EPITAXIAL OXIDES ON SILICON

BY

PULSED LASER DEPOSITION

DAVID DUBBINK

Epitaxial Oxides on Silicon by Pulsed Laser Deposition

David Dubbink

Cover

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Chapter 1

Epitaxial oxides on silicon

1.1 Motivation

The urge to develop electronic devices with new and improved functionalities is the motivation for lots of research and technological development. Existing devices should become faster, smaller and more energy efficient, but also new concepts and functionalities have to be developed [1]. An example of a new concept is brain inspired computing, which receives much attention because of its capability to efficiently perform tasks which are not easily done with the current computers [2]. One of the many possible applications is in smart cameras for self driving cars, since brain inspired computers are very efficient in pattern recognition. A second example of a new concept is the development of wearable sensors for health care. These sensors should be able to accurately and energy efficiently gather the relevant information, and also be integrated in devices which allow for direct analysis of this information [1]. One of the fundamental issues in both examples is the development of materials with the necessary functionalities, such as memristive or ferroelectric. The class of metal oxides may contribute significantly due to its diverse range of functional properties [3]. Since the microelectronic industry is based on fabrication of devices on silicon wafers, integration of these oxides on silicon, the topic of this thesis, is required for many of its applications [4].

Within the oxides, the perovskite oxides, represented by the generalized formula ABO_3 , form an interesting subclass. Depending on the used cations on the A and B positions, materials with a wide variety of physical properties can be obtained [5]. Today's Physical Vapor Deposition (PVD) techniques enable these perovskite oxides to be grown atom layer by atom layer in epitaxial registry with an underlying substrate. By growing thin films of one perovskite oxide or heterostructures of different perovskite oxides, properties can be obtained which are fundamentally different compared to the corresponding bulk materials [6–8]. Those properties are often highly anisotropic due to coupling to the

structure. Preparation of fully epitaxial thin films is necessary in order to make use of these properties and to obtain optimal properties [5].

In order to grow such epitaxial films, a suitable template is necessary. Single crystalline perovskites offer superior templates due to the matching structure [9–11]. However, single crystalline perovskite substrates are costly and not easily prepared with large dimensions, which limit the attractiveness from industrial point of view. As an alternative, single crystalline silicon wafers are considered to offer a good platform for growth of single crystalline perovskite films, because the crystalline quality of today's silicon wafers is high, the costs are low and manufacturing and processing of devices is already highly evolved. More importantly, this opens a route towards integration of the diverse class of oxide materials with existing commercial microelectronics [4]. Therefore, growth of epitaxial oxides on large silicon wafers receives lots of attention in the oxide research community [12–15].

Growth of epitaxial perovskite oxides on silicon is not straightforward. Most of the perovskite oxides are chemically unstable on silicon [16]. Furthermore, the unavoidable presence of an amorphous silicon native oxide prevents the silicon lattice to influence the orientation of the growing film. Finally, a transition should occur from the covalently bonded diamond structure to the more ionic perovskite one [14, 17]. Therefore, most functional perovskite oxides need to be grown on a buffer layer of one of the few oxides which can be grown epitaxially on silicon. Yttria-stabilized zirconia (YSZ) and SrTiO_3 (STO) are the most used buffer layers. YSZ layer can be grown by several (PVD) techniques [18, 19], among which Pulsed Laser Deposition (PLD) [20], directly on the silicon with native oxide. In reducing conditions, YSZ will decompose the native oxide, after which a chemically stable film can crystallize on the silicon lattice [21]. YSZ has a fluorite structure with lattice parameters different from typical perovskites, but use of intermediate layers allow for growth of (001) oriented functional perovskites [22, 23]. Growth procedures for epitaxial (001) oriented STO buffer layers were first developed for Molecular Beam Epitaxy [17]. These buffer layers are attractive due to the high crystalline qualities and the smooth surfaces, while the perovskite structure directly enables the growth of functional perovskite oxides [24–26]. Recently, a similar growth procedure was developed for PLD [27, 28], the deposition technique used in this thesis.

PLD is a very suitable technique for growth of perovskite oxides. Proper choice of the deposition parameters enables stoichiometric transfer of the target material to the growing film, while the deposition can be performed in high oxygen pressures, often favorable for the resulting properties of the oxide film [29]. Moreover, thorough understanding of the PLD process enabled development of industrial scale systems. Commercial systems are available for reel-to-reel deposition on tapes, but also, more important regarding the motivation behind this work, for deposition on silicon wafers up to 200 mm [30, 31].

This work focusses on the use of PLD for epitaxial integration of perovskite oxides on silicon. Although PLD of epitaxial perovskites on silicon is investigated for years,

several aspects of the growth procedures are still subjected to research. First, the initial growth of YSZ on silicon with native oxide by PLD is not fully understood [32]. More knowledge is necessary in order to obtain complete control of the growth process, enabling reproducible growth of YSZ buffer layers with high crystalline and morphological qualities. Therefore, the growth mechanism of YSZ on Si by PLD was investigated in chapter 2. Obtaining (001) oriented perovskites on top of the YSZ fluorite structured surface is not straightforward [33]. Although successful methods are reported [22, 23], the understanding of the underlying mechanisms of this nonisostructural epitaxial growth is limited. Furthermore, surface roughening and loss of crystalline quality occurs during the fluorite to perovskite transition [15]. In chapter 3, the specific case of the growth of perovskite SrRuO_3 on fluorite buffered silicon (CeO_2 on YSZ on silicon) was investigated, aiming to understand the necessary conditions for growth of perovskites on fluorites.

The existing route to obtain epitaxial STO on Si requires an elaborative growth scheme and ultra-high vacuum (UHV) conditions. The growth starts with deposition of a Sr monolayer on the silicon surface. This layer prevents unwanted reactions between titanium and silicon, and forms the necessary template for STO crystallization [34]. However, very reactive silicon dangling bonds are always exposed during the procedure to form the Sr monolayer. UHV conditions are necessary to prevent silicon carbide and amorphous silicon oxide formation [17, 35, 36]. The crystallization of STO on the Sr template has again to be performed at controlled temperatures and oxygen pressures in order to prevent regrowth of silicon oxide and reactions between STO and Si. In this work, less demanding routes to obtain perovskite oxides directly on Si were studied. Chapter 4 concerns the possibility to grow epitaxial perovskite SrZrO_3 (SZO) on Si without removing the native oxide in advance, i.e. with a similar growth procedure as used for YSZ. In chapter 5, the formation of a Sr-silicate template was studied in order to replace the Sr monolayer template. This silicate could be made by reaction between SrO and the silicon native oxide, in this way avoiding the exposure of Si dangling bonds.

The investigated routes to obtain (001) oriented perovskites on Si are indicated in figure 1.1, which have all in common that growth was initiated on silicon without removal of the native oxide. In the next section, the contents per chapter are introduced in more detail.

1.2 Thesis outline

In chapter 2, the growth mechanism of YSZ by PLD was investigated. Attention was paid to the possibilities to control the chemical interactions between silicon, oxygen and YSZ during initial growth. Specifically, the contributions of the different sources of oxygen, i.e. oxygen from the background gas, the plasma and the silicon native oxide, to the initial growth was studied. The obtained knowledge can be used to tune these contributions in order to obtain reproducible growth of high quality YSZ.

Figure 1.1: Schematic representation of the work presented in this thesis. The numbers indicate the corresponding chapters.

Chapter 3 concerns the transition of a (001) oriented fluorite to a (001) oriented perovskite. Direct growth of SrRuO_3 on (001) oriented fluorite CeO_2 surfaces always results in predominantly (110) oriented films. However, when a seed layer of SrRuO_3 was deposited in reducing conditions, a completely (001) oriented film was obtained. This change in orientation was attributed to the phase separation between SrO and metallic Ru in the deposited seed layer. The resulting presence of SrO at the interface between CeO_2 and SrRuO_3 promoted the (001) orientation. This growth mechanism was investigated on CeO_2 surfaces with different morphologies. The roughness of the CeO_2 played an important role. The presence of $\{111\}$ facets enhanced the growth of (001) oriented perovskites, most probably due to matching between the SrO (111) and CeO_2 (111) planes.

In Chapter 4, the possibility was investigated to grow a perovskite via the oxygen scavenging method, i.e. the method used to grow YSZ without removing the silicon native oxide in advance. The perovskite SrZrO_3 was used for this work because of the known scavenging capabilities of Zr and the expected chemical stability on silicon. First, the chemistry of SrZrO_3 and its constituting binary oxides in contact with silicon and silicon oxide at different temperatures was investigated by X-ray Photoelectron Spectroscopy. Secondly, the necessary conditions to perform the scavenging procedure with SrZrO_3 were investigated. Due to different chemical behavior of Sr and Zr, stable epitaxial films could not be obtained in conditions necessary to decompose the silicon native oxide. Especially, formation of amorphous Sr-silicates was shown to hinder the epitaxial relation between Si and SZO. Stable (110) oriented epitaxial SZO films could be obtained

when the contact between Sr and Si was prevented by starting the growth with a thin layer of Zr.

In chapter 5, the mechanism of SrO-assisted silicon deoxidation was investigated. The deoxidation occurred via decomposition of the silicate Sr_2SiO_4 , which formed during heating of SrO films on the silicon native oxide. By controlling the decomposition time and temperature, it was possible to crystallize this silicate epitaxially on the silicon lattice. Epitaxial (001) oriented perovskites could be crystallized directly on this silicate.

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Chapter 2

Growth mechanism of epitaxial yttria-stabilized zirconia on Si

Abstract: The epitaxial growth of yttria-stabilized zirconia (YSZ) on silicon with native oxide was investigated in order to gain more insight in the growth mechanism. Specifically, attention was paid to the possibilities to control the chemical interactions between YSZ, silicon and oxygen during initial growth. The sources of oxygen during growth proved to play an important role in the growth process, as shown by individual manipulation of all sources present during Pulsed Laser Deposition. Partial oxidation of the YSZ plasma and sufficient delivery of oxygen to the growing film were needed to prevent silicide formation and obtain optimal YSZ crystalline qualities. The necessary oxygen pressure led to a significant increase of the silicon oxide thickness at the YSZ growth temperature of 800 °C. Therefore, the YSZ deposition had to be started as soon as the silicon substrate reached the growth temperature. The work presented in this chapter shows that all sources of oxygen present during growth should be controlled to obtain reproducible growth of high quality YSZ.

2.1 Introduction

Epitaxial integration of oxides on silicon is a challenging task, mainly because of the chemical interactions between silicon, oxygen and metal oxides. Most of the metal oxides react with silicon to form silicide and/or silicate phases [1, 2], which prevents epitaxial crystallization of the growing oxide and can deteriorate the functional properties of the film. Besides, an amorphous native oxide always forms on silicon, preventing growth of the oxide directly on the silicon crystal lattice. This native oxide can be removed prior to growth, but ultra-high vacuum conditions are required to keep the very reactive bare silicon surface free from carbide and amorphous silicon oxide formation [3, 4]. These conditions are hard to reach in growth systems, while a low oxygen pressure is contrary to the necessity to supply sufficient oxygen to the growing oxide film [5]. In order to avoid these issues, yttria-stabilized zirconia (YSZ) can be used as a buffer layer to incorporate epitaxial oxides on Si.¹ During growth in reducing conditions, the deposited YSZ decomposes the native oxide through redox reactions, after which a chemically stable film crystallizes epitaxially on the Si crystal lattice [7]. In this way, formation of unstable surfaces is avoided, and therefore the need to work in ultra high vacuum conditions. Very smooth surfaces can be obtained by a variety of Physical Vapor Deposition techniques, e.g. Pulsed Laser Deposition (PLD) [8–10], radio-frequency magnetron sputtering [11] and electron-beam evaporation [7, 12]. The highest quality films have a full width at half maximum (FWHM) of the X-ray Diffraction (002) rocking curve of around 0.7° . Growth of epitaxial (001) oriented perovskites with good functional properties on top of these buffer layers is well established [13, 14]. However, the growth mechanism of YSZ on Si is not known in detail, which is important to obtain reproducible growth of smooth films with high crystalline qualities.

In this work, the growth mechanism of epitaxial YSZ on Si by PLD was investigated. In order to understand the issues assessed in this work, general aspects of the YSZ-Si chemistry are described in the next section, followed by a summary of the existing knowledge about the growth mechanism by PLD. Finally, the research described in this chapter is introduced.

2.1.1 Chemistry of YSZ on Si

Thermodynamics as well as kinetics of the chemical interactions between Zr, Y, O, and Si have to be considered in order to understand in which growth conditions YSZ decomposes the native oxide and forms a stable epitaxial film. At different stages in the growth process, different chemical interactions are important, as indicated schematically

¹ZrO₂ has a monoclinic structure. Y₂O₃ can be added to ZrO₂ in order to stabilize a cubic fluorite structure, favorable for the growth on the cubic Si lattice. Although the cubic fluorite structure can be obtained using doping levels between 6 and 45 % [6], the commonly used composition contains 8-10% Y₂O₃.

Figure 2.1: Schematic representation of the growth process of YSZ on Si, indicating which chemical interactions should be considered. During the first part of the growth, Zr and Y are in contact with the native oxide. The native oxide decomposes due to transfer of oxygen to Zr and Y. At certain moment, yttria and zirconia come in contact with Si, whereafter YSZ crystallizes epitaxially. Here, silicide formation is possible in certain conditions. Leftover or regrown SiO_2 leads to an interface between SiO_2 and YSZ. Interdiffusion between YSZ and SiO_2 can lead to silicate formation.

in figure 2.1. Below, a short overview of the existing knowledge of these chemical interactions is provided. Thermodynamic data is only known in detail for reactions of binary oxides with silicon, and furthermore interfacial energies are never taken into consideration [15]. However, together with experimental observations, sufficient information is present to understand the processes qualitatively.

ZrO_2 and Y_2O_3 have lower Gibbs free energies of formation compared to SiO_2 . Therefore, Zr and Y will scavenge the oxygen from the silicon native oxide when brought into contact with the silicon native oxide at low oxygen pressures [16, 17]. Two reactions are possible, as exemplified for the case of Zr:

In the first reaction, volatile SiO is formed, which evaporates from the surface. In the second reaction, atomic Si is formed, which can be incorporated in the substrate. The scavenging process has to be performed at elevated temperatures (typically above 750 °C) in order to maintain a sufficiently high reaction speed and to promote SiO evaporation in the first reaction.

Once enough native oxide is removed, yttria and zirconia come into contact with the crystalline silicon, where epitaxial crystallization of YSZ can occur. In this stage, the interface between YSZ and Si should be considered. At these interfaces, formation of silicides is often observed alongside with epitaxially crystallized YSZ, especially at low oxygen pressures. Silicide formation is possible for both Y_2O_3 [18] and ZrO_2 films on Si [19, 20], but Zr-silicide formation is more thoroughly researched and most often the only considered silicide in the case of YSZ [21]. The exact reaction pathway for the formation

of Zr-silicides is not known. As shown by Stemmer [22], most of the possible reaction pathways result in a positive change in Gibbs free energy (ΔG°) or are unlikely, because of kinetic constraints. Since silicide formation is often observed in low oxygen pressures, oxygen deficiency in the ZrO_2 was proposed to promote silicide formation. The reaction

was calculated to have a negative free energy of formation for defect concentrations larger than 6%. Alternatively, Locquet *et al.* [23] proposed the formation of a solid silicon suboxide, for example via:

with $\Delta G_{1000\text{ K}}^0 = -112\text{ kJ/mol}$. If this mechanism is true, silicide formation will always occur at a Si- ZrO_2 interface.

As described above, silicide formation is related to low oxygen pressures. At higher oxygen pressures, these silicides are not present, but an amorphous layer is always observed between YSZ and silicon. YSZ is a good oxygen conductor, allowing regrowth of amorphous SiO_2 at the Si-YSZ interface [24]. Additionally, interdiffusion between YSZ and leftover or newly formed SiO_2 could lead to amorphous silicate formation. The ΔG° for silicate formation from the binary oxide

is slightly negative in the case of Zr ($\Delta G_{1300\text{ K}}^0 = -2.96\text{ kJ/mol}$), while a bigger driving force exists for Y-silicate formation ($\Delta G_{1300\text{ K}}^0 = -135\text{ kJ/mol}$) [22]. However, only limited silicate formation is observed experimentally. Most probably, silicate formation is kinetically hindered due to low diffusivity of cations in the silicate layer [25]. In this manner, a thin silicate layer may also act as a barrier against Si diffusion through the YSZ buffer layer to the functional oxide. The final YSZ- SiO_2 interface, with or without silicates, is chemically very stable. For example, YSZ films on Si can be annealed at 1000 °C in oxygen atmosphere in order to grow a thick interfacial SiO_2 layer, while the YSZ structure remains intact and Si does not diffuse through the YSZ [26].

2.1.2 PLD of epitaxial YSZ

Epitaxial YSZ films on Si have been grown by PLD since the 90s. Initially, YSZ films were grown on Si with the native oxide removed in advance [8]. Growth on silicon

with native oxide, using the scavenging reaction, was demonstrated a short time later [16]. This method led to films with higher crystalline qualities compared to films grown directly on the silicon lattice [7, 11, 27]. Typically, a two step growth process is used [9, 14]. The first couple of nm are deposited at low oxygen pressure to perform the scavenging reaction. The used pressures vary from base pressure (often in the 10^{-7} mbar range) to 10^{-4} mbar O_2 . Crystallization of YSZ is typically observed after deposition of about 1 nm [7, 10]. After deposition of about 5 nm, the growth is continued at higher oxygen pressures in order to fully oxidize the growing film.

The scavenging growth process and the fact that YSZ grows better on silicon with native oxide have been investigated by several groups. De Coux *et al.* [28] observed with Transmission Electron Microscopy (TEM) on 2.2 nm epitaxial YSZ that only at a limited amount of locations crystalline YSZ was in contact with crystalline Si. A lateral overgrowth mechanism was proposed, meaning that these locations may have acted as seeds for crystallization of the YSZ film on top of leftover silicon native oxide. Therefore, it was not necessary to reduce the native oxide completely. However, when the YSZ thickness was increased to 6.6 nm, the native oxide was completely removed. With TEM, silicide formation and increased strain in the YSZ film were observed, accompanied by increased disorder at the YSZ-Si interface. These observations are consistent with earlier work on the influence of native oxide thickness on growth of YSZ by PLD [27]. On a thin amorphous silicon oxide (0.49 nm), the YSZ film grew initially strained to the silicon. On thicker silicon oxide (0.68-1.1 nm), Reflection High-Energy Electron Diffraction (RHEED) showed that the YSZ was not strained to the silicon already directly after crystallization. The crystalline qualities for growth on these thicker silicon oxide layers were significantly higher.

All these experiments suggest that silicide formation and the silicon oxide play an important role in the growth process. Although a clear relationship is not described in literature, the formation of silicides at the YSZ-Si interface seems to decrease the quality of the YSZ film. The native oxide may play an important role in avoiding silicide formation. If lateral crystallization occurs, the native oxide does not need to be removed completely during growth via the oxygen scavenging method. The leftover silicon oxide can act as a buffer against silicide formation, since contact between YSZ and Si is minimized. Furthermore, formation of dislocations due to the 5.7 % misfit strain² is avoided since the YSZ can crystallize freely on the silicon oxide [29, 30]. Finally, silicon oxide might play a role in the crystallization process and strain relaxation in a more direct way. As posed in several studies, SiO_x is crystalline close to the Si- SiO_x interface, with lattice parameters close to YSZ [31, 32]. Possibly, YSZ crystallizes on the crystalline part of the native oxide, again avoiding both silicide formation and the large lattice mismatch with Si [27, 33].

The work described above shows the occurrence and importance of several chemical

²YSZ with 8% Y_2O_3 , the composition used in this work, has lattice parameters of 5.14 Å, while the silicon lattice parameters are 5.43 Å.

Figure 2.2: Schematic indication of the sources of oxygen during PLD. Oxygen is present in the silicon native oxide, the plasma plume and the background gas.

processes during initial growth of YSZ on Si by PLD, e.g. silicon oxide reduction and silicide formation. However, limited attention has been paid to the possibilities to control these different chemical processes. A unique feature of the PLD process is the interaction of the plasma with the background gasses present in the deposition chamber. The metals in the plasma can obtain different degrees of oxidation depending on the partial oxygen pressure [34]. As shown for the homoepitaxial growth of SrTiO_3 (STO), stoichiometry and growth kinetics depend heavily on the degree of oxidation of the plasma. Furthermore, the STO substrate proved to supply oxygen to the growing STO film as well [35]. Similar to the growth of STO on STO, three sources of oxygen can be distinguished during growth of YSZ on Si with native oxide, as indicated schematically in figure 2.2. At the substrate/film surface, oxygen can arrive from the plasma as atomic or molecular oxygen, or in the form of (partially) oxidized zirconium and yttrium. The oxygen from the background can oxidize the growing film directly, but also interact with the plasma. Furthermore, oxygen is present in the silicon native oxide. The thickness of this oxide can change during heating to the growth temperature due to reaction with oxygen from the background. Since oxygen is involved in all of the chemical processes described before, tuning the contributions of all sources of oxygen may provide a way to control the chemistry during the scavenging process.

2.1.3 The experiment

In this work, the possibility to control the chemistry of the initial growth of YSZ on Si was investigated, as well as the relationship between the chemistry and the resulting crystalline properties of the YSZ film. Both subjects were assessed by detailed study of the PLD growth process, with a focus on the contributions of the different sources of oxygen. In order to investigate these contributions, all sources were addressed individually:

1. **Background pressure.** The contribution of oxygen from the background was varied by changing the partial oxygen pressure ($p\text{O}_2$) at constant total pressures. Ar was used to reach the total pressure aimed for, since it is inert and has an atomic

weight close to the weight of molecular oxygen. In this way, the plasma plume size and shape was kept similar, meaning the flux of oxygen from the background could be changed independently from the Zr and Y fluxes from the plasma. Additionally, the fluxes of Zr and Y from the plasma could be changed independently by changing the laser repetition rate.

