showing the accuracy of the algorithm. Also a library including the dielectric function of TiO2 and SrO has been built. However, the difference in composition between the dielectric functions of STO films which are the richest in Ti- and Sr- as measured by RBS and the dielectric functions of TiO2 and SrO is much larger than the difference between the single dielectric functions of the STO layers (Figure 4). The accuracy of the library depends on the difference between the dielectric function of known compositions and a poor fit was therefore obtained for layers having \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) \(< 0.42\) or \(> 0.68\). Consequently, more dielectric functions of known compositions are required to have an accurate library also in these ranges. Once the library is built, the ellipsometry data from an as-deposited STO layer with unknown composition can be modeled using only the thickness and the \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio as

near-to-stoichiometric STO films deposited in this work were 1.88 and 1.89 for the FlexAL-A and FlexAL-B reactors, respectively \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio of 0.51). These values are in agreement with our previous work, where the film with \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio of 0.52 had \(n = 1.91,22\) and with literature results, where as-deposited stoichiometric STO films \([\text{Sr}]/([\text{Sr}]+[\text{Ti}]) = 0.5\) with \(n = 1.86\) were obtained from SrTiO3, CuPc, C60 and Ti(OMe)4.36

The indirect bandgap values, \(E_g\), for the STO films were determined by plotting \((\alpha n h)^{1/2}\) versus the photon energy, where \(\alpha = 4\pi k\) is the absorption coefficient, \(n\) and \(k\) are the real and imaginary part of the complex refractive index, and \(h\nu\) is the incident photon energy. The linear part of this function above the transparent region is fitted with a polynomial. In our case, increasing the degree of the polynomials should be optimized accordingly to the case to obtain the best results. The absence of sharp features in the dielectric function of amorphous STO makes it possible to keep the degree of the polynomials low. Higher polynomial degrees can result in interpolation artifacts due to non-linear continuum fitting. In our case, constant fitting of the degree of the polynomials resulted in higher values of the shifts. Since the dielectric function of the mid-point composition is calculated as a weighted average of the two shifted adjacent dielectric functions of known compositions, high values of shifts resulted in misalignment of the transparent region of the two shifted spectra. This led to small non-zero values absorption below the bandgap for the interpolated spectra. Figure 7 displays the B-spline parameterized dielectric functions of STO of known compositions (solid lines) and of the mid-point compositions calculated by the CompleteEASE library (dashed lines), showing the accuracy of the algorithm. Also a library including the dielectric function of TiO2 and SrO has been built. However, the difference in composition between the dielectric functions of STO films which are the richest in Ti- and Sr- as measured by RBS and the dielectric functions of TiO2 and SrO is much larger than the difference between the single dielectric functions of the STO layers (Figure 4). The accuracy of the library depends on the difference between the dielectric function of known compositions and a poor fit was therefore obtained for layers having \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) \(< 0.42\) or \(> 0.68\). Consequently, more dielectric functions of known compositions are required to have an accurate library also in these ranges. Once the library is built, the ellipsometry data from an as-deposited STO layer with unknown composition can be modeled using only the thickness and the \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) ratio as

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Refractive index, \(n\), at 1.96 eV (a) and bandgap, \(E_g\), (b) for STO films deposited with different \([\text{SrO}]/[\text{TiO}_2]\) ALD cycle ratio versus \([\text{Sr}]/([\text{Sr}]+[\text{Ti}])\) content ratio from RBS measurements. Refractive index values are also shown for TiO2 and SrO.
Figure 7. B-spline parameterized dielectric functions of STO films measured by RBS (symbols), and of “mid-point compositions” (average compositions between two adjacent known compositions) calculated by the optical constants library in CompleteEASE (dotted lines).

fit parameters. To test the accuracy of the optical constant library, samples deposited with different [SrO]/[TiO2] cycle ratios were measured by XPS and by SE. The SE data were fitted using this library, and the extracted [Sr]/([Sr]+[Ti]) ratio from SE and XPS were compared. For all samples measured (with 0.42 < [Sr]/([Sr]+[Ti]) < 0.68) the difference in [Sr]/([Sr]+[Ti]) ratio obtained from SE and XPS was < ±0.02, confirming the accuracy of the optical constant library.

Spectroscopic ellipsometry and XRD measurements of annealed STO films.— STO films deposited with different [SrO]/[TiO2] cycle ratios were annealed in flowing N2 atmosphere to achieve crystallization. After an RTA of 10 minutes at 600°C, samples were measured by GI-XRD to determine their crystallinity. GI-XRD spectra of STO films with different compositions are given in Figure 8. Diffraction peaks corresponding to the cubic perovskite structure are clearly observed for films with [Sr]/([Sr]+[Ti]) ratio ranging from 0.48 to 0.63. The relative intensities of the diffraction peaks were comparable to the powder reference standards,40 indicating that there is no preferred crystal orientation. The intensity of the peaks decreased as the composition deviated from the stoichiometric value evidencing that a more pronounced crystallization is achieved for more stoichiometric films. Films deposited with [SrO]/[TiO2] cycle ratios 2:3 and 2:10 were found to be mainly amorphous, suggesting that for Sr-rich and Ti-rich compositions a higher thermal budget is required for crystallization or that full crystallization into the perovskite structure is not achievable for such compositions. When comparing the spectra of the films with [Sr]/([Sr]+[Ti]) ratios 0.63 and 0.42 it is evident that Sr-rich films are more easily crystallized than Ti-rich films. This is in good agreement with the results of Menou et al. who reported higher crystallization temperatures for Ti-rich films.19 Figure 9a shows $\varepsilon_1$ as determined by SE for films that were also analyzed by GI-XRD. Figure 9b displays