2. **Plasma.** The physics and chemistry of the plasma changes drastically with pressure [34, 36]. For instance, the oxidation state of the plasma upon arriving at the substrate can be different for similar pO_2 , while the total pressure influences the arrival time and plasma temperature. For this reason, 2 different total pressures were examined, i.e. $2 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mbar. The resulting physics and chemistry of the plasma were examined with self-emission spectroscopy.
3. **Native oxide.** All 5x5 mm Si substrates were cut from the same 4 inch wafer in order to start with the same native oxide thicknesses in all experiments. However, the thickness can change due to heating of the substrate in the presence of oxygen. Therefore, *in situ* X-ray Photoelectron Spectroscopy (XPS) was used to determine silicon oxide thicknesses of the substrates in different deposition conditions.

Besides addressing these sources of oxygen, the resulting chemical and crystallization processes observed during initial growth were investigated, as well as the resulting crystalline properties of the YSZ film. RHEED was used to monitor the crystallization process during growth. In order to investigate the chemistry after growth, *in situ* X-ray Photoelectron Spectroscopy (XPS) was used. X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM) were used to relate the observed growth processes to respectively the crystalline properties and morphology of the films.

2.2 Methods

Pulsed Laser Deposition All films were grown in a TSST PLD chamber with *in situ* RHEED (STAIB). A 248 nm KrF laser (Coherent LPXpro) was used for ablation from a polycrystalline YSZ target, containing 8% Y_2O_3 . The base pressure of the PLD chamber was in the 10^{-8} mbar range. For low pO_2 , the flow of O_2 was regulated with a needle valve, while the flow of Ar was regulated with a mass flow controller. The substrates were heated via laser heating. The deposition parameters are summarized in tabel table 2.1. Samples examined with *in situ* XPS were cooled down in vacuum, while the thicker samples examined with XRD were cooled down in 100 mbar O_2 .

Characterization and analysis *In situ* XPS was performed with an Omicron XM-1000 monochromated Al-K α source, with the pass energy to the detector set to 20 eV. The angle of the surface normal with respect to the detector was 1° . The method to determine silicon oxide thicknesses was similar to the 5P* method described by Seah and

Table 2.1: Parameters for YSZ deposition. The conditions which were varied will be described in the results section.

Substrate temperature (°C)	800
Heating rate (°C)	50
Cooling rate (°C)	20
Fluency (J/cm ²)	1.9
Spot size (mm ²)	2.4
Laser repetition rate (Hz)	Varied
Total background pressure (mbar)	$2 \cdot 10^{-2}$ or $1 \cdot 10^{-1}$
pO ₂ (mbar)	Varied
Target-substrate distance (mm)	50

Spencer [37]. An R_0 value of 0.80 was determined by measuring silicon substrates with different thicknesses of thermally grown oxides. An attenuation length of photoelectrons in silicon dioxide of 3.448 nm was used [37].

The chemistry of the YSZ plasma plume was assessed by self-emission spectroscopy. An Andor Shamrock 163 spectrograph with a 300 lines/mm grating and an Andor iStar ICCD detector with 1024x1024 pixels were used to collect the data. This combination of spectrograph and detector resulted in a bandpass of 257 nm and a spectral resolution of 1.5 nm. The gate width was adjusted with the delay time after ablation, and typically kept below 2% of the delay time. The resulting images obtained with the CCD camera consisted of one axis representing the wavelength, and the other axis representing the spatial component. In order to compare the measurements, the intensities were summed along the spatial axis. All spectra were normalized between 0 and 1 after subtracting the minimum intensity. The wavelength scale was calibrated using reference tables [38, 39]. In order to obtain information about the individual oxides, sintered powder targets of ZrO₂ and Y₂O₃ were examined as well. The time of arrival and velocity of the YSZ plasma plume at the substrate were measured by imaging the visible part of the plasma, i.e. without a spectrograph between the plasma and the camera.

XRD measurements were performed at a Panalytical X'pert Pro with a nonmonochromated Cu source, using of a nickel filter to remove the K β emission. AFM was performed on a Bruker Dimension Icon in tapping mode.

2.3 Results

This section is divided into three parts. In subsection 2.3.1, chemical and crystallization processes observed during initial growth are described, as well as the resulting crystalline properties. In subsection 2.3.2, the contributions of the different sources of oxygen to these chemical and crystallization processes are investigated. Finally, the phenomena causing the observed low crystalline qualities in oxygen deficient conditions are studied in subsection 2.3.3.

Figure 2.3: a) XPS Zr3d and Si2p spectra of films grown at total pressures of 2×10^{-2} mbar at a) different pO_2 or b) with different laser repetition rates. A low flux of oxygen compared to Zr, caused by low pO_2 or high laser repetition rate, led to silicide formation and an increased ratio of silicate/ SiO_x to SiO_2 bonds.

2.3.1 Correlation between initial growth and crystalline quality

Chemistry during initial growth

First, the influence of pO_2 on the chemical interactions during initial growth was investigated. Figure 2.3a shows XPS spectra of 6 nm YSZ films grown at different pO_2 , while the total pressure and laser repetition rate were kept constant at respectively 2×10^{-2} mbar Ar and 14 Hz. Silicide formation was clearly observed when a pO_2 of 1×10^{-6} mbar was used, as concluded from the existence of Zr^0 peaks together with a shoulder at the low binding energy side of the Si2p bulk peak [40]. The intensities of these features were lower at 1×10^{-5} mbar, and were completely absent when pO_2 of 1×10^{-4} mbar or higher were used. A similar change was obtained by changing the flux of Zr and Y using different laser repetition rates. The XPS spectra in figure 2.3b show that silicide

Figure 2.4: XRD measurements of 100 nm thick YSZ films on top of 5 nm YSZ films grown in varying pressures. a) XRD $\theta - 2\theta$ scans of the films with the first 5 nm grown at a total pressure of 2×10^{-2} mbar Ar. At 33° a multiple reflection peak of the Si can be observed. The variation in intensity of this peak is only related to the in-plane orientation of the sample in the XRD [41]. b) FWHM of the YSZ (002) rocking curves of the samples with the initial 5 nm grown in total pressures of 2×10^{-2} or 1×10^{-1} mbar. The dashed lines are inserted for visual reference.

formation decreased when the laser repetition rate was decreased from 28 to 14 Hz at a constant pO_2 of 1×10^{-5} mbar, whereas no silicide formation was detected anymore at 7 Hz. Thus, the formation of silicides can be controlled by tuning the ratio between flux of oxygen from the background gas and Zr and Y from the plasma.

A second notable difference appeared in the Si2p region indicating oxidized species. In the Si2p region, peaks around 99.7 eV and 103.5 eV indicate the Si^0 substrate and completely oxidized Si^{4+} respectively. In between both extremes, underoxidized Si (SiO_x) and/or silicates (Y/Zr-O-Si) can appear [25]. In principle, at least one monolayer of silicate bonds is expected due to the interface between YSZ and Si or SiO_2 , which contributes significantly to the XPS spectra due to the surface sensitivity of XPS [22]. As visible in figure 2.3, the region indicating SiO_2 increased with respect to the region indicating silicates and SiO_x species when the pO_2 was increased or the laser repetition rate was decreased. Although any quantification cannot be performed without knowledge about the morphology and distribution of the different species, the measurements suggest increasing regrowth of SiO_2 with increasing pO_2 or decreasing laser repetition rate. Quantification of the SiO_2 thickness will be discussed later.

Relation between pO_2 and crystalline quality

In order to investigate the influence of the initial chemistry on the crystalline properties of YSZ, 100 nm YSZ films were grown on top of 5 nm films which were grown under varying pO_2 and a fixed laser repetition rate of 14 Hz. The 100 nm films were all grown with the same deposition conditions ($p = 2 \cdot 10^{-2}$ mbar O_2 , $f = 14$ Hz). In this way, XRD measurements of the thick films acted as a tool to indicate the crystalline properties of the first 5 nm. The XRD measurements presented in figure 2.4 show a clear trend in crystalline properties depending on the pO_2 at $2 \cdot 10^{-2}$ mbar Ar during initial growth. At low pO_2 , (111) oriented YSZ was measured besides the epitaxial (001) orientation. The intensity of the (111) peak decreased with increasing pO_2 . At the same time, the FWHM of the rocking curve of the (002) peak decreased. At a pO_2 of $5 \cdot 10^{-3}$ mbar, the lowest FWHM was measured, while no (111) orientation was visible anymore. Increasing the pO_2 above this value led to increased values of the FWHM and the presence of (111) oriented YSZ again. The presence of the (111) orientation indicated the presence of polycrystalline phases. Although other orientations were hardly visible in the XRD spectra due to the low relative intensities of these peaks, polycrystallinity was consistent with the rings observed in the corresponding RHEED patterns (data not shown).

A similar trend was observed when the initial growth was performed at a total pressure of $1 \cdot 10^{-1}$ mbar (see figure 2.4b). The growth rate per second was kept similar to the $2 \cdot 10^{-2}$ mbar experiments by using a laser repetition rate of 12.5 Hz. Despite the equal growth rate, the lowest FWHM was observed at $5 \cdot 10^{-4}$ mbar, which is one order of magnitude lower compared to the growth performed at a total pressure of $2 \cdot 10^{-2}$ mbar. The lowest FWHM was 1.00° , while an optimum of 0.85° was obtained in the $2 \cdot 10^{-2}$ mbar case. Furthermore, features indicating polycrystallinity started to dominate the RHEED pattern at $5 \cdot 10^{-3}$ mbar, while streaks or spots indicating epitaxial phases were not observed at all at a pO_2 of $2 \cdot 10^{-2}$ mbar. This degree of polycrystallinity differed from the growth performed at a total pressure of $2 \cdot 10^{-2}$ mbar, since only a small amount of polycrystalline phases was observed with XRD when $2 \cdot 10^{-2}$ mbar O_2 was used (see figure 2.4a).

Crystallization behavior

During growth of the films, RHEED movies were recorded with ~ 0.1 frame/s in order to obtain insights about the crystallization behavior in the different growth conditions. Figure 2.5a presents an example of the analysis performed on the RHEED data. Before start of the growth, the pattern of the crystalline surface buried beneath the amorphous silicon oxide was visible. This pattern faded when YSZ was deposited due to increased attenuation by the deposited material. After a certain deposition time, streaks or spots indicating epitaxial YSZ appeared. Typically, streaks, indicating a flat surface, appeared when the FWHM of the XRD (002) rocking curve was below 1° , while spots, indicating

Figure 2.5: a) Snapshots from a RHEED movie recorded during growth at 5×10^{-3} mbar O_2 in a total pressure of 2×10^{-2} mbar Ar. Below the snapshots, the intensity profile derived from the blue box and the streak positions derived from the green box are presented. The dashed line indicates the minimum intensity, which is taken as a measure of the crystallization time/thickness. b) Crystallization times/thicknesses derived with the method depicted in figure a), for samples grown at different pO_2 in total pressures of 2×10^{-2} and 1×10^{-1} mbar Ar. The dashed lines are a guide to the eye.

a rougher surface, appeared above this value. Rings, indicating polycrystalline phases, typically appeared when the FWHM was above 1.5° . The intensity of a disappearing Si spot and evolving YSZ streak or spot was monitored over time. The minimum intensity was used as an indication of the crystallization time. Figure 2.5b shows the crystallization times as well as the corresponding amount of deposited YSZ, determined for samples grown at different pO_2 and total pressures of 2×10^{-2} or 1×10^{-1} mbar Ar. Similar trends were visible in the crystallization time for both total pressures. First the crystallization time decreased with increasing pO_2 , after which it increased again. At a total pressure of 1×10^{-1} mbar, the minimum in crystallization time was observed at the same pO_2 as the optimum crystalline quality (see figure 2.4). At the total pressure of 2×10^{-2} mbar, a minimum was observed at a pO_2 of 1×10^{-5} mbar, after which the crystallization time slightly increased. Crystallization times were notably larger at 1×10^{-1} mbar.

Figure 2.5a shows a typical example of the change of the positions of the Si and YSZ streaks with increasing deposition time. No change in the distance between the YSZ streaks was observed above 2 nm, even after growth of additional 100 nm in oxygen atmosphere. The distance between the YSZ streaks was larger compared to Si, indicating a smaller lattice, as expected. Below 2 nm, the YSZ streak positions were closer to the Si streak positions. Although this may indicate that YSZ was initially strained to the silicon, the shift can be caused by overlap with the Si streaks, which were still weakly present at

Figure 2.6: a) XPS Si2p spectra of Si substrates after heating to 800 °C at different pO_2 . Increase of oxide thickness was observed above 1×10^{-4} mbar. b) Calculated silicon oxide thicknesses for as received and annealed substrates, and after growth of YSZ. The silicon oxide thicknesses for the samples with YSZ film were calculated from the samples shown in figure 2.3a, i.e. 6 nm YSZ films grown at a total pressure of 2×10^{-2} mbar with a laser repetition rate of 14 Hz.

the starting point of YSZ crystallization. Similar fast lattice relaxation during growth was observed for all films.

2.3.2 Contribution of sources of oxygen to the growth process

As mentioned in the introduction, three sources of oxygen exist during growth by PLD. In this section, an attempt was made to determine the contribution of each individual source to the growth process. Therefore, first the thicknesses of silicon oxide before and after growth were determined using XPS. Secondly, the physics and chemistry of the plasma in different deposition conditions are described, as determined with self-emission spectroscopy.

Silicon oxide thickness determination by XPS

Figure 2.6a shows the Si 2p spectra for silicon substrates with native oxide after annealing at 800 °C for 5 minutes at different pO_2 . An increase in the intensity of SiO_2 with respect to Si from the bulk of the substrate was notable above a pO_2 of 1×10^{-4} mbar. The calculated thicknesses are shown in figure 2.6b. A linear increase of oxide thickness with pO_2 was observed. Growth of YSZ was normally started within 30 seconds after reaching 800 °C. This is especially important for the higher pO_2 , since the thickness of the

Figure 2.7: Plot of plasma front positions versus delay times at $2 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mbar O_2 . The solid lines represent a drag model fit, the dashed curve is a linear fit indicating diffusive propagation. The blue line is the substrate position.

silicon oxide is expected to increase approximately linearly with time [42]. For example, when growth is performed at a total pressures of $2 \cdot 10^{-2}$ mbar O_2 , the increase in oxide thickness is expected to be only 0.04 nm when the substrate is kept at 800 °C for 30 s, instead of the observed 0.4 nm when the substrate is kept at 800 °C for 5 min. Indeed, polycrystalline growth was observed in the latter case (data not shown), while epitaxial growth was observed when the growth started immediately after reaching 800 °C (see figure 2.4).

Secondly, the SiO_2 thicknesses after growth of YSZ were calculated for the samples grown in a total pressure of $2 \cdot 10^{-2}$ mbar. In order to perform the calculation, a homogeneous Si- SiO_2 -YSZ stacking sequence was assumed. After fitting, only the part of spectrum indicating SiO_2 and Si were taken into account by subtracting the silicide, silicate and SiO_x contributions, which were especially present in the low pO_2 samples. A significant increase in silicon oxide thickness with increasing pO_2 was calculated, as shown in figure 2.6b. Although the samples were cooled down in vacuum directly after growth, the oxide thicknesses were much larger compared to the bare substrates annealed at the same pO_2 . In the case of growth at $pO_2 = 5 \cdot 10^{-3}$ mbar, where an optimum crystalline quality was observed with XRD, a silicon oxide thickness of 2.6 nm was determined.

Plasma Spectroscopy

The chemistry and kinetics of the plasma were investigated for different pO_2 at total pressures of $2 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mbar. Figure 2.7 presents the front position versus delay time of the plasma plume at pressures of $2 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mbar O_2 . The plasmas propagated differently in both pressures. At $2 \cdot 10^{-2}$ mbar, the plasma arrived at the substrate 6 μs after ablation, with a velocity of 5 km/s. The propagation could be fitted with a simple kinetic drag model [43]. In this model, the plasma has a ballistic like propagation, while minor deceleration occurs due to drag forces on the particles in the plasma.

Figure 2.8: Self emission spectra of the plasma at total pressures of a) 2×10^{-2} and c) 1×10^{-1} mbar after arriving at the substrate, respectively 6 and 20 μs after ablation. The YO line at 597 nm is indicated with a black arrow. b) and d) show the relative intensities of the YO line at 597 nm after different delay times for total pressures of 2×10^{-2} and 1×10^{-1} mbar respectively. The color scales correspond to figures a and c, the arrival of the plasma plume at the substrate is indicated with a dashed line.

At 1×10^{-1} mbar, the plasma front position changed linearly with delay time after 12 μs , which indicates propagation by diffusion. The plasma reached the substrate after 20 μs with a velocity of 1 km/s. The plasma propagation behavior and arriving velocities were very similar to other oxide plasmas [36].

Figure 2.8a and c shows the spectra of the plasmas at different pO_2 just after arriving at the substrate. The spectra show a clear trend depending on pO_2 for both 2×10^{-2} and 1×10^{-1} mbar total pressures. Comparison with spectra from the binary oxides and the reference tables showed that the plasmas were dominated by atomic Zr lines at low pO_2 . Especially, the lines between 400 and 500 nm can be assigned to atomic Zr species. The

Figure 2.9: AFM images of films grown in pO_2 of a) 1×10^{-6} and b) 5×10^{-3} mbar, at a total pressure of 2×10^{-2} mbar. These images are typical for growth at pO_2 where silicides are formed or formation of silicides is prevented. In conditions where silicide formation was avoided, the surface was smoother compared to conditions where silicide formation occurred (the peak-to-peak roughnesses were respectively 0.8 and 1.5 nm).

relative intensity in this region decreased with increasing pO_2 . Simultaneously, between 500 and 600 nm bands originating from zirconia increased. With increasing oxidation, the contribution of yttria to the spectra became stronger as well. Especially, a strong YO band showed up at 597 nm. In order to compare the oxidation of the plasmas, the relative intensity of this line was determined for all pO_2 after different delay times. Figure 2.8b and d show the results for the total pressures of 2×10^{-2} and 1×10^{-1} mbar respectively. The presence of the YO line was noted above pO_2 of 1×10^{-4} mbar in 2×10^{-2} mbar total pressure, and 5×10^{-4} mbar in the 1×10^{-1} mbar case. When the plasma arrived at the substrate, the YO line was more pronounced at total pressures of 1×10^{-1} mbar, compared to similar pO_2 in 2×10^{-2} mbar. However, at 2×10^{-2} mbar, the relative intensity of the YO still increased after arrival, while the increase hardly occurred at 1×10^{-1} mbar. For both total pressures, oxidation was observed at pO_2 corresponding to optimal YSZ quality (5×10^{-3} and 5×10^{-4} for 0.02 and 1×10^{-1} mbar respectively, see figure 2.4).

2.3.3 Instability of silicides in oxygen atmosphere

Figure 2.9 shows typical AFM images of 6 nm thick films grown in conditions where silicides formed, as well as an image of a film grown in optimized conditions. The surface of the film with silicides was grainy and had an RMS of 0.39 nm (peak-to-peak roughness 1.5 nm). The film grown in optimized conditions was much smoother, and had an RMS of 0.18 nm (peak-to-peak roughness 0.8 nm).

A similar observation was made by RHEED (see figure 2.10). The film grown in optimized conditions had a streaky pattern, indicating a flat film, while the film grown in oxygen deficient conditions had a spotty pattern, indicating island formation. Although both patterns indicate epitaxially grown films, a big difference was observed when O_2 was

Figure 2.10: a) RHEED image of a film grown at a $p\text{O}_2$ of $1 \cdot 10^{-6}$ mbar in a total pressure of $2 \cdot 10^{-2}$ mbar Ar, where silicides were observed with XPS. b) RHEED image grown in the same conditions, but after cooling down in O_2 . c) RHEED image of a film grown at $5 \cdot 10^{-3}$ mbar O_2 in a total pressure of $2 \cdot 10^{-2}$ mbar Ar, showing the streaks consistent with a flat surface. No changes were observed in the pattern when more O_2 was added to the system.

Figure 2.11: XPS Zr3d and Si2p spectra of two films grown at $1 \cdot 10^{-6}$ mbar O_2 in a total pressure of $2 \cdot 10^{-2}$ mbar Ar. The features indicating silicide formation were not visible in the sample which was cooled down in O_2 .

added directly after growth. Patterns of films grown in optimized conditions remained streaky. However, rings indicating polycrystallinity appeared in the film grown in the more reducing conditions. In the XPS measurements performed on this film, no features indicating silicides were visible anymore, while the ratio of SiO_2 with respect to silicates/ SiO_x increased (see figure 2.11).

2.4 Discussion

2.4.1 Relation between silicide formation and crystalline quality

A high ratio of Y/Zr to oxygen during growth caused formation of silicides, which could be tuned by changing the $p\text{O}_2$ and the laser repetition rate. As shown for the case

of a laser repetition rate of 14 Hz and a total pressure of $2 \cdot 10^{-2}$ mbar, silicide formation occurred at pO_2 below $1 \cdot 10^{-5}$ mbar. At these conditions, plasma spectroscopy did not show any oxidation of the plasma. Initially, Y and Zr can take sufficient oxygen from the native oxide to form YSZ. However, oxygen deficiency may occur due to ongoing deposition of metal atoms. As described in the introduction, oxygen deficiency at the YSZ-Si interface will lead to silicide formation (via equation 2.3 or equation 2.4). At a pO_2 of $1 \cdot 10^{-5}$ mbar, the thermodynamically expected amount of vacancies is much lower than the amount causing instability [22], while the flux of O_2 from the ambient was sufficient to provide the necessary oxygen for complete oxidation of the growing film³. Apparently, excess of O_2 at the film surface is necessary to completely oxidize the film during growth.

The silicide formation may explain the trend in the crystallization time at low pO_2 . In principle, the scavenging process, followed by YSZ crystallization, should be fastest in the most oxygen deficient conditions, i.e. when Y and Zr do not oxidize in the plasma and regrowth of the silicon oxide due to O_2 from the background gas is limited. Instead, increased crystallization times were observed under the most oxygen deficient conditions, which can be caused by competition between silicide formation and YSZ crystallization at the silicon-YSZ interface.

XPS measurements showed that silicides were not stable in oxygen, and transformed to SiO_2 and YSZ, while formation of polycrystalline phases was observed with RHEED. Most probably, addition of O_2 before growth of the 100 nm YSZ film led to formation of polycrystalline YSZ and amorphous SiO_2 phases due to reaction between the silicides and oxygen. The presence of these phases resulted in a low crystalline quality when the YSZ growth was continued. This process could still occur in pO_2 above which silicide formation was detected with XPS. Before the XPS measurements, small amounts of silicides could have been transformed to YSZ and SiO_2 during cool down. This explains why an optimum quality was not reached at a pO_2 of $1 \cdot 10^{-4}$ in $2 \cdot 10^{-2}$ mbar Ar yet, while no silicides were measured anymore.

2.4.2 YSZ growth in higher oxygen pressures

At higher pO_2 , the crystallization time increased with increasing pO_2 . For both total pressures of 0.02 and $1 \cdot 10^{-1}$ mbar, the increase occurred at pO_2 where the plasma started to oxidize. Due to this partial oxidation, the scavenging possibility per Zr or Y atom was lower, as shown by the following modification of equation 2.1.

³At $1 \cdot 10^{-5}$ mbar, approximately 10 monolayers of oxygen arrive at the surface per second, which is much more than the oxygen necessary, considering the used YSZ growth speed of ~ 0.5 unit cells per second.

Therefore, deposition of more YSZ was needed to decompose the silicon native oxide. Two additional mechanisms were found to contribute to the increased crystallization times. First of all, at pressures above $1 \cdot 10^{-3}$ mbar, the silicon oxide thickness started to increase before the start of the growth. This contribution was largely circumvented by starting the growth quickly after reaching the growth temperature. More importantly, the thickness of the silicon oxide after growth of YSZ depended heavily on the pO_2 , and showed a growth rate much higher than the growth rate on the as received silicon. Similar growth rate enhancements with over an order of magnitude has been described for thin metal overlayers of e.g. Ba [44], Cu [45], Sr [46] and Y [47]. Apparently, YSZ catalyzes the absorption of oxygen by the silicon oxide. Therefore, silicon oxide regrowth competes with the scavenging process as soon a YSZ is present at the silicon surface. In the case of growth at a total pressure of $2 \cdot 10^{-2}$ mbar, the optimum pO_2 was found at conditions where severe regrowth of the silicon oxide was observed. Together with the observed partial oxidation of the plasma, the scavenging process in optimum conditions can now be summarized by the following reaction:

When the oxygen pressure was too high, (partly) polycrystalline films grew due to insufficient scavenging, caused by overoxidation of the plasma and regrowth of the native oxide.

The observed phenomena agree very well to the lateral overgrowth mechanism proposed by De Coux *et al.* [28]. Regrowth of silicon oxide does not necessarily prevent lateral crystallization. The observed lattice relaxation from the start of crystallization occurs because the YSZ is not coupled to the Si lattice. Lateral overgrowth is a well known method in growth of semiconductors, and proved to increase the crystalline quality due to avoidance of defect formation because of strain [29, 30]. Similarly, this mechanism explains the high YSZ crystalline qualities in conditions where residual SiO_2 was present, since the large mismatch of 5.7 % between YSZ and Si is avoided.

2.4.3 Differences between $2 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ mbar total pressures

The trends described above hold in general for both total pressures of $2 \cdot 10^{-2}$ mbar and $1 \cdot 10^{-1}$ mbar. However, differences were observed in the optimal pO_2 , crystallization times, the obtained crystalline quality and the limiting pO_2 at which epitaxial growth was not possible anymore. Some aspects of the growth process were similar for both total pressures. The silicon oxide thicknesses at the start of YSZ growth were similar, since the increase in thickness depends on the pO_2 only. For the same reason, the fluxes of oxygen from the ambient to the growing film were similar. Finally, the flux of YSZ per second was kept constant by using a slightly lower laser repetition rate in the $1 \cdot 10^{-1}$ mbar case

(12.5 Hz instead of 14 Hz). Therefore, the differences in growth behavior can only be explained by differences in the behavior of the plasma.

First, differences can be caused by the different kinetic regimes of the plasma. At 2×10^{-2} mbar, the velocity of the plasma arriving at the substrate was much higher compared to 1×10^{-1} mbar. High energetic particles may assist in breaking of silicon-oxygen bonds within the native oxide layer. Secondly, differences can be caused by the plasma chemistry. A higher degree of oxidation is expected at 1×10^{-1} mbar, since the plasma is thermalized [35]. Furthermore, the interaction between the plasma and background gas is expected to be increased at 1×10^{-1} mbar, because of the diffusion like propagation. Surprisingly, the pO_2 at which plasma oxidation started was in the same order of magnitude for both total pressures. This observation is however in agreement with the observations made on plasmas ablated from an $YBiO_3$ target [48]. In that case, oxidation of Y was observed quickly after ablation because of reaction with oxygen ablated from the target. At lower pO_2 , the pressure dependent degree of oxidation was explained by a pressure dependent oxygen nonstoichiometry of the target. If this mechanism is true, the degree of oxidation is indeed expected to be comparable in both total pressures. At low pO_2 , the interaction of the plasma with oxygen from the background is low in both total pressures. Therefore, the oxidation of the plasma is dominated by the oxygen present in the target, which depends only on the pO_2 . The plasma chemistry can however still be responsible for observed differences in growth behavior due to different arrival times. In the 2×10^{-2} mbar case, the plasma just started to oxidize when arriving at the substrate, while the amount of oxidation was higher in the 1×10^{-1} mbar case due to the increased arrival time. Therefore, the average amount of oxidized species arriving at the substrate was lower at 2×10^{-2} mbar compared to 1×10^{-1} mbar.

More work should be performed in order to elucidate the details of the influence of the plasma kinetics and chemistry on the growth process. This is important, since a proper choice of the total pressure can be used to tune the oxygen arriving from the plasma with respect to the oxygen arriving from the ambient. Furthermore, the velocity of the particles arriving at the substrate can be optimized in order to optimize the scavenging process.

2.5 Conclusion

In this work, the growth mechanism of epitaxial YSZ on Si with native oxide by PLD was investigated. The possibility to control different sources of oxygen in the PLD process was exploited to control the chemistry during the scavenging of oxygen from the native oxide by YSZ. In conditions corresponding to optimum YSZ crystalline quality, silicide formation was prevented due to partial oxidation of the YSZ plasma and sufficient flux of oxygen from the ambient to the growing film. In this regime, significant regrowth of silicon oxide occurred, catalyzed by the deposited YSZ film. Thickness increase of the silicon oxide before growth had to be prevented by starting the deposition as soon as

possible after reaching growth temperature. These findings show that the contributions of all sources of oxygen can and should be controlled in order to obtain reproducible YSZ growth.

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Chapter 3

Growth of (001) oriented SrRuO_3 on YSZ- CeO_2 buffered silicon

Abstract: Limited knowledge exists concerning the growth of (001) oriented perovskites on (001) oriented fluorite surfaces. Therefore, the specific case of growth of epitaxial (001) oriented perovskite SrRuO_3 on (001) oriented fluorite CeO_2 was investigated. In order to obtain the (001) orientation, growth of a SrRuO_3 seed layer in reducing conditions was necessary. XPS and RHEED were used to investigate why this seed layer was necessary. The most important aspect of the seed layer turned out to be the phase separation between SrO and metallic Ru. The resulting presence of SrO at the interface between CeO_2 and SrRuO_3 promoted the (001) orientation. In agreement with these findings, (001) oriented SrRuO_3 could be obtained when a seed layer of SrO was deposited. The growth of SrRuO_3 with use of a seed layer was investigated on CeO_2 surfaces with different morphologies. The roughness of the CeO_2 played an important role. The presence of $\{111\}$ facets enhanced the growth of (001) oriented perovskites, most probably due to lattice matching between the SrO (111) and CeO_2 (111) planes.

3.1 Introduction

Epitaxial integration of (001) oriented perovskites on yttria-stabilized zirconia (YSZ) buffered silicon is not straightforward. First of all, a transition from a fluorite to perovskite structure is necessary. Even if the unit cell dimensions are close, mismatch between bonds at the interface easily causes noncoherent growth [1, 2]. In the case of YSZ, the lattice parameters are far from typical perovskite values. The closest match between (001) oriented fluorites and perovskites can be found when the perovskite unit cell is rotated in plane by 45°. This rotation still leads to lattice mismatches between perovskites, with lattice parameters typically between 3.67 (LuAlO₃) and 4.05 (LaScO₃) Å [3], and YSZ, with lattice dimensions of $5.14/\sqrt{2} = 3.63$ Å, from 1 to 12 %. Additionally, in some cases chemical interactions between cations of the film and Zr cause chemical and structural inhomogeneity at the fluorite-perovskite interface [4]. For these reasons, use of an additional fluorite CeO₂ layer was suggested already 30 years ago [5, 6].

Growth of (001) oriented perovskites with high crystalline quality on the CeO₂ buffer layer remains challenging. Taken the 45° rotation into account, CeO₂ has lattice dimensions of $5.41/\sqrt{2} = 3.83$ Å, leading to mismatches with the perovskites between -4 and 6 %. Although this is more in the range of the perovskites, the mismatch with for example the electrode material SrRuO₃ (3.2 %) is still considerable. Equally important, due to a lattice mismatch between YSZ and CeO₂ of 5.5 %, growth of CeO₂ islands instead of smooth films occurs from the very first stage of the growth [7, 8]. This leads to defects in both the CeO₂ and, as a results, the perovskite [9]. Finally, the transition from a fluorite to perovskite structure should still occur.

In literature, growth of (001) orientated perovskites on CeO₂/YSZ buffered silicon is demonstrated only for a limited number of perovskites. Most of the work is dedicated towards the conducting LaNiO₃ (LNO) [10–12] and SrRuO₃ [13] for use as bottom electrodes, or towards SrTiO₃ (STO) [14, 15] as typical template for growth of functional perovskites. (001) oriented LNO buffer layers can be grown in a one step process. However, Dekkers *et al.* [13] showed that growth of SrRuO₃ required an extra step, since the orientation could only be switched from mainly (110) to completely (001) when a monolayer of SrRuO₃ was grown in reducing conditions at high temperatures¹. The same seed layer was necessary to induce the (001) orientation in La_{0.67}Sr_{0.33}MnO₃ films [16]. In the case of STO, two opposing growth procedures are described in literature. While Sanchez *et al.* [14] were able to grow (001) oriented STO on CeO₂ directly, Yamada *et al.* [15] only succeeded in (001) oriented growth of STO when a monolayer of TiO₂ was grown first, while the (110) orientation was obtained when growth was initiated with STO directly.

Limited knowledge exists about the mechanisms causing the differences between the mentioned growth studies. Although lattice mismatch is often considered as the critical

¹(Pseudo)cubic indices are used for all perovskites mentioned in this chapter.

Table 3.1: Parameters for deposition of CeO_2 on Al_2O_3 (102) substrates and (001) oriented YSZ (the same growth parameters were used for growth on single crystal YSZ and YSZ buffered Si).

	On Al_2O_3 (102)		On YSZ (001)	
	CeO_2 (111)	CeO_2 (001)	Grainy CeO_2	Rough CeO_2
Substrate temperature ($^{\circ}\text{C}$)	850	800	800	800
Fluency (J/cm^2)	2	2	2	2
Spot size (mm^2)	1.2	1.2	0.59	2.3
Laser repetition rate (Hz)	1	1	1	4
Pressure (mbar)	0.01 O_2	0.3 O_2	0.1 O_2	0.02 O_2

parameter in heteroepitaxial growth [11], the mentioned growth of SrRuO_3 and STO using thin seed layers suggests that chemistry and structure at the fluorite-perovskite interface are more important. This work aims to uncover why these seed layers are necessary for the (001) fluorite to (001) perovskite transition. Therefore, attention was paid to the procedure of obtaining (001) oriented SrRuO_3 using a seed layer grown in reducing conditions [13, 16]. The purpose was to determine the necessary deposition conditions for the seed layer, as well as which properties of the resulting seed layer favored the growth of (001) oriented SrRuO_3 . XPS and RHEED were used to study respectively the chemical and structural properties of the seed layer.

Furthermore, the influence of the CeO_2 morphology on the growth of perovskites was investigated. The roughness of CeO_2 films on YSZ leads to exposure of $\{111\}$ facets, which have the lowest surface energy. The morphology of this surface, and therefore the amount of facets present, varies heavily with deposition conditions [8]. This variation is hardly discussed in studies on growth of perovskites on CeO_2 , but may have a large influence on the results. Tuning the amount of $\{111\}$ facets may be an additional parameter for optimization of perovskite growth on CeO_2 -YSZ buffered silicon. Therefore, the growth of SrRuO_3 was studied on faceted surfaces, but also on smooth (001) oriented CeO_2 surfaces to exclude the influence of the $\{111\}$ facets. The growth on the $\{111\}$ facets itself was further investigated using (111) oriented CeO_2 surfaces. The different CeO_2 templates are described in more detail in the methods section.

3.2 Methods

3.2.1 Preparation of CeO_2 surfaces

Figure 3.1a and b show two types of CeO_2 (001) oriented surfaces with different roughnesses used to study the growth of SrRuO_3 . Surfaces with roughnesses in the nanometer scale were grown on YSZ single crystals or YSZ buffered Si with the parameters shown in table 3.1. These rough surfaces are the type of surfaces typically used

Figure 3.1: AFM micrographs of the CeO_2 templates used in this chapter. a) Typical CeO_2 morphology obtained by deposition in 0.02 mbar O_2 on YSZ substrates or YSZ buffered Si. Nanometer scale roughness is present, as visible in d) the corresponding line profile. b) Flat (001) oriented CeO_2 obtained by annealing CeO_2 layers on YSZ single crystal substrates. Mainly 0.5 unit cell steps are present, as shown in e) the corresponding line profile. c) (111) oriented CeO_2 prepared by annealing CeO_2 layers on Al_2O_3 (102) substrates. The height differences between the flat terraces correspond to the distance between the CeO_2 (111) planes, as shown in f) the corresponding line profile.

to integrate perovskites on CeO_2/YSZ buffered silicon. Smooth surfaces, used to study the growth of SrRuO_3 without the influence of side facets, were prepared in two steps. First, CeO_2 with a grainy morphology was deposited on YSZ single crystals using the parameters shown in table 3.1. After deposition, these films were annealed in a tube furnace for 10 h at 1000 °C in flowing oxygen. Low miscut substrates were used to avoid step bunching. The resulting surfaces showed only 0.5 unit cell height differences (see figure 3.1e). The methods to obtain these surface are discussed in more detail in the appendix (subsection 3.7.1 starting on page 56).

The CeO_2 (111) oriented surfaces were prepared on Al_2O_3 (102) substrates. CeO_2 films, grown using the deposition parameters shown in table 3.1, were annealed in a tube furnace for 10 h at 1000 °C in flowing oxygen. A surface consisting of flat terraces was obtained, with height differences between the terraces corresponding to the distance between the (111) planes (see figure 3.1c and f). More details about the procedures to obtain these (111) surfaces are presented in the appendix (subsection 3.7.1 starting on page 56).

Before deposition, the Al_2O_3 (102) and YSZ (001) single crystal substrates were annealed for 4 h. at 1000 °C in flowing oxygen. In order to obtain YSZ buffer layers on

Table 3.2: Parameters for deposition of SrO, STO and SrRuO₃

	SrO	STO	SrRuO ₃ seed	SrRuO ₃ full layer
Substrate temperature (°C)	800	800	800	600
Fluency (J/cm ²)	1.3	1.3	2	2
Spot size (mm ²)	2.3	2.3	2.3	2.3
Laser repetition rate (Hz)	50	1	1	1
Pressure (mbar)	0.13 O ₂	0.1 O ₂	Var.	0.15 O ₂ + 0.15 Ar

Si, the optimized procedure described in chapter 2 was used.

3.2.2 Growth of SrRuO₃

The method known for growth of (001) oriented SrRuO₃ consists of growing 1 mono-layer at 800 °C in base pressure, followed by deposition of the rest of the film at 600 °C in oxygen atmosphere [13, 17, 18]. The hypothesis behind this method was that growth at high temperatures in reducing conditions led to evaporation of Ru. The rocksalt structure of the resulting SrO layer was thought to induce the (001) orientation of the SrRuO₃ grown on top of it. However, the chemical and structural aspects of the formation of the seed layer were not studied in detail, as will be done in this chapter.

In this work, the partial oxygen pressure (pO₂) during deposition of the seed layer was varied in order to investigate the necessary conditions for the formation of the seed layer. The chemistry and structure of the seed layers were examined by *in situ* XPS and RHEED respectively. The influence of the seed layer on the orientation of the SrRuO₃ was verified by deposition of 50 nm of SrRuO₃ at 600 °C. A relatively low temperature and high pressure were chosen. As shown for growth on DyScO₃ substrates with mixed surface terminations, these conditions made the nucleation of SrRuO₃ very sensitive towards differences in surface diffusivity [19, 20]. Therefore, growth of SrRuO₃ could be used to verify whether or not the DyScO₃ substrates were single terminated. Similarly, these growth parameters are useful in this work to study growth on the seed layer. The used parameters for the seed layer and the full layer are shown in table 3.2. In order to investigate the influence of the seed layer on the orientation of another perovskite, STO films were deposited on the SrRuO₃ seed layer using the parameters shown in table 3.2.

The presence of SrO at the CeO₂-SrRuO₃ interface may induce the (001) orientation. In order to verify this idea, seed layers were grown from a SrO target. Interval deposition was used in order to obtain a high nucleation density [21, 22]. Monolayers of SrO were grown by deposition of 60 pulses with a laser repetition rate of 50 Hz. When more than one monolayer was grown, a waiting time of 60 s. was used between each layer. The other growth parameters are shown in table 3.2.

AFM and XRD measurements were performed as described in the experimental section in chapter 2. XPS measurements were performed with a surface normal to detector

Figure 3.2: 50 nm STO and SrRuO_3 films grown with and without SrRuO_3 interlayers. The red line indicates the samples grown with a seed layer consisting of 1 ML of SrRuO_3 deposited at 800 °C in 10^{-5} mbar O_2 . The green line indicates a film grown on a 10 ML SrRuO_3 seed layer deposited at 800 °C in a background gas consisting of 0.15 mbar O_2 and 0.15 mbar Ar. The asterixes label the peaks originating from residual silver glue used to mount the substrates on the sample holders during growth.

angle of 1° , unless stated otherwise.

3.3 Mechanism of SrRuO_3 seed layer formation at low $p\text{O}_2$

First, the growth procedure described in literature [13] was reproduced in the PLD system used in this work. As shown in the XRD scans presented in figure 3.2, growth of SrRuO_3 at 600 °C directly on CeO_2 -YSZ buffered silicon resulted in predominant (110) orientation, while a minor amount of the (001) orientation was present. Insertion of one monolayer of SrRuO_3 , grown at 800 °C in 10^{-5} mbar O_2 , led to clear enhancement of the (001) orientation. A similar enhancement of the (001) orientation was observed when STO was grown on this SrRuO_3 seed layer (see figure 3.2), showing the seed layer causes the enhancement independent of the perovskite grown on top. It must be noted that the enhancement was much stronger for growth of STO instead of SrRuO_3 . As described in the methods section, the growth conditions of SrRuO_3 were not chosen to obtain optimal crystalline qualities, but to have a high sensitivity towards the presence and properties of the seed layer.

In order to verify the influence of reducing conditions on the stoichiometry and chemistry of SrRuO_3 , three samples were grown at 800 °C at different oxygen pressures, i.e.

Figure 3.3: a) XPS measurements of monolayers of SrRuO₃ grown at 800 °C at different oxygen pressures. In case of the 0.15 mbar O₂, also 0.15 mbar Ar was provided to the chamber to obtain the typical SrRuO₃ deposition condition used in this work. b) The same films after annealing in O₂ at 600 °C. The 0.15 mbar sample was not annealed, the shown data is similar as figure a), and just added for comparison. c) Relative intensities calculated after fitting the spectra of a) and b)

base pressure ($2 \cdot 10^{-6}$ mbar after growth of CeO₂ on YSZ buffered silicon), 10^{-5} mbar O₂ and the high oxygen pressure normally used for deposition of SrRuO₃, i.e. a mixture of 0.15 mbar O₂ and 0.15 mbar Ar. The films were cooled to room temperature directly after growth, which was done in vacuum in case of the first two samples. As shown in figure 3.3a, XPS measurements showed a clear relationship between oxygen pressure and SrRuO₃ chemistry. Growth in base pressure resulted in appearance of Ru 3d 5/2 and 3/2 peaks at respectively 282.5 and 286.7 eV, corresponding to a metallic phase. This phase was also present in the 10^{-5} mbar film, but a lower intensity was measured. At high oxygen pressure, no metallic Ru was measured. Instead, peaks appeared at positions corresponding to oxidized Ru, around 287 and 291 eV. In the growth recipe of SrRuO₃, oxygen is added at 600 °C before starting growth of a thicker layer. Therefore, the samples grown in low oxygen pressures were heated again to 600 °C, after which 0.02 mbar O₂ was added to the chamber. After cooling in this pressure, XPS measurements were performed again, as shown in figure 3.3b. The metallic Ru peak disappeared in the films grown at low oxygen pressures, but the peaks corresponding to oxidized Ru appeared instead.