Figure 8. GI-XRD spectra of STO films after RTA at 600°C for 10 minutes in N2. The corresponding [SrO]/[TiO2] cycle ratio and [Sr]/[Ti] content ratio from RBS (when available) are indicated. The powder diffraction spectrum for crystalline STO is plotted as a reference.40

Figure 9. Real part ($\varepsilon_1$) of the dielectric function of STO films. Data of deposited films after RTA at 600°C for 10 minutes in N2 (a). Reference data from literature (b), $\varepsilon_1$ of bulk STO and of crystalline 10 nm, 20 nm STO films prepared by pulsed laser deposition.29
an incomplete crystallization process. Comparing the dielectric functions of the as-deposited films (Figure 4a) and of the annealed samples (Figure 9a) a transition in $\varepsilon_1$ can be noticed. This suggests that after RTA these films are partially crystalline. This hypothesis is corroborated by GI-XRD that revealed weaker peaks for these films.

The intensity of the peak at $\sim 4$ eV in $\varepsilon_1$ can also be used to estimate the stoichiometry of the crystallized films. As evident from Figure 9a, the intensity of this peak is maximum for the more stoichiometric film ([SrO]/[TiO2] = 2.8) and decreases gradually when deviating from the stoichiometric composition. This demonstrates that SE can be used to estimate the crystallinity of the STO films as well as the stoichiometry of both as-deposited and crystallized films.

**Film thickness influence on dielectric function.**—Films with different thicknesses (10–40 nm), deposited at 250°C with [SrO]/[TiO2] ALD cycle ratio 1:3 in the FlexAL-B reactor, were annealed at 650°C for 10 min. The real parts of the dielectric functions of these layers are shown in Figure 10. Compared to the real part of the dielectric function of bulk STO the peaks are broadened and the amplitude is reduced. Furthermore, thinner films showed lower amplitudes of $\varepsilon_1$ and decreased refractive indexes at 1.96 eV (2.35, 2.13, 2.12 and 2.08 respectively for bulk, 40 nm, 20 nm and 10 nm thick STO). This is an important consideration to take into account when comparing the dielectric function of thin films to estimate their composition. To establish an accurate relation between dielectric function and stoichiometry, layers with the same thickness should be used. In this work all layers were $\sim 30$ nm in thickness. A similar trend for STO films deposited on Si was also reported by Zollner et al.\(^a\) as illustrated in Figure 9b. The broadening of the peaks at the critical points compared to the reference dielectric function of bulk STO was ascribed to the polycrystalline structure and defects in the film.\(^a\) The decrease in refractive index films can be explained by the more prominent influence of the low refractive index interfacial oxide (formed at the Si/STO interface) on the dielectric function of thinner STO films. The influence of the interfacial oxide is also increased upon annealing the STO films. XPS depth profiles (not reported here) showed Si diffusion into the STO film after the annealing step leading to silicate formation. This could also explain the lower amplitude of $\varepsilon_1$ for crystalline STO reported in this work ($\sim 30$ nm thick, Figure 9a and 10) compared to the one reported by Zollner et al.\(^a\) (20 nm thick STO, Figure 9b).\(^a\) In the latter case the STO films deposited by Pulsed Laser Deposition (PLD) were crystalline as-deposited and did not require an annealing step. This probably limits the formation of silicates, thus yielding a better quality interface between the STO and the Si substrate.

Conclusions

Strontium titanate films were deposited by plasma-assisted ALD from Ti-Star ([pentamethyl-cyclopentadienyl] trimethoxy-titanium), Hyper-Sr [bis(tri-isopropylcyclopentadienyl) strontium-DME] and O2 plasma. The ALD temperature window for this process was found to be between 150°C and 350°C. RBS analysis confirmed that the stoichiometry of the STO film is determined by the ALD cycle ratio employed and that the Sr-content is higher than expected from the [SrO]/[TiO2] ALD cycle ratio. This was imputed to a slightly enhanced growth of SrO on a TiO2 surface. Spectroscopic ellipsometry was employed to determine the dielectric functions of the STO films in the as-deposited state and after RTA. Using an optical constants library, built in the SE software (CompleteEASE), it was proven possible to determine the composition of amorphous STO thin films from the ellipsometric angles using RBS measurements as a cross-reference for the Sr and Ti content in the compositional range examined ([Sr]/([Sr]+[Ti])) from 0.42 to 0.68. It was also demonstrated how the composition of as-deposited films can be derived from the refractive index and bandgap values. GI-XRD was employed to determine the crystallinity of the layers after RTA in N2 for 10 minutes at 600°C. Diffraction peaks corresponding to the cubic perovskite structure were observed for films with [Sr]/([Sr]+[Ti]) ratio ranging from 0.48 to 0.63. SE analysis of annealed films evidenced also that only films appearing as crystalline from GI-XRD measurements, showed also a pronounced peak at $\sim 4$ eV in the real part of the dielectric function ($\varepsilon_1$). This implies that SE, in addition to being an in situ film growth monitoring tool, is an effective technique to determine the crystallinity of STO films and also to probe the stoichiometry of as-deposited and crystalline STO films.

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