The relative intensities were determined by fitting the spectra using Shirley backgrounds and Scofield cross sections. In case of the samples with metallic Ru, the overlapping Ru 3d 5/2 and Sr 3p 1/2 peaks were used to determine the relative intensities. In these samples, the contribution of oxidized Ru was too small to take into account. In case of the samples with oxidized ruthenium, the complete region between 297 and 279 eV was fitted using the contributions of Ce 4s, Ru 3d and Sr 3p 1/2 peaks (see figure 3.16 in the appendix on page 61). The Ru 3d contribution needed to be fitted by 6 peaks, i.e. 3 peaks contributed to each of both spin-orbit doublets, in consistency with the work of Simons *et al.* [23]. The calculated relative intensities are shown in figure 3.3c, and led to two important observations. First of all, the measured relative intensities of Ru in the

Figure 3.4: XRD θ - 2θ scans of 50 nm SrRuO_3 films grown on YSZ- CeO_2 buffered silicon using 3.5 nm SrRuO_3 seed layers. The seed layers were grown at 800 °C at varying $p\text{O}_2$, while additional Ar was provided to reach a total pressure of 0.1 mbar. The inset shows the relation between the relative peak intensity of the (002) peak with respect to the (110) peak and the $p\text{O}_2$. The colors used in the θ - 2θ graphs correspond to the colors shown in the inset. The asterixes label the peaks originating from residual silver glue used to mount the substrates on the sample holders during growth.

samples containing metallic Ru increased after exposure to oxygen. The increase can be caused by transformation of Ru metallic islands into more homogeneously distributed oxidized Ru, thereby decreasing the attenuation of the Ru signal. Secondly, the relative intensities of Ru after annealing in O_2 at 600 °C depended only slightly on the oxygen pressure during deposition at 800 °C.

The XPS measurements showed the dependence of chemistry and amount of Ru on the oxygen pressure during growth at 800 °C. In order to verify which conditions are favorable in order to obtain the (001) orientation, 50 nm thick SrRuO_3 films were grown on YSZ- CeO_2 buffered silicon using 3.5 nm seed layers grown at 800 °C with varying $p\text{O}_2$, while Ar was used to reach a total pressure of 0.1 mbar. Figure 3.4 shows the XRD measurements of the corresponding samples. All samples showed predominant (110) and/or (001) orientations for SrRuO_3 , but the intensities varied with $p\text{O}_2$. A visualization of the effect of the $p\text{O}_2$ on the presence of the (001) and (110) orientation was made using the peak intensities of the (110) and (002) peaks, after correction for relative sensitivities of respectively 100 and 35 % [24]. As shown in the inset of figure 3.4, a clear trend was present, showing the (110) orientation was favored at high $p\text{O}_2$, while the (001) orientation started to increase when the $p\text{O}_2$ was decreased. Only in the case of the lowest $p\text{O}_2$, i.e. $3 \cdot 10^{-5}$ mbar, the contribution of the (110) orientation was not visible in

the XRD spectrum anymore. This dependency on pO₂ was also verified for thinner seed layers, down to one ML (data not shown).

Figure 3.5 shows the RHEED images obtained during growth of SrRuO₃ at 600 °C on YSZ-CeO₂ buffered silicon using seed layers prepared at 800 °C at different background pressures. In case no seed layer was used, the RHEED pattern of the CeO₂ increasingly blurred during ongoing deposition of SrRuO₃ at 600 °C. After deposition of 50 nm, spots and circles were visible in a diffuse background, as indicated in figure 3.5a. This pattern corresponded well with the low intensity of the SrRuO₃ peaks measured with XRD, as already presented in figure 3.2. In case one ML of SrRuO₃ was grown at 800 °C in 0.15 mbar O₂ and 0.15 mbar Ar, the crystallization slightly improved. The influence of a seed layer grown in these conditions was enhanced when 10 ML were grown in these conditions, as presented in figure 3.5c. As shown in the corresponding XRD measurements (figure 3.2), the (110) orientation was strongly enhanced due to this seed layer. Since the RHEED spectrum of the complete film was similar to the spectrum after growth of the seed layer, it can be concluded that (110) oriented SrRuO₃ was already formed during growth of the seed layer at 800 °C. The RHEED patterns of the seed layers prepared at low pO₂ showed completely different behavior. Additional spots appeared besides the CeO₂ in case one monolayer was grown in 10⁻⁵ mbar O₂ (figure 3.5d). These spots disappeared after adding oxygen at 600 °C. Instead, new spots appeared at positions corresponding to perovskite (001) oriented grains viewed along the [100] direction, as indicated with arrows in the corresponding image. The intensity of these spots increased with respect to the intensity of the CeO₂ spots when the deposition of SrRuO₃ was continued at 600 °C. After deposition of 2 ML, the CeO₂ spots were not visible anymore, while only a pattern typical for (001) oriented SrRuO₃ was left. Finally, in figure 3.5e the patterns are shown for a 10 ML SrRuO₃ seed layer prepared at base pressure. After 10 ML, spots appeared similar to the 10⁻⁵ case, but with higher intensities. Now, a hexagonal pattern was clearly visible, which corresponded well to the hexagonal structure of metallic Ru. After adding oxygen at 600 °C, this pattern was transformed into a perovskite (001) pattern, while the CeO₂ pattern was not visible anymore.

As shown by RHEED, oxidation of the SrRuO₃ layer after growth in reducing conditions led to formation of (001) oriented seeds. In order to obtain more insight in the formation process of the seed layer, the morphology of the seed layers on different surfaces was investigated by AFM. Monolayers of SrRuO₃ were deposited in reducing conditions, after which 0.02 mbar O₂ was added at a temperature of 600 °C. A deposition pressure of 10⁻⁵ mbar instead of base pressure was chosen in order to avoid differences between the experiments due to fluctuations of the base pressure. On STO (001) single terminated substrates², deposition of the monolayer led to formation of transmission spots in the RHEED image (not shown), indicating the presence of islands. After adding O₂, the transmission pattern disappeared, while a diffraction pattern corresponding to an atom-

² STO (001) substrates were treated with BHF according to [25, 26] in order to obtain TiO₂ terminated surfaces.

Figure 3.5: RHEED images captured during different steps in the growth process of SrRuO_3 on CeO_2 buffer layers, using different seed layers prepared at 800°C before growth of SrRuO_3 at 600°C . The RHEED images were taken along the $\text{Si}[110]/\text{YSZ}[110]/\text{CeO}_2[110]$ direction. The labels denoting SrRuO_3 - 1 and SrRuO_3 - 2 correspond to respectively the seed layer deposited at 800°C and the rest of the film deposited at 600°C . a) Without seed layer. The arrows in the image after growth of 50 nm SrRuO_3 indicate rings corresponding to phases with random in-plane orientations. b) 1 and c) 10 ML grown in 0.15 mbar O_2 and 0.15 mbar Ar. The circles indicate the spots which can be attributed to the (110) orientation of SrRuO_3 , which appeared already after growth of the seed layer at 800°C . d) 1 ML grown in 10^{-5} mbar O_2 . The circles indicate the spots appearing due to deposition of the SrRuO_3 in reducing conditions. The arrows indicate the spots appearing due to formation of the SrRuO_3 (001) orientation. e) 10 ML grown at base pressure, around 3×10^{-6} mbar. The hexagonal lattice of the phase formed after deposition in reducing condition is indicated in blue. In green, the lattice of the CeO_2 is indicated for comparison, as constructed from the image after deposition of the CeO_2 .

Figure 3.6: SrRuO₃ seed layers, grown at 800 °C in 10⁻⁵ mbar O₂, after addition of O₂ at 600 °C, on different substrates. The AFM images before and after growth of the seed layers are shown. All images are 1x1 μm. a) On single termination STO (001) oriented substrates. Only unit cell height differences can be observed in both images. b) On the (001) oriented CeO₂ exhibiting the step and terrace morphology. The height differences between the CeO₂ terraces are 0.5 unit cells. The height of the islands after deposition of SrRuO₃ was around 4 nm. c) On a CeO₂ (111) oriented template prepared on Al₂O₃ (102) substrates. The height differences between the terraces correspond to the distance between the CeO₂ (111) planes. After deposition of SrRuO₃, the peak-to-peak roughness on the terraces was around 0.3 nm. d) On a rough CeO₂ (001) oriented surface (peak-to-peak roughness of 3 nm), grown in 0.02 mbar O₂ on an YSZ single crystal substrate. After oxidation, regions appeared which were smoother compared to the original CeO₂ morphology. Examples are indicated with blue ellipses.

ically flat surface appeared. The AFM micrograph presented in figure 3.6a shows the formation of an almost closed layer with height differences corresponding to the pseudocubic unit cell of SrRuO₃. This experiment shows that epitaxial SrRuO₃ can form after phase separation, while the diffusivity of the involved species is high enough to cover the surface completely.

On flat (001) oriented CeO₂, transmission spots were formed as well after deposition in 10⁻⁵ mbar, but addition of oxygen led to appearance of spots and rings indicating the presence of islands and disordered phases. The AFM micrograph in figure 3.6b shows the presence of well separated islands, with a total volume corresponding to the deposited monolayer. On the rougher CeO₂ (001) oriented surface, formation of these islands was not visible. Instead, a decreased roughness appeared in regions on the surface, indicating improved wetting of the SrRuO₃ seed layer on this surface compared to the flat CeO₂ surfaces (see (figure 3.6d)).

Figure 3.7: AFM micrographs of 50 nm SrRuO_3 films grown on flat CeO_2 templates using a) 0, b) 1, c) 3 or d) 10 ML of SrO in between the CeO_2 and SrRuO_3 . All images are $5 \times 5 \mu\text{m}$. The blue circle in subfigure b) indicates an example of a region with a smooth morphology. The peak-to-peak roughnesses of these images are respectively 40, 22, 21 and 12 nm. e) The corresponding XRD θ - 2θ scans. The asterixes label the peaks originating from residual silver glue used to mount the substrates on the sample holders during growth.

The roughness of the (001) CeO_2 surface proved to be key for obtaining (001) oriented SrRuO_3 . On the flat CeO_2 , it was not possible to crystallize the (001) orientation using similar procedures as growth on the rougher surface. This behavior may be caused by $\{111\}$ side facets, which are always present in rough (001) oriented CeO_2 films [8]. In order to test this possibility, a monolayer of SrRuO_3 was grown on the CeO_2 (111) templates prepared on Al_2O_3 (102) substrates. RHEED showed formation of islands at 800°C , but the 3D spots disappeared after adding oxygen (data not shown). The AFM micrograph (figure 3.6c) shows that the film completely covered the surface, comparable to the situation on STO.

3.4 SrO seed layer

The previous experiments showed that phase separation between a metallic Ru phase and SrO was necessary to obtain (001) oriented growth. In all cases when oxidized Ru and Sr were provided simultaneously, poor crystallization or enhanced (110) orientation was

Figure 3.8: AFM micrographs of 50 nm SrRuO₃ films prepared on YSZ-CeO₂ buffered silicon with a) no seed layer, b) a SrRuO₃ seed layer deposited in 10^{-5} mbar at 800 °C and c) a seed layer consisting of 10 ML of SrO. All images are 5x5 μm. The peak-to-peak roughnesses of these images are respectively 20, 16 and 3 nm (disregarding the 10 nm deep pits in the last image). d) The corresponding XRD scans. The asterixes label the peaks originating from residual silver glue used to mount the substrates on the sample holders during growth. e) RHEED image of the CeO₂ surface along the [110] direction. f) After deposition of 10 ML SrO. The blue arrows point to the streaks indicating formation of a smooth surface.

observed. Possibly, the phase separation is necessary to form a layer between CeO₂ and SrRuO₃ which purely consists of SrO. In order to test this hypothesis, SrO layers were grown by interval deposition before growth of SrRuO₃ at 600 °. Figure 3.7 shows the AFM spectra and XRD scans of 50 nm SrRuO₃ films grown on flat CeO₂ with 0, 1, 3 and 10 ML of SrO. In case no SrO was used, a rough surface was visible, while XRD showed a mixed (110)/(001) orientation. Using 1 ML of SrO changed the surface significantly. Smooth regions appeared in between the grains. XRD showed an increased amount of (001) oriented SrRuO₃, but a significant amount of the (110) orientation was still present. The RHEED images obtained during deposition indicated that the SrO formed island instead of completely covering the surface (data not shown). The same observations were made when 3 ML of SrO were used. In order to try to obtain a complete coverage of the CeO₂ surface, the amount of SrO was increased to 10 ML. XRD showed a clear decrease in (110) orientation. The surface of the film only consisted of separated square grains, typical for a (001) oriented perovskite film grown with a high initial nucleation density [22].

A similar experiment was performed on YSZ-CeO₂ buffered silicon, with a CeO₂ morphology similar to the one shown in figure 3.6d. After growth of SrRuO₃, a rough surface was formed when no seed layer was used, as presented in figure 3.8a. When an SrRuO₃ seed layer was grown first at 800 °C in 10⁻⁵ mbar O₂, similar sized grains were present, although the roughness decreased and the grains had a square shape, as expected for (001) oriented grains (see figure 3.8b). A completely different surface was obtained when 10 ML of SrO were used, as shown in figure 3.8c. The surface was much smoother with a peak-to-peak roughness of 3 nm, although some 10 nm deep pits were present. The XRD graph presented in figure 3.8d shows that the (110) orientation was completely suppressed, while the intensity of (002) peak increased strongly compared to the samples without seed layer and with the SrRuO₃ seed layer. Interestingly, the crystalline and morphological qualities of this film were much better compared to the film deposited in the same conditions on the flat CeO₂ template. The difference between growth on both surfaces can be caused by the different growth behavior of the SrO seed layer. As visible in RHEED by formation of streaks (see figure 3.8e and f), the rough CeO₂ surface became smoother after deposition of the SrO, indicating the tendency of SrO to completely cover the rough CeO₂ surface. Instead, SrO islands were formed on the flat CeO₂ surface. The grainy morphology and presence of the (110) orientation of the SrRuO₃ suggests that even after 10 ML of SrO the CeO₂ surface was not completely covered.

3.5 Discussion

3.5.1 Importance of phase separation

As shown, the characteristics of the SrRuO₃ seed layer depended heavily on the oxygen pressure used during deposition. At 800 °C, the formation of volatile RuO₄ due to reaction of SrRuO₃ or Ru with oxygen can cause offstoichiometry in SrRuO₃ [27, 28]. The oxygen pressure necessary to form RuO₄ from RuO₂ or SrRuO₃ at 800 °C is well above (>1000 mbar) the pressures used in this work [29], but at this temperature a small vapor pressure of RuO₄ can be observed during exposure of metallic Ru to O₂ [27]. Therefore, as shown in literature for the growth of SrRuO₃ on STO, loss of Ru can occur before formation of a stable SrRuO₃ film [30]. Similarly, the observed loss of Ru in the SrRuO₃ seed layers deposited this work can be attributed to evaporation of RuO₄, formed due to reaction between O₂ and Ru species before a stable SrRuO₃ phase was formed. However, even in 0.15 mbar O₂, enough Ru was left to form thermodynamically stable (110) oriented SrRuO₃ phases.

In low pO₂, loss of oxygen can lead to decomposition of the SrRuO₃ film into metallic Ru and Sr rich oxidized phases [29, 33, 34]. In order to visualize the relevant dissociation pressures, an Ellingham diagram was constructed³, as shown in figure 3.9. As can

³ The diagram was constructed as follows. The oxidation of a metal A occurs due to reaction with molecular

Figure 3.9: Ellingham diagram indicating the standard Gibbs free energy of formation (solid lines) and equilibrium oxygen pressure (dashed lines) for formation of SrO, RuO₂, CeO₂ and SrRuO₃. The diagram was constructed using the data from [27, 31, 32]

be seen in the diagram, the calculated dissociation pressures of RuO₂ and SrRuO₃ are $1 \cdot 10^{-3}$ and $1 \cdot 10^{-5}$ mbar respectively at 800 °C⁴. These pressures correspond well with

oxygen from the background pressure:

The Gibbs free energy of formation (ΔG) is 0 at the equilibrium oxygen pressure (p_{O_2} , also known as dissociation pressure), as described for the previous oxidation reaction by:

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{1}{p_{O_2}} \right) = 0 \quad (3.2)$$

The standard Gibbs free energy of formation (ΔG^0) can be calculated via:

$$\Delta G^0 = \Delta H^0 + T \Delta S^0 \quad (3.3)$$

in which ΔH^0 and ΔS^0 are respectively the standard enthalpy and entropy of formation. The solid lines in the diagram are constructed using this formula, assuming temperature independent standard enthalpies and entropies of the reactions [27, 31, 32]. Note that all energies are calculated per mole of oxygen.

The oxygen equilibrium pressure at given temperature can directly be obtained from equation 3.2:

$$\Delta G^0 = RT \ln(p_{O_2}) \quad (3.4)$$

The equilibrium pressure can be visualized in the diagram by drawing a linear line from the origin through a point on the solid line indicating the standard Gibbs free energy of formation, at the temperature of interest. The slope of this line equals $R \ln(p_{O_2})$. A nomographic scale was added to the diagram in order to be able to read out the equilibrium pressure. In the diagram, the dashed lines were constructed representing the dissociation pressures at 800 °C, i.e. the temperature used for growth of the seed layer.

⁴Previously published experiments indicate an oxygen pressure of at least $5 \cdot 10^{-3}$ mbar is necessary to stabilize a stoichiometric grown SrRuO₃ film against reduction completely [35].

the experimental observations in this work. After deposition of the SrRuO_3 seed layer in oxygen pressures of $1 \cdot 10^{-5}$ and lower, metallic Ru was measured by XPS. The calculated formation energies also explain why the metallic Ru was not oxidized via reduction of the CeO_2 surface, since the energy of formation is much lower for CeO_2 compared to RuO_2 .

Importantly, presence of SrO is thermodynamically expected in all experimentally obtainable pressures as a result of its very low dissociation pressure of $1 \cdot 10^{-43}$ mbar. The fact that oxidized Ru was hardly measured after deposition in low $p\text{O}_2$, combined with the thermodynamically expected presence of SrO, therefore points to a complete phase separation between SrO and Ru. This phase separation is the most plausible explanation for the low $p\text{O}_2$ needed to obtain (001) oriented growth, because of the following reasons:

- Minor differences in Ru content were found between growth of the seed layer at high oxygen pressure or 10^{-5} mbar. Therefore, differences in Ru content are unlikely to be the cause of the different crystallographic orientations. Note that this observation contradicts the hypothesis described in earlier work [13], as mentioned in the methods section. There, evaporation of metallic Ru was expected due to reducing conditions. In this work an opposite trend was observed, i.e. the highest amount of Ru was measured in the most reducing conditions (see figure 3.3c). This observation is in agreement with the volatility of oxidized Ru species described above, as well as the low vapor pressure of metallic Ru [36].
- When the phase separation occurs, regions can form consisting of SrO and metallic Ru. As shown by growing seed layers consisting of SrO only, the SrO can promote the formation of (001) oriented SrRuO_3 . When a phase separation was not promoted, i.e. oxidized Ru and Sr were provided simultaneously during growth at higher oxygen pressures, predominantly (110) oriented SrRuO_3 was always formed, irrespective of whether the deposition was performed at 600 or 800 °C.
- The observation that $p\text{O}_2$ below 10^{-4} were necessary to obtain the (001) orientation (see figure 3.4) corresponds closely to the thermodynamically expected dissociation pressure of SrRuO_3 .
- An alternative explanation is the occurrence of structural changes at the CeO_2 surface due to loss of oxygen in reducing conditions. As shown in the Ellingham diagram, reduction of the surface occurs only at oxygen pressures much lower (10^{-21} mbar) than the pressures used in this work. Even the formation of oxygen vacancies is negligible at 800 °C [37]. Therefore, the CeO_2 surfaces are considered to be identical during growth of the seed layer at different oxygen pressures.

If the SrO covered CeO_2 areas indeed induce the (001) orientation of SrRuO_3 , the formation of (001) oriented SrRuO_3 could occur due to diffusion of oxidized Ru towards the SrO covered areas. In this way, the rocksalt structure of the SrO still induces the

(001) orientation of SrRuO_3 , confirming part of the hypothesis described in the methods section.

3.5.2 Lattice matching

In order to gain more insight in the initial nucleation of perovskites on fluorites, structures of the lattice planes involved in the growth process are shown in figure 3.10. In the [001] direction, the fluorite CeO_2 structure consists of alternating planes of Ce and O. The Ce forms a face-centered cubic sublattice, whereas the O forms a simple cubic lattice. The positions of the Sr atoms in the SrO plane and the O atoms in the RuO_2 plane of SrRuO_3 are similar to the positions of Ce atoms and O atoms in CeO_2 . However, the SrO and RuO_2 planes consist of anions and cations and are charge neutral, while the CeO_2 planes consist of only cations or anions and are therefore charged. In terms of coordination chemistry and electrostatics, these conditions are not favorable for formation of a coherent interface. The (110) oriented SrRuO_3 consists of alternating planes of SrRuO and O_2 , which have charges of +4 and -4 respectively. When oxidized Sr and Ru are provided simultaneously to the CeO_2 surface, the problems regarding polar discontinuity are therefore solved partially. However, the structures of these planes do not match to the CeO_2 planes, which explains the observed difficult crystallization (see e.g. figure 3.5a). The (001) oriented rocksalt SrO consists of planes similar to the SrO plane of SrRuO_3 (with slightly smaller dimensions of 5.16 Å), and therefore forms a perfect template for growth of (001) oriented SrRuO_3 . Although the experiments clearly show growth of this rocksalt on the CeO_2 (001) planes is possible, the exact structure at the film-substrate interface should still be determined. Finally, the structures of the CeO_2 (111) and SrO (111) planes indicate why existence of {111} facets can be beneficial for the growth process. In this orientation, the CeO_2 consists of Ce planes alternated by two oxygen planes. SrO consists of alternating planes of Sr and O. In terms of structure the cation and anion planes of both materials are completely similar.

3.6 Conclusion and outlook

The mechanism behind the method to obtain (001) oriented SrRuO_3 on (001) oriented CeO_2 was investigated. Key behind successfully obtaining (001) oriented SrRuO_3 was to have at least one monolayer of SrO between CeO_2 and SrRuO_3 . This was possible by deposition of SrO, or by deposition of SrRuO_3 in reducing conditions, which led to phase separation between SrO and Ru. In the last case, (001) oriented SrRuO_3 seeds were formed after oxidation of the Ru. The roughness of the CeO_2 had a large influence on the growth of SrRuO_3 . The presence of {111} CeO_2 facets on rough CeO_2 surfaces improved the growth of SrRuO_3 , probably due to the matching structures of the SrO (111) and CeO_2 (111) planes.

Figure 3.10: Representation of the structure of the a) CeO_2 (001), b) SrRuO_3 (001), c) SrRuO_3 (110), d) CeO_2 (111) and e) SrO (111) planes. All dimensions are scaled with respect to each other. Blue spheres represent the Ce atoms, red spheres the oxygen atoms, orange spheres the Sr atoms and green spheres the Ru atoms.

Figure 3.11: Schematic indication of the multilayer grown in this work and the corresponding lattice parameters.

Based on this work, some possibilities are proposed to improve the crystalline quality of perovskites grown on YSZ/CeO₂ buffered silicon. The discussed phase separation of SrRuO₃ implies that SrRuO₃ films grown via this method will always consist of grains, since (001) oriented SrRuO₃ seeds will only form in separate areas covered with SrO. Deposition of a seed layer of only SrO led to significantly smoother surfaces. This was not only caused by formation of a continuous seed layer, but also because growth of perovskites on this rocksalt layer leads to A-site terminated growth, which is known to favor the growth of smooth perovskite layers due to increased diffusivity [22]. The growth of this rocksalt seed layer can be improved further. As shown, the presence of {111} facets increased the wetting of SrO. The morphology of CeO₂ can be tuned by changing the deposition conditions [8] in order to find an optimum balance between the amount of {111} facets and surface roughness. On the other hand, the problem of SrO island formation on flat (001) oriented CeO₂ surfaces may be solved by decreasing the lattice mismatch between CeO₂ and the rocksalt. For example, a lattice matched rocksalt can be formed by a solid solution of BaO (lattice parameters of 5.54 Å) and SrO [38].

As shown in figure 3.11, each layer in the stack has a large lattice mismatch with the underlying layer. Besides optimizing the composition of the rocksalt layer, which reduces the mismatch towards CeO₂ and SrRuO₃, the YSZ to CeO₂ transition could also be optimized. As shown in the supporting information (page 59), CeO₂ on YSZ buffered

silicon never reaches the smoothness of the YSZ surface, even after annealing. Insertion of one or more layers with lattice parameters between YSZ and CeO_2 may aid a smooth transition between both materials. These layers can be chosen based on the possibility to modify the fluorite lattice parameters by doping with a wide range of cations [39]. For example, the Y doping in YSZ can be increased to increase the YSZ lattice parameters [40], or the lattice parameters of CeO_2 can be decreased by doping with Zr [41].

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3.7 Appendix

3.7.1 Preparation of CeO₂ templates

On Al₂O₃ substrates

As previously described in literature, deposition of CeO₂ on Al₂O₃ (102) substrates followed by an annealing step leads to atomically flat CeO₂ (001) surfaces [42–45]. Furthermore, depending on the used deposition conditions, (111) orientated CeO₂ can be obtained on these substrates as well [46, 47]. As shown in figure 3.12, predominant (001) or (111) orientated CeO₂ films were obtained in this work, using the different deposition conditions mentioned in the methods section to deposited films with thicknesses of respectively 14 and 21 nm. In both cases, minor amounts of the other orientation, respectively (111) or (001), were present as well ⁵. The AFM micrographs (figure 3.12c and f) showed rough surfaces for both orientations, which however flattened after post annealing at 1000 °C. The improvement of the surface morphology also appeared in the XRD scans as a more pronounced presence of Laue oscillations. In the case of the (111) orientation, a shift in the peak position was observed to higher 2θ values, to a value corresponding to the bulk lattice parameters of 3.11 Å. Steps corresponding to this lattice size were observed in the AFM micrograph (figure 3.12d), although straight coherent step edges were not present. Formation of these coherent step edges was not expected, since two in-plane orientations were present, rotated with 30° with respect to each other. These different orientations were caused by two possible orientations of the hexagonal structured (111)

⁵Note that the cross sections of intensity from the (111) and (002) are 100% and 30% respectively [48]

Figure 3.12: a) XRD θ - 2θ scans of a predominantly (111) oriented CeO_2 film on an Al_2O_3 (102) substrate, before and after annealing at 1000 $^\circ\text{C}$. b) Similar scans for the predominantly (002) oriented film. c) AFM micrograph of the as deposited (111) oriented film and d) the AFM micrograph and e) line profile of this film after annealing at 1000 $^\circ\text{C}$. In f-h), similar images are shown for the (001) oriented CeO_2 .

lattice on the close to square Al_2O_3 (102) lattice, as described by Bick *et al.* [47]. In case of the predominantly (001) oriented film, the unwanted (111) orientation disappeared completely during post annealing. The AFM micrograph (figure 3.12g) showed clear terraces, but step bunching occurred. Between most of the terraces height differences of 1 unit cell, i.e. 5.41 $\text{\AA}$, were observed, while half a unit cell height differences are typical for single crystal fluorite surfaces.

On YSZ substrates

In order to obtain flat (001) oriented CeO_2 templates, growth on YSZ (001) substrates seems to be a more logical choice due to matching structures. Although CeO_2 always grows (001) oriented on these substrates, it was not possible to obtain flat CeO_2 directly. Dewetting and roughening occurred always after deposition of more than 1 ML, in agreement with observations made in other work [7]. Therefore, similar to the Al_2O_3 case, annealing steps were introduced to decrease the roughness of the film. In figure 3.13,

Figure 3.13: a-d) 0.5, 4, 8 and 22 nm CeO_2 films on YSZ (001) oriented single crystal substrates. e-h) The same films after annealing for 10 h. at 1000 °C.

AFM micrographs are shown of films of different thicknesses before and after annealing. Deposition of one unit cell of CeO_2 led to a smoothly covered surface, showing the morphology of the underlying YSZ substrate clearly. However, CeO_2 islands were formed after annealing. The sides of these islands were clearly oriented along two in-plane diagonals, corresponding to the $[110]$ directions of the substrate, as expected for the presence of the lowest energy $\{111\}$ facets [43]. When the CeO_2 thickness was increased to 4 nm, a rough surface formed. After annealing, grain growth clearly occurred, but holes were visible. Again, these holes were oriented in-plane in the $[110]$ directions. AFM indicated these holes reached to the substrate surface. Similar behavior was observed in the 8 nm case, but the amount of holes decreased. Above 12 nm, the layer was completely closed after annealing. However, as shown for a 22 nm film, a clear step and terrace morphology was not always observed. The thickness dependent CeO_2 dewetting is similar to the behavior described in literature when annealing (001) oriented CeO_2 films on Al_2O_3 (102) substrates [44]. There, the thickness dependent dewetting was shown to result from minimization of the interfacial and surface energies, elastic energy and energy of the grain edges.

As stated before, annealing of the CeO_2 did not always led to formation of a surface with clear step and terrace morphology. As shown by Develos *et al.* [49], the initial morphology of the CeO_2 surface has large influence on the morphology after annealing. Therefore, different deposition conditions were chosen to obtain different initial CeO_2 morphologies. When the CeO_2 was deposited in 0.1 mbar O_2 with a smaller laser spot size, grains around 20 nm were visible at the surface. Annealing these surfaces led to the formation of flat CeO_2 surfaces, with terrace widths corresponding to the underlying YSZ substrates, as shown in figure 3.14. The height differences between the steps corresponded to the expected 0.5 unit cells. Although the morphology of the CeO_2 deposited

Figure 3.14: AFM micrograph of the grainy CeO₂ a) before (peak-to-peak roughness of 4 nm) and b) after annealing. c) AFM micrographs of annealed grainy CeO₂ on a lower miscut substrate and d) after additional homoepitaxial growth of 5 unit cells of CeO₂. e) RHEED intensity variations of the homoepitaxial growth. One oscillation corresponds to one monolayer, i.e. half an unit cell.

in 0.02 mbar O₂ was initially smoother (see figure 3.13d), formation of clear steps and terraces was never achieved after annealing. The dependence on initial morphology explains why formation of flat (001) oriented CeO₂ on YSZ substrates with clear steps and terraces was not always shown in similar work [50–52]. In this work, no further attempts were made to clarify the underlying mechanism.

In order to improve the surface morphology even further, low miscut substrates were used to obtain clear separation between the terraces, as shown in figure 3.14c. Homoepitaxial growth was performed on this surface in order to verify the quality of the surface⁶. As shown by the corresponding RHEED intensity oscillation of the specular spot in figure 3.14e, layer-by-layer growth was obtained. XRR reflectivity confirmed that each oscillation corresponded to the deposition of one monolayer, i.e. half an unit cell. The AFM after growth (figure 3.14d) showed a morphology similar to the morphology before growth. This experiment also confirmed that the roughening of CeO₂ on YSZ during initial growth is not intrinsically caused by the deposition of CeO₂.

On YSZ buffered Si

In order to improve the morphology of CeO₂ on YSZ buffered silicon, annealing steps were introduced on grainy CeO₂ films with thicknesses of 21 nm. Typical results from two different procedures are discussed now. In the first procedure, the annealing step was

⁶This deposition was performed at 850 °C in 0.02 mbar O₂ with a spot size of 0.59 mm²

Figure 3.15: a) AFM micrograph of the YSZ surface as deposited on Si. b) The same sample after annealing for 1 h. at 1000 °C. c) Typical morphology of the deposited CeO₂ on either two of the surfaces shown in a) and b). d) AFM micrograph of a CeO₂ film on YSZ buffered silicon after annealing. e) AFM micrograph after annealing of a CeO₂ film deposited on an annealed YSZ buffered silicon. f) FWHM of the XRD (002) rocking curves.

performed after deposition of both YSZ and CeO₂. In the second procedure, an additional annealing step was performed before deposition of the CeO₂. As shown in figure 3.15a, YSZ surfaces were very flat after deposition, with peak-to-peak height variation below 0.5 nm. The peak-to-peak roughness was similar after annealing these surfaces for 1 h. at 1000 °C in flowing oxygen, but a larger in-plane coherency was visible, as shown in figure 3.15b. Deposition of CeO₂ led to similar morphologies on both surfaces, which was also comparable to the films deposited in similar conditions on YSZ substrates (compare figure 3.15c and figure 3.14a, peak-to-peak roughness of 4 nm). However, annealing both CeO₂ films led to different morphologies and crystalline properties, as shown in figure 3.15d and e. In case the sample was annealed after deposition of both YSZ and CeO₂, peak-to-peak roughness was about 1 nm, while a minor amount of small holes around 2 nm deep were visible. The FWHM of the XRD (002) rocking curves increased for YSZ and CeO₂, from 0.79° and 0.91° to 0.54° and 0.76° respectively (see figure 3.15f). In case an anneal step was introduced before deposition of the CeO₂, the FWHM of the YSZ increased even more, from 0.78° to 0.48°. Deposition of CeO₂ on top of this YSZ layer led to an initial lower FWHM compared to the CeO₂ deposited on unannealed YSZ. Annealing decreased the FWHM even more to 0.60°. The morphology was different as well, since very flat square grains were observed. However, the height variation increased significantly, and holes with depths to 10 nm were present.

3.7.2 Fitting of XPS spectra

Figure 3.16: Fits of the XPS spectra presented in figure 3.3, corresponding to the samples deposited in a) base pressure, b) 10⁻⁵ mbar O₂ and c) 0.15 mbar O₂.

Chapter 4

Growth of SrZrO_3 on silicon with native oxide

Abstract: In this chapter, the possibility to grow a perovskite directly on silicon with native oxide was investigated. In this way, exposure of silicon dangling bonds was avoided, and therefore the need for elaborative growth procedures and UHV conditions. SrZrO_3 (SZO) was chosen for this study because of the scavenging capabilities of Zr and the expected chemical stability on Si. First, the chemical interactions between SZO and silicon were investigated. When thin films of SZO were heated on silicon with native oxide, Sr silicate formation was always observed. This silicate formation led to Zr enrichment of the SZO film, and lowered the thermal stability compared to yttria-stabilized zirconia (YSZ). Sr silicate formation prevented crystallization of epitaxial SZO when the growth was performed in reducing conditions at elevated temperatures. Low oxygen pressures were necessary to allow contact between the crystalline silicon and the growing film. However, these reducing conditions led to formation of zirconium silicides, and not to epitaxial SZO. When higher oxygen pressures were used, amorphous silicate formation prevented sufficient decomposition of the silicon native oxide. Stable epitaxial SZO films could only be obtained by preventing the interaction between Sr and Si, as shown by initiating growth with a thin layer of YSZ. (110) oriented SZO was obtained due to crystallization on the fluorite structured YSZ seeds.

4.1 Introduction

4.1.1 SrZrO_3 as alternative buffer layer

Yttria-stabilized zirconia (YSZ) and SrTiO_3 (STO) have its own advantages and disadvantages considering the use as buffer layers for epitaxial integration of (001) oriented perovskites on Si. YSZ buffers can be grown directly on the silicon native oxide via the oxygen scavenging method, as shown in chapter 2. However, integration of perovskites on the YSZ fluorite surfaces is not straightforward, as described in chapter 3. The perovskite structure of STO buffer layers directly enables the growth of functional perovskites, but a demanding procedure is required to grow this buffer material. One of the reasons is the chemical instability of titania on Si [1, 2], which means contact between Si and the TiO_2 plane of STO should be avoided. Therefore, the growth procedure of STO on Si starts with the formation of a Sr template on the bare Si substrate [3]. Ultra-high vacuum (UHV) conditions are necessary in this process to prevent contamination of the very reactive bare silicon surface. Crystallization of STO on this template should be performed in carefully controlled temperatures and oxygen pressures to avoid unwanted reactions between the Si substrate and TiO_2 and oxygen. The aim of the work in this chapter was to find an alternative to YSZ and STO buffers, avoiding both the difficulties regarding the fluorite to perovskite transition as well as elaborate growth procedures. Therefore, the possibility was investigated to grow a perovskite via the oxygen scavenging method.

A perovskite was chosen based on the chemistry of the individual cations. First of all, the constituting metals of the perovskite oxide should be capable of scavenging oxygen from the silicon native oxide, i.e. perform the following reaction:

Furthermore, the perovskite oxide should be chemically stable on Si. Since knowledge about the reactions and stability of ternary oxides on Si and SiO_2 is limited, choices were made based on theoretical and experimental knowledge about the constituting binary oxides [2, 4, 5]. For these reasons, SrZrO_3 (SZO) was chosen in this work. As shown in chapter 2, Zr can be used to decompose the silicon native oxide, while ZrO_2 is chemically very stable on Si. As shown in studies on the growth of STO on Si, the presence of Sr at the STO-Si interface enhanced the stability of STO on Si [3]. Furthermore, Sr could aid the transition of the Si diamond to the perovskite structure, as well as the transition from a covalent to more ionic type of bonding [6].

An unsuccessful attempt to grow epitaxial SZO on Si via the scavenging method was already made some years ago by Miu and coworkers [7]. However, the variation in used deposition parameters was limited, and the reasons for failure were not studied. This

work aims to add the necessary knowledge about the chemical interactions between SZO and Si, as well as a method to grow SZO on Si without removing the native oxide in advance.

4.1.2 The experiments

As described above, two existing methods to obtain epitaxial oxides on Si are combined in order to develop an alternative method:

- The growth of YSZ via the oxygen scavenging method. Since SZO is used in this work, the influence of Sr on the scavenging process should be studied.
- The method of using Sr to chemically and structurally enable growth of STO on Si. By using SZO instead of STO, the problems due to the instability of titania on Si are avoided. However, the expected higher stability of SZO on Si has never been verified experimentally. Furthermore, it is not known if Sr will aid the Si to perovskite transition during growth via the scavenging method.

Two experimental approaches were used in this chapter to study these aspects. First, the chemistry of SrZrO_3 in contact with Si and SiO_2 as a function of temperature was investigated with X-ray Photoelectron Spectroscopy (XPS). In order to be able to distinguish the effect of the constituting oxides, SrO and YSZ layers were investigated as well. YSZ was chosen instead of ZrO_2 in order to be able to compare SZO to a material which can be grown via the scavenging method. Furthermore, STO layers were investigated to verify whether or not the presence of Zr instead of Ti leads to a more stable perovskite on Si. The chemistry of metal oxides on Si is known to depend on silicon oxide composition [8] and thickness [9], as well as the amount of oxygen vacancies in the film [10, 11]. Therefore, in the cases of STO and SZO, two opposing situations were investigated. Films were grown in oxygen atmosphere on silicon with native oxide in order to investigate an oxygen rich situation. In contrast, oxygen deficient films were grown in Ar atmosphere on silicon without native oxide. These different conditions are important to investigate, since growth via the scavenging method depends heavily on the amount of oxygen present during growth (see chapter 2).

Secondly, the growth of SZO on silicon with native oxide via the oxygen scavenging method was studied. Among the parameters which can be varied in the Pulsed Laser Deposition (PLD) process, this work focussed on the deposition temperature and partial oxygen pressure ($p\text{O}_2$). Growth of YSZ via the oxygen scavenging method occurs typically at temperatures between 750 and 800 °C, which serves as a good indication for the temperature necessary to grow SZO. However, varying the temperature may enable thermodynamic and kinetic control of the chemical reactions during growth. Furthermore, as shown in chapter 2 for the growth of YSZ, the $p\text{O}_2$ can be used to control the chemistry as well. Chemistry and structure after growth in the different conditions were

analyzed with Reflection High-Energy Electron Diffraction (RHEED), XPS, Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). In the next section, the used methods will be described in detail, after which the results of both experimental approaches are presented in two separate sections.

4.2 Methods

4.2.1 General methods

All samples were grown in a PLD system with *in situ* RHEED. The base pressure of the PLD/RHEED chamber was in the 10^{-8} range. Polycrystalline SZO and YSZ targets were used, whereas the used SrO and STO targets were single crystalline. The used growth parameters were varied between the different experiments, as will be described below.

In situ XPS was performed using an Omicron XM-1000 monochromated Al-K α source, with the pass energy to the detector set to 20 eV. The angle of the surface normal with respect to the detector was 1°, unless stated otherwise. The spectra were fitted with Voigt curves after subtracting Shirley shaped backgrounds. Relative intensities were calculated from the obtained areas using the Scofield cross sections [12].

TEM was performed at EMAT in Antwerp. Samples prepared for TEM analysis were capped *in situ* with carbon and gold to prevent reactions between the samples and atmosphere. The TEM specimen were prepared¹ by focussed ion beam milling in vacuum and transported to the TEM using vacuum transfer instrumentation in order to avoid reactions between samples and air. The electron energy loss spectroscopy (EELS) spectral signatures were recorded using low electron beam currents (about 40-50 pA) to prevent beam damage effects.

XRD measurements were performed on a Panalytical X'pert Pro with a nickel filtered nonmonochromated Cu source. Tapping-mode AFM was performed on a VEECO Dimension Icon.

4.2.2 Methods regarding investigation of the chemistry

The Si substrates were mounted on holders by clamping, as will be described in detail in chapter 5. Before deposition, the holders with Si substrates were degassed in vacuum at elevated temperatures, after which deposition was performed at room temperature. The deposition parameters of the different materials are summarized in table 4.1.

The oxygen rich films were deposited in oxygen atmosphere on silicon with 0.6 nm native oxide. The oxygen deficient STO and SZO samples were deposited in 0.1 mbar Ar

¹Preparation of the TEM specimen and the TEM measurements were performed by R. Egoavil

Table 4.1: Parameters for deposition of the films for the XPS heating experiments.

	YSZ	SrO	SZO	STO
Substrate temperature (°C)	RT	RT	RT	RT
Fluency (J/cm ²)	1.9	1.3	2	1.3
Spot size (mm ²)	2.3	2.3	2.3	2.3
Laser repetition rate (Hz)	1	1	1	1
Pressure (mbar)	0.02 O ₂	0.13 O ₂	0.1 O ₂ or Ar	0.1 O ₂ or Ar
Thickness (nm)	5	0.9	2	2

atmosphere on silicon without native oxide. The native oxide was removed by etching in 1 % HF for 3 min.

Heating was performed by radiative heating in the XPS chamber. This chamber had a base pressure in the 10^{-11} mbar range. The pressure during heating always stayed below 1×10^{-8} mbar. Typically, samples were heated to the desired temperatures in 5 minutes, at which point the cool down was initiated immediately. The temperature was determined by measuring the emission from the front of the sample. The XPS measurements were performed after cooling to room temperature.

The binding energy (BE) scale of the XPS spectra were normalized with respect to one of the peaks in the O1s spectrum. Although bulk Si (labelled as Si⁰, around 99.3 eV) may often serve as a good reference, the dielectric character of the oxide overlayer can easily alter the Si⁰ peak position due to formation of trapped charges in the oxide overlayer during X-ray irradiation and subsequent band bending in the Si close to the overlayer [13–15]. Furthermore, the C1s peak positions of the contamination cannot be used as a reference. Upon heating, these position shifted due to changes in thickness and composition of the contamination. For these reasons, the strongest O1s peak of the oxide overlayer was used, i.e. the peak of SiO₂ at 533 eV, or the peak around 531 eV corresponding to phases containing metal-oxygen bonds. Although the position of these peaks can shift due to the chemical interactions occurring at the different temperatures, at least a reference is present to compare the peak positions of the elements in the oxide overlayer with respect to each other.

No corrections were applied to normalize the absolute intensities of the spectra. Intensity variations of the individual peaks can occur due to changes in the efficiency of the XPS source and removal of contamination during heating, but also due to changes in film morphology and altered distribution of different phases in the film. Therefore, the relative intensities of the species present in the layers above the silicon substrate were primarily taken into consideration for the analysis.

Table 4.2: Parameters for SZO and YSZ deposition. The conditions which were varied will be described in the results section.

	SZO	YSZ
Substrate temperature (°C)	varied	800
Fluency (J/cm ²)	2	2
Spot size (mm ²)	2.3	2.3
Laser repetition rate (Hz)	14	14
Total background pressure (mbar)	0.02	0.02
pO ₂ (mbar)	Varied	Varied

4.2.3 Methods regarding the scavenging experiments

The used deposition parameters for growth of SZO via the scavenging method are summarized in table 4.2. In some experiments, the scavenging process was initiated by deposition of a layer of YSZ, using the parameters shown in the table as well. Oxygen pressures below 10⁻⁴ mbar were regulated with a needle valve. In all experiment, Ar was provided to reach a total pressure of 0.02 mbar. Samples were heated to the chosen temperature with 50 °C/min, while cool down was performed with 20 °C/min.

4.3 Chemistry of metal oxides on silicon

4.3.1 Results

In the next paragraphs, a description of the results is provided per metal oxide. The XPS spectra of the films deposited in oxygen atmosphere on silicon with native oxide are shown in figure 4.1. Graphs showing the relative intensities, derived from fitting of the spectra, are presented in the appendix on page 86.

YSZ

After deposition, the O1s spectrum showed a peak around 531 eV which can be assigned to oxidized Zr and Y. A second peak was visible at 533 eV, which can be assigned to SiO₂ and carbonate contamination. The latter one was in agreement with the presence of a C1s peak around 291 eV [16]. The peaks corresponding to the carbonates decreased upon heating. After heating to 660 °C, the carbonates were burned off completely. During heating, the Si 2p peak indicating oxidized silicon only slightly broadened towards lower binding energy, indicating only a small amount of silicates was formed. The absence of significant peak shifts in the O1s and Zr3d spectra supported this conclusion [17, 18]. Heating above 760 °C resulted in a slight increase of the O and Zr intensity, probably caused by further removal of carbon contamination. After heating to 1000 °C, the Si2p

Figure 4.1: XPS spectra of a) 5 nm of YSZ, b) 0.9 nm of SrO c) 2 nm of SZO, and d) 2 nm of STO on silicon with native oxide after heating to different temperatures.

peak corresponding to oxidized species decreased significantly, as well as the O1s shoulder at 533 eV, indicating decomposition of the silicon oxide started at this temperature. No changes were observed in the Zr3d or Y3d spectra and the O1s peak corresponding to YSZ, i.e. the decomposition of the silicon oxide occurred without affecting the chemistry of YSZ. After heating to 1040 °C, the O1s peak completely disappeared due to loss of all oxygen. The Zr peak shifted to lower binding energy as a result of silicide formation, which was also visible in the appearance of a shoulder at the low binding energy side of the Si2p peak, around 98 eV [19]. The intensity of the Zr3d peak decreased due to diffusion of Zr into the Si substrate or the formation of silicide islands instead of a continuous film. Furthermore, a relatively large amount of carbon remained at the surface. The position of the C 1s peak of 283 eV and the broadening of the Si2p peak around 100 eV indicated formation of the chemically and thermally very stable silicon carbides [20].

SrO

Similar to the YSZ sample, the intensity in O1s spectrum of the SrO sample could be assigned to SiO_2 and carbonates at 533 eV, and phases containing Sr-O bonds at 531 eV. Sr silicate formation was already observed directly after deposition, as visible in the Si2p spectrum around 102.5 eV. During heating to 770 °C, the C1s peak indicating carbonates (291 eV) gradually disappeared. Simultaneously, the O1s peak at 533 eV decreased while the peak at 531 eV increased. This change can be explained partly by oxygen loss due to carbonate decomposition and oxygen transfer from the carbonate to the oxide film, according to the following reaction:

The second reason for the observed changes in the O1s spectra was silicate formation. The silicate region in the Si2p spectrum increased with temperature, especially above 650 °C. Silicate formation should result in disappearance of SiO_2 , as observed in the decrease of intensity at 533 eV, and appearance of oxygen in silicate environment, as visible in the increased intensity in the lower BE part of the O1s spectrum [21–24]. At 810 °C, the highest intensity of the O1s peak around 531 eV was measured, at which point the stoichiometry of the silicate corresponded to a Sr_2SiO_4 phase. Above this temperature, loss of oxygen started to occur. After heating to 840 °C, all oxygen was removed, together with a major part of the Sr.

SZO

Similar to the YSZ and SrO sample, the O1s spectrum of the SZO sample consisted of two peaks separated by about 2 eV. However, the intensity of peak around 533 eV could not be explained by carbonates and SiO_2 only, considering the relative intensities of the

corresponding C and Si peaks. Furthermore, the intensity of the peak around 531 eV was too low considering the amount of oxygen expected in completely oxidized Sr and Zr. Both observations led to the conclusion that hydroxides contributed to about 10 % of the O1s intensity. Hydroxide formation leads to an O1s peak at 533 eV and is known to occur on perovskite oxide surfaces at room temperature due to dissociative adsorption of water molecules [25–27]. The hydroxide and carbonate contamination gradually disappeared during heating to 750 °C, as concluded from the decrease of the C1s peak corresponding to carbonates, and the increase in O1s intensity at 531 eV at the expense of intensity of the peak at 533 eV. The observed changes in intensity were in agreement with the carbonate decomposition reaction shown in equation 4.2, and the following reaction for removal of dissociatively adsorbed water [26]:

Above 770 °C, the intensity of the Si2p peak around 102 eV increased strongly, indicating silicate formation. Simultaneously, the ratio between Zr and Sr increased. Considering the silicate formation measured in the SrO sample and the stability of the YSZ sample against silicate formation, the increase in ratio can be explained by Sr silicate formation at the SZO-SiO₂ interface and, as a consequence, Zr enrichment of the SZO film. Decomposition of the oxides was observed after heating to 980 °C. Oxygen and strontium were removed completely, leaving zirconium silicides and silicon carbides.

STO

The chemistry of the STO sample was similar to the SZO samples at temperatures below 760 °C. At 770 °C, formation of silicates was clearly observed in the Si2p spectrum, again similar to the temperature at which silicate formation was observed in the SZO sample. However, while the silicate formation led to ZrO₂ enrichment of SZO, reduction of TiO₂ occurred in the STO sample. Furthermore, the decomposition of the STO sample started at a lower temperature compared to the SZO sample, since all oxygen was removed at 870 °C. Ti silicides remained, as well as silicon carbides.

Comparison of the decomposition temperatures

In figure 4.2, the temperature regions where loss of oxygen occurred for the different metal oxides are visualized, as derived from the XPS measurements. The lower limit of the bar represents the temperature at which the film was still completely oxidized, whereas the upper limit represents the temperature at which oxygen loss from the metal oxide was observed. The temperature regions shown are quite large, because of the differences in temperatures between subsequent measurements. However, a clear difference of about 200 °C was observed between deoxidation of YSZ and SrO. In order to compare

Figure 4.2: Bars representing the temperatures at which loss of oxygen occurred, as derived from the data in figure 4.1. Data for STO and SZO films deposited in Ar on silicon without native oxide are added as well.

these temperatures to the deoxidation of the silicon native oxide itself, a silicon substrate with native oxide was heated with similar procedures to similar temperatures. Loss of oxygen was not observed after heating to 840 °C, the temperature at which all oxygen was lost in the SrO sample. On the contrary, the silicon native oxide was completely decomposed after subjecting to conditions where native oxide decomposition only started in YSZ sample.

The presence of Zr had also a stabilizing effect in the SZO sample, since decomposition started at higher temperatures compared to the sample with only SrO. However, the thermal stability was lower compared to YSZ. In the case of STO, the presence of Ti did not increase the stability of the oxide film significantly compared to SrO.

In figure 4.2, the decomposition temperatures are also shown for STO and SZO samples in oxygen poor conditions, i.e. when the films were deposited in Ar atmosphere on silicon without native oxide (the corresponding XPS spectra are shown in the appendix on page 87). The chemistry of these films below the decomposition temperature was comparable to the oxygen rich cases. However, the stability of the SZO sample against reduction was significantly lower compared to the SZO sample made in oxygen rich conditions. This difference was not observed between both STO films, although small changes may have been overlooked due to the large steps in temperatures between subsequent measurements.

4.3.2 Discussion

Contamination issues

Although all experiments were performed *in situ*, contamination by hydroxides and/or carbonates was measured in all samples. These contaminations can easily occur due to typical PLD deposition conditions. First of all, most of these contaminations can originate from the background gasses used during deposition. The gasses were not filtered before introduction into the system, which means that water and carboneous contamination present in the gasses and gas lines could enter the deposition chamber. Furthermore, the base pressure of the deposition chamber was only in the 10^{-8} mbar range. Since major part of the contamination was evaporated before the temperatures at which the chemical reactions of interest started to occur (< 700 °C), the influence on the results is considered negligible.

Sr silicate formation

Both STO and SZO films on silicon showed silicate formation around 750 °C. In the case of STO, reduction of titania was measured at the same temperatures. Similar observations were made by Liang and coworkers [28, 29] by XPS on a 4 nm STO film on Si without native oxide. In their experiment, titania reduction started at 630 °C together with oxidation at the STO-Si interface in the form of silicates and SiO_2 , while the oxide completely decomposed at 880 °C. Goncharova *et al.* observed interfacial silicate formation after annealing to 780 °C, while desorption of SrO, SiO and O_2 was measured by mass spectrometry at 850 °C [30]. The described phenomena and temperatures correspond well to the observations made in this work.

Although formation of Sr silicates occurred in the SZO sample at similar temperatures as the STO sample, reduction of zirconia did not occur. Instead, a Zr enrichment of the top part of the film was measured. This observation is in agreement with the expected stability of zirconia on Si in oxygen rich conditions, as well as the expected limited silicate formation². The observations can be described by the following reaction:

In the case of STO, a similar reaction leads to formation of TiO_2 , which is easily reduced in contact with Si [1, 31].

²See chapter 2 for a more thorough description of the chemistry of zirconia on Si.

Metal oxide decomposition

Regarding the decomposition of the metal oxide, the effects of the presence of Sr or Zr were clearly observed. The SrO catalyzed the decomposition of the native oxide, in agreement with studies on Sr or SrO assisted silicon deoxidation [32, 33]. At the temperature at which the decomposition started, the silicon oxide layer was almost completely transformed into a Sr silicate. Large amounts of Sr disappeared during decomposition, caused by diffusion of Sr into the Si bulk or due to Sr evaporation³.

A layer of YSZ increased the stability of the native oxide layer against deoxidation. The decomposition of the native oxide started before the decomposition of the YSZ. Probably, the YSZ overlayer slowed down the formation and evaporation of SiO, while it remained stable against reduction. This stability was lost when the native oxide was completely removed, in agreement with studies on stability of ZrO_2 on Si, which show ZrO_2 becomes unstable in direct contact with Si [9, 34, 35]:

The observed phenomena in the binary oxides help to explain why SZO decomposed at lower temperatures compared to YSZ. The formation of Sr silicate catalyzed the silicon deoxidation, which resulted in contact between the ZrO_2 rich SZO and Si at lower temperatures compared to the YSZ case. The even lower stability of SZO on silicon without native oxide can be explained likewise. The contact between Si and SZO could occur at a lower temperature compared to the situation where a thicker silicate layer prevented this interaction. Moreover, oxygen vacancies due to the deposition in Ar atmosphere may have decreased the stability of the SZO even more [10, 36]. In the case of STO, no differences were observed between the oxygen rich and oxygen poor samples, because even completely oxidized titanium is unstable on Si [1].

4.3.3 Conclusion

In this section, the chemistry of SZO films on Si with and without native oxide was investigated by XPS after heating to different temperatures. This chemistry was compared to the chemistry of STO, SrO and YSZ films, which was determined using similar measurements. Sr silicate formation due to reaction between the silicon native oxide and the film occurred in all Sr containing films. In the case of SZO, the Sr silicate formation led to Zr enrichment of the SZO film. Furthermore, the presence of Sr lowered the thermal stability of SZO compared to YSZ due to formation of the Sr silicate, which decomposed at lower temperatures compared to the silicon native oxide. The difference between SZO

³More details regarding this decomposition process will be discussed in chapter 5

Figure 4.3: RHEED after growth of 5 nm SZO at a) 800 °C , v) 775 °C and 750 °C in 0.02 mbar Ar with d) the corresponding XPS measurements

and STO was mainly found in the reduction of TiO₂ well before the decomposition temperature, whereas zirconium remained completely oxidized until the point the decomposition started. As a result, the decomposition of SZO on silicon with native oxide started at a higher temperature compared to STO. However, on silicon without native oxide this increased thermal stability was lost due to earlier contact between oxidized zirconium and Si of the substrate.

4.4 Growth of SZO via the oxygen scavenging method

4.4.1 Results

Varying temperature and pO₂

First, the possibility to grow epitaxial SZO via the oxygen scavenging method was studied by growth in 0.02 mbar Ar. Films with thicknesses of 5 nm were grown at temperatures between 750 and 800 °C. When the growth was performed at 800 °C, the RHEED pattern of the Si substrate initially disappeared due to attenuation by the deposited overlayer. However, after deposition of a few nm, a new pattern appeared indicating formation of an epitaxial phase, as shown in figure 4.3a. A similar pattern appeared after growth at 775 °C, but was hardly observed at 750 °C (see respectively figure 4.3b and c). XPS was performed after cooling these samples in vacuum (figure 4.3d). Zirconium silicide formation was clearly visible in the 800 and 775 °C samples, as concluded from the co-existence of Zr⁰ peaks together with a shoulder at the low binding energy site of the Si2p

Figure 4.4: Experiments performed on samples grown at 775 °C and cooled in O_2 or vacuum. a) and b) represent the RHEED patterns of the sample cooled down in vacuum along respectively the [110] and [100] axis of the silicon substrate. c) RHEED image of the film grown in the same conditions, but cooled down in O_2 . d) XPS spectra of the films cooled down in vacuum and O_2 . e) and f) TEM images of the films cooled down in respectively vacuum and O_2 . The red arrows indicate Zr and Si rich crystallites, the yellow arrows indicate amorphous phases.

spectrum. The amount of silicides was much lower in the film grown at 750 °C. Growth at all of the temperatures led to formation of silicates, as clearly visible in the appearance of a peak at 102 eV.

In order to gain information about the stability of the observed epitaxial phases in O_2 , 5 nm thick SZO films were grown in 0.02 mbar Ar at 775 °C, after which the samples were cooled down in vacuum or in 0.02 mbar O_2 . Figure 4.4a and b show the RHEED images of the sample cooled down in vacuum. A four fold symmetry was present in the epitaxial phase, as concluded from the patterns visible along the Si $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. When O_2 was added directly after deposition, the RHEED patterns disappeared

immediately (figure 4.4c). The corresponding XPS measurements in figure 4.4d show the disappearance of the silicide phase, as well as an increase of the Si2p peak indicating silicates and SiO₂. Therefore, the observed RHEED pattern after growth can be most likely attributed to the presence of zirconium silicides, which are known to be unstable in O₂, according to the following reaction:

The suggested presence of epitaxial ZrSi₂ was supported by the four fold symmetry observed with RHEED, corresponding to the structures of these type of silicides as determined by Schönbohm *et al.* [37]. The formation of SiO₂ due to reaction between the silicide and O₂ was observed in the XPS spectrum as the appearance of intensity around 103.5 and 533 eV. Additional SiO₂ may have been formed due to reaction between O₂ from the background and Si of the substrate. An indication for this additional SiO₂ formation was the observation of a significant decrease of the intensity of the Si 2p peak corresponding to the Si substrate, most probably caused by an increased thickness of the oxide overlayer.

As described in the previous section by equation 4.4, reaction between SZO and SiO₂ leads to Sr silicate formation. Therefore, the newly formed SiO₂ can lead to further formation of Sr silicates. The stoichiometries of the samples supported this possibility. The sample cooled down in vacuum had a 1:1 Zr:Si ratio, as determined from the Zr 3d and Si 2p peaks. The sample cooled down in O₂ had a Zr:Si ratio of 1.2:1. As shown in the previous section, this can be caused by formation of Sr silicates near the Si substrate and, as a consequence, Zr enrichment of the top part of the film.

The interpretation of the XPS and RHEED measurements were confirmed by TEM measurements of the samples (figure 4.4e and f). In the sample cooled down in vacuum, epitaxial grains were visible. EELS indicated these crystallites were Zr and Si rich, corresponding to the formation of zirconium silicides. In between these crystallites, oxygen rich amorphous Sr silicate phases and amorphous metal oxide (Sr_xZr_yO_z) phases were present. In the sample cooled down in O₂, only limited amount of the crystallites were present close to the Si substrate. The thickness of this sample was 9 nm instead of the 7 nm of the sample cooled down in O₂. Since both samples were deposited in exactly similar conditions, the thickness increase can be explained by the reaction between O₂ from the background and the silicide and Si substrate.

In order to suppress silicide formation during growth, O₂ was added to the 0.02 mbar Ar. When growth was performed at 800 °C, epitaxial phases appeared up to 10⁻⁵ mbar O₂, but the corresponding RHEED patterns disappeared quickly after growth. When 10⁻⁴ mbar O₂ was used, no RHEED pattern appeared during growth. In the XPS measurements of the corresponding samples (data not shown) similar observations were made compared to the sample cooled down in O₂ (see figure 4.4d), i.e. silicate formation together with Zr

enrichment of the top part of the film.

Growth in conditions favoring Sr silicate decomposition

In order to avoid the formation of an amorphous Sr silicate phase, which prevented SZO epitaxy, SZO was deposited at higher temperatures, favoring the decomposition of this silicate. A typical example is discussed now. Two similar 300 nm thick samples were grown at 825 °C using a $p\text{O}_2$ of 10^{-5} mbar in 0.02 mbar Ar. One sample was analyzed *in situ* by XPS and TEM, and one sample was analyzed *ex situ* by AFM and XRD (see figure 4.5). XRD showed at least a part of the film consisted of polycrystalline SZO. However, XPS revealed other phases were present in the film besides SZO. First of all, Si was present in the top part of this film in the form of silicates, SiO_2 and silicides. The presence of silicides was confirmed by performing the XPS measurements at two different surface normal to detector angles. At higher emission angles, both Zr^0 and Si^0 peaks decreased in intensity compared to the lower emission angle, indicating both elements were present in the same part of the film. Finally, Sr enrichment of the surface of the film was observed. The Zr:Si ratio was 0.94 at a take off angle of 1° and 0.76 at a take off angle of 70° .

The TEM image and corresponding EELS measurements (in figure 4.5c) revealed more details. Near the substrate, the film consisted of a Sr rich layer, followed by a Zr rich and O deficient layer. Pores were visible running from the substrate to the top of the film, in correspondance with the porous surface morphology observed with AFM (figure 4.5d). The walls of the pores were O deficient, but Zr and Si rich. Si was measured throughout the whole film, but more in the Zr rich and O deficient parts of the film, i.e. in the layer close to the substrate and at the walls of the pores. The observations made with TEM were in agreement with the phenomena observed with XPS, and can be explained by the instability of the Sr silicate. Decomposition of this silicate may lead to pore formation due to ongoing evaporation of SiO and Sr^4 . The Sr and SiO can deposit on the walls of the pores and on the film surface, leading to the Sr and Si enrichment of the surface measured by XPS. Furthermore, the evaporated SiO can react with the deposited SZO to form the observed zirconium silicides.

Avoiding Sr silicate formation using YSZ

Control of the chemistry of SZO on Si proved to be difficult, especially due to the chemical interactions between Sr, Si and O. In order to prevent contact between SrO and Si, a 0.7 nm of YSZ was grown at 800 °C in $p\text{O}_2$ of $1 \cdot 10^{-6}$, $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ mbar. A clear RHEED pattern was not present after deposition of this layer. When the growth was continued with 5 nm of SZO at the same pressures and at the same temperature, RHEED

⁴The decomposition is discussed in more detail in chapter 5

Figure 4.5: Experiments performed on 300 nm SZO films grown at 825 °C in a pO_2 of 1×10^{-5} and cooled vacuum. a) XPS measurements at photoelectron take off angles of 1° and 70° with respect to the surface normal. b) XRD θ - 2θ scan of the sample compared with the scan of the used target. c) TEM and EELS measurements of the sample. d) AFM images showing a porous surface. The data shown in this figure is from two different samples grown in the same conditions. a) and c) are from one sample which was analyzed completely *in situ*. b) and d) correspond to the sample prepared for *ex situ* analysis.

patterns appeared. In the case of 10^{-6} and 10^{-5} mbar, the pattern resembled the patterns without YSZ interlayer, as shown in figure 4.6a-b. In the corresponding XPS spectra, formation of silicides was observed (figure 4.6d). The RHEED pattern after growth in 10^{-4} mbar also showed spots, but at different locations. Reduced Zr was not observed with XPS. Besides, silicate formation was prevented, as visible in a clear decrease in

Figure 4.6: a-c) RHEED patterns of the SZO films grown in $p\text{O}_2$ of respectively 1×10^{-6} , 1×10^{-5} and 1×10^{-4} mbar on 0.7 nm YSZ grown in the same pressures. d) The corresponding XPS Zr3d spectra. e) XRD θ - 2θ scan of 300 nm film grown on the YSZ-SZO template prepared with a $p\text{O}_2$ of 1×10^{-4} mbar. The asterisks indicate the peaks originating from residual silver glue used to mount the substrate on the sample holders during growth.

intensity of the Si2p peak between 101 and 103 eV. Furthermore, the RHEED pattern did not disappear when more O_2 was added to the PLD chamber. This enabled to continue growth of a thick epitaxial SZO layer in 0.02 mbar O_2 . After growth of a 300 nm thick layer, XRD showed a predominant (110) orientation (figure 4.6e).

4.4.2 Discussion

The observed phenomena during growth can be understood using the knowledge obtained from investigation of the metal oxide on Si chemistry in the previous section. First of all, Sr silicate formation was observed in all experiments. The formation of silicates hindered the formation of epitaxial SZO for two reasons. The silicate phase itself was amorphous, as shown by TEM, which prevented contact between the crystalline silicon and SZO. Secondly, the formation of Sr silicates led to Zr enrichment of other parts of the film, preventing formation of stoichiometric SZO. When the temperature was above

the stability limit of the Sr silicate, decomposition of the silicate led to Sr evaporation and increased Zr silicide formation. These phenomena are comparable to experiments on the stability of STO on Si performed by Yong *et al.* [38]. In their work, formation of pores and titanium silicides were observed as well, together with formation of SrSiO_3 structures on top of the film due to reaction between the film and gaseous SiO and SrO.

Zirconium silicide formation was observed in growth conditions necessary to crystallize an epitaxial phase. Very reducing conditions (10^{-5} mbar O_2 or lower) were necessary to decompose the native oxide sufficiently. As shown in the previous section, oxygen deficiency significantly lowered the stability of SZO against reduction. The used $p\text{O}_2$ were in the range where silicide formation was observed in growth with YSZ as well (see chapter 2). In the YSZ case, silicide formation could be avoided by increasing the $p\text{O}_2$. However, in the case of SZO, formation of epitaxial phases was not observed anymore in these conditions. The lower amount of Zr in SZO compared to YSZ, together with Sr silicate formation, required more reducing conditions compared to YSZ.

The problem of the presence of Sr was its tendency to form silicates instead of scavenging the oxygen from the silicon native oxide. Starting growth with an 0.7 nm YSZ interlayer in a $p\text{O}_2$ of 10^{-4} mbar chemically stabilized the SZO film by preventing contact between Sr and SiO_2 . This allowed epitaxial crystallization of the SZO. The resulting orientation can be seen as a result of the presence of YSZ. As shown in chapter 2, crystallization of (001) oriented YSZ started below a thickness of 0.7 nm. As shown in literature, SZO tend to crystallize (110) oriented on (001) oriented YSZ [7]. The formation of a stable film was only observed using a $p\text{O}_2$ of 10^{-4} mbar. In $p\text{O}_2$ of 10^{-5} and 10^{-6} mbar, formation of Sr silicates and Zr silicides was observed, similar to the case when growth was performed with SZO only. In these conditions, formation of silicides was also observed for growth of YSZ (see chapter 2). Clearly, an oxygen rich Zr phase between SZO and Si is necessary to stabilize the film completely.

As will be shown in chapter 5, Sr silicate formation could enable epitaxial crystallization of SZO. An epitaxial silicate formed during heating of SrO on silicon with native oxide, in conditions favoring controlled decomposition of the silicon native oxide. The results presented in this chapter suggest it was not possible to obtain such epitaxial silicates during growth of SZO, or epitaxial crystallization of SZO on top of this silicate did not occur. In the reducing conditions necessary to form the epitaxial silicate template, oxygen deficiency prevented formation of a stable SZO layer.

4.5 Conclusion

In this chapter, growth procedures were investigated to grow epitaxial SZO on Si via the oxygen scavenging method, i.e. without removing the silicon native oxide in advance. First, the chemical interaction between Si and SZO at different temperatures was investigated by XPS. The presence of Zr proved to increase the stability of the SZO film against

decomposition compared to STO films. However, due to the formation of Sr silicates, the SZO stability was lower compared to YSZ. Secondly, the growth of SZO on silicon with native oxide was investigated. It proved to be possible to decompose the silicon native oxide during growth at elevated temperatures in reducing conditions. However, the obtained epitaxial phases consisted of Zr silicides, which formed due to the necessary reducing conditions. When higher oxygen pressures were used, epitaxial phases were not observed. The main reason was formation of amorphous Sr silicates between the Si lattice and the SZO film, which prevented epitaxial crystallization and formation of stoichiometric SZO. Formation of epitaxial SZO via the oxygen scavenging method was only possible by initiating the growth with a thin layer of YSZ in order to prevent contact between Sr and Si. (110) oriented growth was obtained due to crystallization of SZO on epitaxial (001) oriented YSZ seeds.

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4.6 Appendix

4.6.1 Stoichiometries

Figure 4.7: Normalized and relative intensities of the YSZ, SrO, SZO and STO films, as determined from the XPS spectra shown in figure 4.1.

4.6.2 Annealing on silicon without native oxide

Figure 4.8: a) XPS spectra of the SZO film deposited in Ar on silicon without native oxide, and b) the normalized and c) relative intensities determined from these measurements.

Figure 4.9: a) XPS spectra of the STO film deposited in Ar on silicon without native oxide, and b) the normalized and c) relative intensities determined from these measurements.

Chapter 5

Formation of a Sr silicate template for epitaxial crystallization of perovskites

Abstract: Current methods to obtain epitaxial SrTiO_3 on Si require formation of a Sr silicide template in ultra-high vacuum conditions. In this chapter, the formation of a Sr silicate template was studied in order to develop a less demanding alternative. SrO assisted silicon deoxidation was considered as a possible route to prepare a silicate template. First, the mechanism of the deoxidation procedure was investigated. The deoxidation was shown to occur via decomposition of Sr_2SiO_4 , which formed during heating due to reaction between the silicon native oxide and thin SrO films. Controlling the decomposition time and temperature enabled epitaxial crystallization of the silicate. This silicate template proved to be suitable for crystallization of (001) oriented perovskites, as shown by growing epitaxial SrTiO_3 and SrZrO_3 films on top of it, and is therefore an usefull pathway for integration of epitaxial perovskites on Si.

5.1 Introduction

To date, epitaxial SrTiO_3 (STO) films prepared on Si by MBE are, in terms of crystalline properties, the best buffer layers for heteroepitaxial integration of perovskite oxides on Si. A growth procedure to obtain STO directly on Si was first developed by McKee and coworkers [1], and further developed and investigated by several groups [2–8]. The main philosophy behind the growth procedure is to facilitate the Si to STO transition layer-by-layer, thereby seeking thermodynamic or kinetic control of each step [9]. Mainly, interactions between Si and titania and between Si and O have to be avoided, because of unfavorable formation of respectively titanium silicides or amorphous silica. Therefore, the growth procedure starts with the formation of a Sr 2×1 reconstructed Si surface, consisting of half a monolayer of Sr on the native oxide free silicon [10]. The Sr layer acts as a template for crystallization of (001) oriented STO, which should be done in optimized pressures and temperatures to prevent degradation of the Sr template and reactions between STO and Si. Normally, cycling is performed between low temperature deposition and oxidation of STO, followed by crystallization at higher temperatures in vacuum [11]. The main advantages of this approach are the obtained high crystalline qualities and smooth surfaces, while the resulting STO can directly serve as a template for growth of any (001) oriented functional perovskite of choice [11–15]. Because of these advantages, similar procedures were recently developed for PLD [16, 17].

As mentioned, the growth procedure of STO on Si starts with the formation of a Sr reconstructed surface, which can be obtained via two procedures. In the first procedure, the Sr is provided to the Si substrate after flash annealing in ultra-high vacuum (UHV) in order to remove the native oxide and obtain a clean flat Si surface [1, 18, 19]. UHV conditions are necessary in order to prevent degradation of the surfaces during this procedure due to the presence of Si dangling bonds. The second procedure is the so called Sr assisted deoxidation process. Deposition of a small amount of Sr on the native oxide will catalyze the decomposition of the native oxide, after which metallic Sr remains at the oxide free surface. Additional Sr deposition to complete half a monolayer leads to formation of the reconstructed surface as well [5, 20, 21]. Use of SrO for the deoxidation process gives similar results, and is therefore used in PLD, since SrO is easier to handle and ablate compared to metallic Sr [22–24]. UHV conditions are still necessary, since the coverage of Sr after the deoxidation procedure is always below 0.5 monolayers, which means reactive Si dangling bonds are present [10].

Some disadvantages are inherent to the growth procedures described above, mainly because they will always be very complex and time consuming and will require ultra-high vacuum conditions, even when the Sr assisted deoxidation procedure is used [24, 25]. Therefore, it would be useful to find less demanding procedures. As shown in literature, crystallization of STO does not necessarily have to be performed on the reconstructed silicide surface itself. In some procedures, the Sr reconstructed Si surface is carefully

Figure 5.1: Structure of Sr_2SiO_4 . Si is surrounded by O (red spheres) forming small tetrahedra (indicated by the blue facets). Sr^{2+} ions (green spheres) are in between these tetrahedra, forming large polyhedra.

oxidized to obtain a silicate like template [18, 19]. Possibly, direct formation of a Sr silicate template, thus avoiding the procedure to obtain the Sr reconstructed surface, can be the starting point of the alternative procedure aimed for.

Sr silicates can easily be formed via solid state synthesis by annealing Sr and Si containing precursors (e.g. SrCO_3 and SiO_2). Sr_2SiO_4 is known to be the first silicate to form in bulk solid state synthesis procedures, while conversion to for example SrSiO_3 occurs at temperatures above 800°C [26, 27]. Annealing of SrO, or chemically equivalent BaO, thin films on Si can also lead to formation of silicate phases [28, 29]. Sr is a network modifier according to the classification of Zachariasen, which means that it tends to disrupt the network of SiO_2 [30]. In Sr_2SiO_4 , this leads to formation of isolated SiO_4 tetrahedra alternated by Sr cations. Crystallization of these types of silicates easily occurs [30], which in the case of Sr_2SiO_4 leads to formation of an orthorhombic structure with lattice parameters of $a = 5.663 \text{ \AA}$, $b = 7.084 \text{ \AA}$ and $c = 9.767 \text{ \AA}$ [31–35], as shown in figure 5.1. These silicates can crystallize epitaxially on Si. As shown in literature for Ba_2SiO_4 silicates with similar structures, crystallization on silicon occurs (001) oriented. Two domains will form, with the [100] of the silicate parallel to the [110] or [-110] of the Si [36, 37]. For example, this silicate can be grown by e-beam evaporation of Ba in oxygen atmosphere directly on a Si surface at 650°C [36]. By intermixing of Si with the growing BaO, an epitaxial crystalline silicate is formed. Furthermore, deposition of BaO on a Sr silicide template at 600°C in oxygen atmosphere also resulted in epitaxial Ba_2SiO_4 [37]. Similarly, formation of an epitaxial phase was observed when growing 6 ML of SrO on (001) oriented silicon without native oxide at 500°C in oxygen atmosphere [21].

Formation of epitaxial silicates using the silicon native oxide as one of the precursors

Figure 5.2: Sample holder used for all experiments presented in this chapter.

would be favorable compared to the reported methods, since difficulties regarding silicon native oxide removal are avoided. Interestingly, Imanaka *et al.* reported formation of a Sr silicate buffer layer after SrO assisted silicon deoxidation [22], but it is not clear why their process led to a silicate, and not to a silicide as reported in all the studies discussed above. More knowledge about the mechanism behind the SrO assisted deoxidation is necessary in order to know which conditions can lead to formation of a Sr silicate template.

In this chapter, the possibility was investigated to prepare an epitaxial Sr silicate template via reaction between SrO and the silicon native oxide. Special attention was paid to the use of a SrO assisted silicon deoxidation procedure to obtain this silicate. Therefore, the mechanism of SrO assisted deoxidation was studied first. The chemistry behind the deoxidation process was monitored by heating SrO films on silicon with native oxide in the X-ray Photoelectron Spectroscopy (XPS) chamber. Next, the deoxidation process was monitored in the Pulsed Laser Deposition (PLD) chamber by Reflection High-Energy Electron Diffraction (RHEED) to make the link between the chemistry and the occurring structures. Finally, PLD of SrZrO_3 (SZO) and STO layers was performed in order to verify which of the formed silicate templates were suitable for crystallization of perovskites. RHEED, X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM) were used to analyze the resulting structure and morphology of the films.

5.2 Methods

All samples were grown in a PLD system with *in situ* RHEED and XPS. The base pressure of the PLD/RHEED chamber was in the 10^{-8} range. All experiments were performed with 7x7 mm Si substrates cut from the same wafer, in order to keep the contribution of the native oxide constant. As determined with the procedure described in chapter 2, the estimated native oxide thickness was 0.6 nm.

For the experiments in this chapter, sample holders were designed with a clamping mechanism to hold the Si substrates. In this way, silver glue was not necessary to mount the sample, which decreased the amount of carbon contamination in the chamber caused by outgassing of this silver glue. Furthermore, these sample holders allowed for direct heating of the substrate with an infrared laser, which increased the possibilities regarding

Figure 5.3: Procedure used for deposition of STO or SZO on silicate buffers.

Table 5.1: Parameters for deposition of the different materials.

	SrO	SZO	STO
Substrate temperature (°C)	RT	Varied	Varied
Fluency (J/cm ²)	1.3	2	1.3
Spot size (mm ²)	2.3	2.3	2.3
Laser repetition rate (Hz)	1	1	1
Ar pressure (mbar)	0.13	Varied	Varied

fast thermal cyclings. Photographs of the front and back of the holder carrying a silicon substrate are shown in figure 5.2. The base of the holder consisted of Inconel 600. An alumina spacer was used for thermal isolation of the substrate with respect to the holder. An Inconel spring was fixed to the holder base with screws in order to fix the sample to the holder. An opening was left in the base and the alumina spacer to enable heating of the back side of the substrate with an infrared laser. A pyrometer was used to measure the temperature via this opening as well.

The parameters used during PLD are summarized in table 5.1. Single crystalline SrO and STO targets were used, whereas the SZO target was polycrystalline. The procedure to obtain silicate templates via annealing of SrO films will be explained in more detail in the results section. Crystallization of perovskites on top of these silicate templates was performed using the procedure summarized in figure 5.3. After preparation of the silicate template, two monolayers of the perovskite were deposited at room temperature and crystallized at 600 °C. After repeating this step, growth was continued at 600 °C. The first few nm were deposited at a low oxygen pressure in order to prevent degradation of the film due to reactions between oxygen and the underlying silicon. Thereafter, growth was continued at higher oxygen pressure to fully oxidize the growing film .

Experimental details regarding heating samples in the XPS chamber, as well as regarding the other characterization techniques used, can be found in chapter 4.

Figure 5.4: a) XPS spectra of the 0.9 nm SrO film on Si with native oxide after heating to different temperatures. b) Normalized and c) relative areas of the different species. The square markers indicate where the stoichiometry of the silicate was close to Sr₂SiO₄.

Figure 5.5: a) XPS spectra of the 0.22 nm SrO film on Si with native oxide after heating to different temperatures. The decomposition started slowly at 800 °C. The sample was heated 6 times to this temperature in order to monitor the decomposition in detail. b) Normalized and c) relative areas of the different species.

Figure 5.6: Proposed SrO assisted deoxidation mechanism as deduced from the XPS measurements. Deposition of SrO at room temperature led to formation of some SrCO_3 . This carbonate was decomposed during heating, while Sr_2SiO_4 formed. The deoxidation occurred via decomposition of the silicate, at a temperature of 800 °C. The silicate was regenerated until all native oxide was consumed. At this point, ongoing decomposition led to complete deoxidation. Some Sr was left at the surface, while Si carbides were formed due to the reaction between exposed Si and contamination present in the film or due to degassing of the sample holder.

5.3 Results

5.3.1 Mechanism of SrO-assisted deoxidation

Figure 5.4a shows the temperature dependent XPS data measured on a 0.9 nm SrO film grown on a Si substrate with native oxide, as already presented in chapter 4. In addition, the normalized and relative intensities of all the species are shown in figure 5.4b and c. In summary of the analysis described in chapter 4, at increasing temperatures a SrCO_3 phase was decomposed, while SiO_2 reacted with SrO into a silicate phase. Just before decomposition of the complete oxide film, the silicate phase had a stoichiometry close to Sr_2SiO_4 .

In order to investigate the decomposition in more detail, a similar experiment was performed with a 0.22 nm SrO film, as presented in figure 5.5. This low amount of SrO was chosen in order to have more SiO_2 left at the start of the decomposition, which aided

the analysis of the decomposition of this phase. The decomposition was performed in several steps by carefully tuning the temperature to obtain a slow decomposition rate. Below 800 °C, similar behavior was observed as the 0.9 nm case, i.e. disappearance of a SrCO_3 phase and formation of a silicate phase with a stoichiometry of Sr_2SiO_4 . However, due to the lower amount of SrO, a significant amount of SiO_2 remained present as well, as concluded from the observed intensities around 533 eV and 103.5 eV. As visible in figure 5.5b, loss of O and Si started to occur after heating the first time to 800 °C. The loss of O and Si only occurred due to disappearance of the SiO_2 phase, as visible in the decrease in intensity of the peaks around 533 eV and 103.5 eV and disappearance of Si and O in a 1:2 ratio. The amount of O, Sr and Si in the silicate phase remained constant and kept a stoichiometry corresponding to Sr_2SiO_4 .

As shown in the previous chapter, the presence of SrO lowered the stability of the SiO_2 layer against decomposition. Therefore, although SiO_2 disappeared first during decomposition, the decomposition process most likely occurred in the silicate layer. The following decomposition reaction can therefore be given, taken into account the observed relative intensities of Si and O removal:

The formed SrO can react with the remaining SiO_2 to form a silicate again. In this way, the XPS intensity of O and Si in the silicate remained constant during the decomposition, while the intensities of Si and O from the SiO_2 gradually decreased.

After heating the 4th time to 800 °C, major part of the SiO_2 phase was removed. At this point, not enough SiO_2 was left to form the silicate phase, which led to a decrease in the intensities of the peaks corresponding to the silicate phase. In the final step, significant decrease of the amount of Sr occurred. Similar disappearance of Sr is observed in all studies on SrO or Sr assisted silicon deoxidation, but the cause was never determined, and was not studied in this work. The two possible causes are Sr diffusion into the Si substrate or evaporation of Sr containing material [37]. It must be noted that metallic Sr has a high vapor pressure at 800 °C [38]. Therefore, partial evaporation of Sr is plausible, which means the decomposition can be described by the following reaction:

A significant contribution of Si carbides was visible after complete deoxidation. The carbon can originate from incomplete degassing of the sample holder or was present in the film due to contamination. Quantification of the contamination present in the film was not possible due to the overlap between the C1s corresponding to contamination (around 284.8 eV) and the Sr 3p 1/2 peaks.

The decomposition mechanism described above is summarized in figure 5.6.

Figure 5.7: SrO assisted deoxidation in PLD chamber. a) 2.5 nm SrO annealed for 90 s. at 800 °C, b) 1.7 nm SrO annealed for 10 s. at 800 °C. The distances indicated with the blue arrows correspond closely to the Si lattice size, i.e. 5.4 Å. c) 2.1 nm SrO annealed for 3 min at 800 °C. Some transmission spots are indicated with blue circles. The blue arrow indicates the specular spot, which moved with tilt angle, indicating flat regions were present at the surface. d) 0.9 nm SrO annealed for 10 s at 800 °C.

5.3.2 Silicate template formation

SrO assisted deoxidation was performed in the PLD/RHEED chamber to monitor the crystalline properties of the surface during the process. SrO layers were deposited in 0.13 mbar Ar¹ at RT, after which the films were heated with 50 °C/min to 800 °C in vacuum. After keeping the sample at 800 °C for the chosen amount of time, fast cool down was performed by turning off the infrared heating laser. In this way, the temperature dropped below 300 °C in tens of seconds.

In figure 5.7, RHEED images from typical results are shown. Annealing SrO films with thicknesses above 2.5 nm for 3 min did not lead to appearance of a RHEED pattern (figure 5.7a). Only increasing the temperature could force the deoxidation process, but formation of polycrystalline phases was observed always. Annealing SrO films with thicknesses below 2.5 nm led to formation of epitaxial phases, which started to appear when the temperature reached 780 °C during the heating process. figure 5.7b shows the RHEED image observed after annealing a 1.7 nm thick film for 10 s. at 800 °C. A transmission pattern emerged, which was still present after cooling the sample to room temperature. The lattice size, as determined from the RHEED pattern, corresponded closely to the Si lattice size, i.e. 5.4 Å. Similar patterns were obtained when film thicknesses between 1.3 and 2.1 nm were annealed for similar amounts of time. When the annealing time of these films was increased above 1 min, the pattern evolved to a mix between spots indicating flat and ordered regions on the surface, and transmission spots. A typical image is shown in figure 5.7c, as resulting from annealing a 2.1 nm thick film for 3 min. Transmission spots were never observed when layer thicknesses below 1 nm were used. Instead, streaks or spots indicating flat surfaces appeared. Figure 5.7d shows such a pattern, obtained after annealing a 0.9 nm film for 10 s.²

¹ Similar behavior was observed when the SrO was deposited in 0.13 mbar O₂ instead of Ar.

² The results obtained by heating this sample and the experiment shown in figure 5.4 indicate the temperatures in the XPS chamber were slightly overestimated compared to the temperatures determined in the PLD chamber.

Figure 5.8: a) XPS of SrO assisted deoxidized samples prepared in the PLD chamber. The RHEED images of the measured samples were already shown in figure 5.7. b) XPS of the 1.7 nm sample annealed for 10 s, measured with different photoelectron takeoff angles.

XPS measurements (see figure 5.8a) were performed on the samples shown in figure 5.7. The layers which showed formation of a clear RHEED pattern, i.e. layers with thicknesses below 2.5 nm, showed spectra which could be assigned to one of the steps of the deoxidation mechanism described before (see figure 5.6). Prolonged annealing, i.e. 3 min at 800 °C, or annealing a thin layer of SrO, i.e. 0.9 nm for 10 s, led to removal of almost all O. The XPS spectra corresponded to the final stage of the described deoxidation mechanism, i.e. the film after complete deoxidation. However, some leftover O was always measured, which can be caused by slightly incomplete deoxidation, but also by reaction of the sample with O₂ due to the vacuum conditions of the PLD chamber. The pressure after the deoxidation process was typically in the 10⁻⁸ mbar range, which was high enough to provide the measured amount of O to the surface during cool down and subsequent transfer of the sample from the PLD chamber to the better vacuum conditions of the XPS chamber. Formation of Si carbides was always observed as well, especially in the case of the sample annealed for 3 min at 800 °C. The presence of carbides could lead to the transmission pattern shown in figure 5.7c [25].

The XPS spectra of the 1.7 nm films annealed for 10 s. were completely different. Significant amounts of O, Sr and silicate bonds were left. The stoichiometry corresponded to Sr₂SiO₄, similar to the 3th stage of the described deoxidation mechanism. figure 5.8b shows the spectra of this sample measured at different detector to surface normal angles. Only intensity variations of the Si substrate peak with respect to the other

Figure 5.9: RHEED of the crystallization of perovskites on the different silicate templates. a-d) STO on the Sr_2SiO_4 template prepared by annealing 1.3 nm SrO for 10 s at 800 °C. a) Silicate template. b) After 2 ML STO, deposited at RT and annealed for 1 min at 600 °C, c) After subsequent 2 ML deposited at RT and annealed at 600 °C. d) After subsequent growth of 45 nm STO at 600 °C in 0.02 mbar O_2 . e-h) SZO on a 1.7 nm SrO layer annealed for 3 min at 800 °C. e) Template. f) After 2 ML SZO, deposited at RT and annealed for 1 min at 600 °C, g) After subsequent 2 ML deposited at RT and annealed at 600 °C. h) After subsequent growth of 50 nm at 600 °C in 0.02 mbar O_2 . i-k) On a template prepared by annealing 0.9 nm SrO for 10 s. i) Template. j) After 2 ML STO, deposited at RT and annealed for 1 min at 600 °C, k) After subsequent 2 ML deposited at RT and annealed at 600 °C.

peaks were visible, indicating a chemically homogeneous Sr_2SiO_4 was formed. Apparently, this silicate crystallized on the Si lattice during the deoxidation procedure.

The spectra of the 2.5 nm film, i.e. the film which remained amorphous after annealing, had a stoichiometry close to Sr_2SiO_4 as well. However, a shoulder at the low binding energy side of the O1s spectrum indicated SrO was still present. This SrO was predominantly present at the surface of the film, as concluded from XPS measurements at different surface normal to detector angles (data not shown).

Figure 5.10: a) XRD θ - 2θ scan of 50 nm STO and SZO films grown buffer layers prepared by annealing respectively a 1.3 and 2.1 nm film for 10 s. or 3 min. b) XRD ϕ scan of a 50 nm SZO film grown on a buffer layer prepared from annealing a 1.7 nm SrO film for 10 s.

5.3.3 Crystallization of perovskites

In order to investigate the possibility to use the different crystalline templates for epitaxial crystallization of perovskites, the procedure described in the methods sections was used. Similar results were obtained for both STO and SZO, of which typical RHEED images are shown in figure 5.9. In case the Sr_2SiO_2 template was used, prepared from annealing a 1.3 nm SrO film for 10 s., a perovskite transmission pattern was already observed after annealing the first 2 ML, as shown for STO in figure 5.9b. The sharpness of the spots increased when additional 2 ML were crystallized. After deposition at 600 °C in oxygen atmosphere, the shape of the spots became more streaky, indicating increased smoothness (see figure 5.9d). When a template was used prepared from annealing a 1.7 nm SrO film for 3 min, much weaker RHEED spots were observed after crystallization of the first couple of monolayers, as shown for SZO in figure 5.9f and g. After growth of 50 nm, rings and a diffuse background were present besides the epitaxial pattern (figure 5.9h). On a template prepared from annealing 0.9 nm SrO for 10 s., no crystallization of the perovskite was observed (see figure 5.9j and k).

XRD was performed on the crystalline perovskite films, as shown in figure 5.10. The growth of STO on the Sr_2SiO_4 template, prepared from annealing a 1.3 nm film for 10 s., resulted in a predominantly (001) oriented film, while a minor secondary orientation was measured at $2\theta = 57.7^\circ$, which is attributed to the (211) orientation. The FWHM of the (002) rocking curve was 1.6° . Growth of SZO on a template prepared from annealing a 2.1 nm SrO film for 3 min resulted in a lower crystalline quality. The (002) peak was much weaker, whereas the (110) orientation was visible as well³. The FWHM of the (002) rocking curve was $> 3^\circ$.

In order to obtain information about the in-plane orientation of the films grown on

³The SZO pseudocubic unit cell is used in this chapter.

Figure 5.11: AFM micrographs of a) a silicate template prepared from annealing a 1.7 nm SrO film for 10 s. at 800 °C, and c) a 50 nm STO film grown on top of it, the same sample as presented in figure 5.10a. b) and d) are the corresponding line profiles, showing similar peak-to-peak roughnesses around 1.6 nm.

a Sr_2SiO_4 template, ϕ scans were performed on a 50 nm SZO film grown on a Sr_2SiO_4 template prepared from annealing a 1.7 nm SrO film for 10 s. The (110) and (220) peaks of respectively SZO and Si were used. For both materials, 4 peaks appeared in the spectra which were separated by 90° , corresponding to single in-plane orientations. The unit cell of SZO was rotated 45° with respect to the unit cell of Si, i.e. the SZO [100] was parallel to the silicon [110].

The morphology of the surface is an important property of a buffer layer. Therefore, AFM was performed on the Sr_2SiO_4 buffer, as well as on the 50 nm perovskite films grown on top of it. figure 5.11a shows AFM images of the silicate template prepared by annealing 1.7 nm SrO for 10 s., corresponding to the sample measured with XPS in figure 5.8. The surface was covered with separated grains around 1.6 nm in height. The AFM micrograph of a 50 nm STO film, corresponding to sample measured with XRD in figure 5.10, showed similar height variations (figure 5.11b). This morphology was typically observed for all perovskite films crystallized via the procedure used in this chapter.

5.3.4 Stability in oxygen

Finally, the stability of the Sr_2SiO_4 template in oxygen atmosphere at the typical perovskite growth temperature of 600 °C was addressed. A silicate layer was prepared by annealing a 1.7 nm SrO film for 10 s, leading to the expected RHEED pattern (fig-

Figure 5.12: a) RHEED image of a silicate template prepared via annealing 1.7 nm SrO for 10 s. at 800 °C. b) After annealing for 1 and c) 10 min at 600 °C in 0.02 mbar O₂. d) 50 nm STO film grown at 600 °C in 0.02 mbar O₂ on a template prepared from annealing 1.7 nm SrO for 10 s. at 800 °C. e) XPS measurements of the template after annealing in O₂ atmosphere. For comparison, the measurements of a sample without annealing is added.

ure 5.12a). After cooling to 600 °C, 0.02 mbar O₂ was added. The sample was kept in these conditions for 10 min. The RHEED pattern started to change quickly after adding oxygen, as shown for annealing times of 1 and 10 min in respectively figure 5.12b and c. Although the original spots remained visible, the background became more and more diffuse. Comparison of XPS measurements with and without the 10 minutes anneal (figure 5.12e) indicated the silicate was stable in O₂. The peaks at 531 eV and 102 eV were still present after annealing, while the Sr3p spectrum remained unchanged. The stoichiometry determined from these peaks still corresponded to Sr₂SiO₄. However, additional peaks appeared in the O1s and Si2p spectra at positions corresponding to SiO₂. Therefore, the diffuse background observed with RHEED could be assigned to the growth of SiO₂ in between the silicate grains. Since the silicate phase remained present, perovskites could still be crystallized in these conditions. For example, obtaining epitaxial STO was still possible at 600 °C in 0.02 mbar O₂ when growth was initiated within 2 min (see figure 5.12d), although the FWHM of the XRD (002) rocking curve increased to 2.1°.

5.4 Discussion

As discussed previously, Sr_2SiO_4 plays a central role in the SrO assisted silicon deoxidation procedure. The observations made in this work are in agreement with the knowledge about this silicate described in the introduction. First of all, the formation of a Sr_2SiO_4 phase at temperatures below 800 °C due to reaction between SrO and SiO_2 was in agreement with the cited studies on bulk and thin film synthesis methods. Furthermore, the tendency of Sr to disrupt the SiO_2 network, as shown in figure 5.1, may explain why the decomposition temperature of the silicon native oxide was decreased due to the presence of SrO. The Si-O network in the silicate is not as evolved as in SiO_2 , which means that less Si-O bonds have to be broken in order to make evaporation of SiO possible.

Whether or not epitaxial Sr_2SiO_4 islands were formed, depended on the SrO thickness. When thin layers of SrO were used, almost all native oxide should be removed before epitaxial crystallization of the silicate could occur. Therefore, the ongoing decomposition, as described by equation 5.2, quickly led to removal of almost all O and Sr. On the other hand, when the amount of SrO largely exceeded the amount necessary to form the Sr_2SiO_4 phase, a SrO layer remained on top of the film. SrO will not decompose or evaporate easily at 800 °C [39, 40], which means it stabilized the film against decomposition and prevented formation of a stoichiometric Sr_2SiO_4 phase. In between both extremes, sufficient amount of Sr_2SiO_4 was formed, which could crystallize in islands after enough native oxide at the Sr_2SiO_4 -Si interface was consumed. The SrO thicknesses at which the epitaxial silicate formed exceeded the amount necessary considering only the native oxide thickness, i.e. about twice the native oxide thickness of 0.6 nm. Besides small errors in determination of the silicon native oxide thickness and the thickness of the deposited SrO, two additional factors should be taken into account. First of all, the thickness of the native oxide could increase during heating due to reaction with O_2 present in the chamber. As shown in chapter 2, the presence of a metal oxide layer can significantly increase the SiO_2 growth rate. Furthermore, although limited evaporation of SrO is expected due to its low vapor pressure [39, 40], small amounts of SrO may still evaporate. For example, a small amount of SrO evaporation was shown in literature during reaction between STO and silicon [41, 42].

The structure of the silicate prepared in this work has still to be determined, as well as the epitaxial relationships to the Si substrate and perovskite film. For sure, the presence of silicate islands allowed easy crystallization of perovskites. On the other hand, when the deoxidation procedure was performed with longer annealing times or by using a low amount of SrO, crystallization of a perovskite was hardly possible. This observation is in agreement with existing knowledge about Sr and SrO assisted deoxidation. When a silicide template is prepared using a SrO or Sr assisted deoxidation procedure, always some additional Sr has to be deposited after the deoxidation in order to obtain a coverage of 0.5 monolayers [5, 20, 21]. In this work, additional deposition was not performed,

which means the amount of Sr present at the Si surface was too low to prevent unwanted reactions between Si and STO.

The quality and stability of the Sr_2SiO_4 template may be further improved. One possibility may be to crystallize the silicate without using the decomposition method, by prolonged annealing at lower temperatures. Furthermore, the silicate thickness can be increased by using a thicker SiO_2 layer, in order to ensure a complete coverage of the Si substrate. Finally, Ba or Ca can be mixed with the SrO in order to obtain a silicate with better matching to the Si or perovskite [31, 35].

5.5 Conclusion

In this chapter, the mechanism of SrO assisted silicon deoxidation was investigated by XPS. The deoxidation occurred via decomposition of an intermediate Sr_2SiO_4 phase, which formed due to reaction between SrO and the silicon native oxide. This silicate phase crystallized epitaxially on the underlying Si substrate just before complete decomposition of the oxide layer. When the deoxidation was stopped at this moment by lowering the temperature, a suitable template was formed for crystallization of (001) oriented epitaxial perovskites. The work presented in this chapter shows a promising pathway to develop less demanding procedures for integration of (001) oriented perovskites on Si.

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Summary

Within the perovskite oxides a wide range of physical properties can be found, making this class of materials interesting for use in new types of microelectronic devices. The microelectronic industry is silicon based, which requires integration of these oxides on silicon. This integration should be epitaxial, because the functional properties depend on the crystalline quality of the perovskite oxide and because of the ability to make use of anisotropy in these properties. Epitaxial growth on silicon is not straightforward. Most of the perovskite oxides are chemically unstable on silicon, while the amorphous silicon native oxide prevents the silicon lattice from influencing the perovskite orientation. Therefore, a buffer layer should be incorporated between silicon and most of the perovskites. In this thesis, several strategies were investigated to obtain such a buffer. Pulsed Laser Deposition (PLD) was used, since this technique is very suitable to grow oxides and can be used to deposit on industrial size silicon wafers.

First, the growth of yttria-stabilized zirconia (YSZ) was studied. This buffer layer can be grown without removing the native oxide in advance, since YSZ will break down the native oxide during growth in reducing conditions. Special attention was paid to the possibilities to control the chemistry of the initial growth, by detailed study of the PLD growth process. Specifically, the contribution of the different sources of oxygen present during the growth process were investigated, i.e. oxygen in the silicon native oxide, in the background gas and in the plasma. All those sources were addressed individually, while the resulting chemical and crystallization processes were monitored, as well as the resulting crystalline properties of the film. Partial oxidation of the plasma and sufficient delivery of oxygen from the background gas to the growing film were necessary to avoid silicide formation and obtain optimal crystalline quality. Since the oxidation of the plasma depended on the total pressure, the necessary partial oxygen pressures were different for different total pressures. The necessary amount of oxygen led to increase of the silicon oxide thickness before start of the growth. Therefore, growth of YSZ had to be started as soon as reaching the deposition temperature. This work shows that all sources of oxygen can and should be controlled to obtain reproducible growth of high quality YSZ.

The YSZ buffer layer has a fluorite structure. Limited knowledge exists about the transition to the perovskite structure, and roughening and loss of crystalline quality often occurs. In this thesis, the growth of (001) oriented perovskite SrRuO_3 on (001) oriented fluorite YSZ- CeO_2 buffered silicon was studied. A growth process was already devel-

oped some years ago, starting the growth of SrRuO_3 with deposition of a monolayer in reducing conditions. The mechanism behind this growth method was studied in detail. Key behind a successful transition was the phase separation between SrO and Ru in reducing conditions. When this phase separation was not promoted, (110) oriented SrRuO_3 was always obtained. In case of the phase separation, the presence of a SrO rocksalt layer at the fluorite-perovskite interface induced the (001) orientation. The morphology of the perovskite could be improved by depositing SrO directly, since a higher coverage of the rocksalt on the CeO_2 surface was obtained. The presence of {111} facets on the CeO_2 surface enhanced the growth of (001) oriented SrRuO_3 . This could be understood by the structural match between the (111) fluorite and (111) rocksalt planes.

In order to avoid the fluorite to perovskite transition, the growth of a perovskite directly on the silicon native oxide was studied. SrZrO_3 (SZO) was used based on its expected stability on silicon and the known capability of Zr to break down the native oxide during growth in reducing conditions. First, the chemistry of SZO and its constituting binary oxides in contact with silicon and silicon oxide was studied. Although Zr can form a chemically very stable oxide in contact with silicon, Sr formed silicates at temperatures above 650 °C. This silicate formation lowered the thermal stability of SZO on silicon compared to YSZ. Moreover, the Sr silicate formation prevented epitaxial crystallization of SZO when the growth was performed on silicon with native oxide in reducing conditions at elevated temperatures. When the growth was initiated with a thin layer of YSZ, stable SZO films could be obtained due to prevention of the interaction between Si and Sr. (110) oriented SZO was obtained due to crystallization on the fluorite structured YSZ seeds.

Finally, an alternative to an existing method to obtain SrTiO_3 (STO) on silicon was studied. As shown in literature, Sr or SrO assisted silicon deoxidation can lead to formation of a Sr silicide template, which allows crystallization of (001) oriented STO. In this thesis, the formation of a Sr silicate template via SrO assisted deoxidation was studied in order to avoid the necessity to use ultra-high vacuum conditions. First, the mechanism of SrO assisted deoxidation was studied. The deoxidation occurred via decomposition of Sr_2SiO_4 , which formed during heating of SrO films on the silicon native oxide. This silicate could be crystallized epitaxially on the silicon when the decomposition time and temperature were controlled. (001) oriented STO and SZO were crystallized on the resulting silicate layers, by alternating deposition of monolayers at room temperature and recrystallization at 600 °C. Optimization of the silicate template formation and perovskite crystallization process may further improve the morphology and crystallinity of the STO film.

Samenvatting

De perovskiete oxides zijn interessant voor gebruik in nieuwe soorten elektronica vanwege de grote variëteit aan fysische eigenschappen in deze materiaalklasse. De microelektronische industrie is gebaseerd op silicium, wat betekent dat deze oxides geïntegreerd moeten worden op silicium. Deze integratie moet epitaxiaal zijn, omdat de functionele eigenschappen afhangen van de kristallijne kwaliteit en vanwege de mogelijkheid gebruik te maken van anisotropie in de eigenschappen. Direct epitaxiaal groeien op silicium is vaak niet mogelijk. De meeste perovskiete oxides zijn chemisch instabiel op silicium, en de amorfe natuurlijke siliciumoxide verhindert de beïnvloeding van de oriëntatie van de perovskiet door het silicium kristalrooster. Daarom is een bufferlaag nodig tussen silicium en de meeste perovskiete oxides. In dit proefschrift zijn verschillende strategieën onderzocht om een dergelijke bufferlaag te verkrijgen. Hierbij is gepulste laser depositie (PLD) gebruikt, omdat deze techniek erg geschikt is voor het groeien van oxides en gebruikt kan worden om te groeien op industriële siliciumwafers.

De groei van yttria gestabiliseerd zirconia (YSZ) was als eerste bestudeerd. Deze bufferlaag kan gegroeid worden zonder de natuurlijke oxide vooraf te verwijderen, omdat YSZ deze afbreekt tijdens groei in reducerende omstandigheden. Aandacht is vooral gegeven aan het controleren van de chemie tijdens de initiële groei, door het PLD groeiprocessen in detail te bestuderen. De bijdragen van de verschillende zuurstofbronnen hieraan werden bestudeerd, namelijk van zuurstof in de natuurlijke siliciumoxide, in het achtergrondgas en het plasma. Deze bronnen werden individueel geadresseerd, en de resulterende chemische en kristallisatieprocessen geanalyseerd, evenals de resulterende kristallijne eigenschappen van de gegroeide film. Gedeeltelijke oxidatie van het plasma en voldoende levering van zuurstof vanuit het achtergrondgas naar de groeiende film waren nodig om vorming van silicides te voorkomen en optimale kristallijne kwaliteit te bereiken. Omdat de oxidatie van het plasma afhangt van de totale druk verschilde de benodigde partiële zuurstofdruk voor verschillende totale drukken. De benodigde hoeveelheid zuurstof zorgde voor een toename van de dikte van silicium oxide voorafgaande aan de groei. Daarom moest de groei van YSZ zo snel mogelijk na het bereiken van de groeitemperatuur gestart worden. Dit werk laat zien dat alle zuurstofbronnen beheerst moeten worden om reproduceerbare groei van YSZ met een hoge kwaliteit te krijgen.

De YSZ buffer heeft een fluoriete structuur. Er is weinig bekend over de overgang naar de perovskiete structuur, en verruwing en verlies van kristallijne kwaliteit komt vaak

voor. In dit proefschrift is de groei van (001) georiënteerd perovskiet SrRuO_3 op (001) georiënteerd fluoriet CeO_2 -YSZ gebufferd silicium bestudeerd. Een groeimethode was al een paar jaar geleden ontwikkeld, waarbij de groei van SrRuO_3 begon met depositie van een monolaag in reducerende omstandigheden. Het mechanisme van deze groeimethode is in detail bestudeerd. De sleutel tot een succesvolle overgang was de fasescheiding tussen SrO en Ru in deze reducerende omstandigheden. Wanneer deze scheiding niet werd bevorderd, groeide SrRuO_3 altijd in de (110) oriëntatie. In geval van de fasescheiding zorgde de aanwezigheid van SrO met de steenzout structuur tussen de fluoriet en perovskiet voor groei in de (001) oriëntatie. De morfologie van de perovskiet kon verbeterd worden door alleen SrO te deponeren, zodat er een grotere bedekking van het steenzout op het fluoriete oppervlak was. De aanwezigheid van $\{111\}$ facetten op het CeO_2 oppervlak versterkte de groei van (001) georiënteerd SrRuO_3 . Dit kan begrepen worden als gelet wordt op de structurele overeenkomst tussen de (111) fluoriet en (111) steenzout vlakken.

Om de overgang van fluoriet naar perovskiet te vermijden werd de groei van een perovskiet direct op de natuurlijke siliciumoxide bestudeerd. SrZrO_3 (SZO) werd gebruikt vanwege de verwachte stabiliteit op silicium en de bekende mogelijkheid van Zr om de natuurlijke oxide af te breken tijdens groei in reducerende condities. Allereerst werden de chemie van SZO en zijn binaire oxides in contact met silicium en siliciumoxide bestudeerd. Hoewel Zr een chemisch erg stabiele oxide kan vormen in contact met silicium, vormt Sr silicaten bij temperaturen boven 650°C . Deze silicaatvorming verlaagde de thermische stabiliteit van SZO op silicium in vergelijking met YSZ. Bovendien verhinderde vorming van Sr silicaten de epitaxiale kristallisatie van SZO wanneer de gegroeid werd op de natuurlijke siliciumoxide in reducerende condities op hoge temperatuur. Wanneer eerst een dun laagje YSZ gegroeid werd, kon een stabiele SZO film verkregen worden omdat contact tussen Sr en Si verhinderd werd. De (110) oriëntatie werd verkregen, omdat SZO kristalliseerde op de fluoriet gestructureerde YSZ nucleï.

Als laatste is een alternatief bestudeerd voor bestaande methoden van groei van SrTiO_3 (STO) op Si. Zoals aangetoond in de literatuur, kan Sr of SrO gesteunde silicium deoxidatie leiden tot vorming van een Sr silicidelaag, wat kristallisatie van (001) georiënteerd STO mogelijk maakt. In dit proefschrift is de vorming van een Sr silicaatlaag via SrO gesteunde deoxidatie bestudeerd, waarmee gebruik van ultrahoog vacuüm vermeden werd. Allereerst is het mechanisme van SrO gesteunde deoxidatie bestudeerd. De deoxidatie vond plaats via decompositie van Sr_2SiO_4 , wat vormt tijdens het verhitten van SrO films op de natuurlijke siliciumoxide. Dit silicaat kon epitaxiaal kristalliseren wanneer de tijd en temperatuur van de decompositie gecontroleerd werden. (001) georiënteerd STO en SZO konden op de resulterende silicaatlagen gekristalliseerd worden, door middel van afwisselend depositie op kamertemperatuur en kristallisatie op 600°C . Optimalisatie van de silicaatvorming en de kristallisatieprocedure van de perovskiet kunnen de morfologie en kristalliniteit van de STO film verder verbeteren.

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David Dubbink
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