Structure and stability of Gd-doped CeO₂ thin films on yttria-stabilized zirconia

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Abstract

25 nm thick Gd-doped ceria thin films were grown on yttria-stabilized zirconia (YSZ) substrates with (110) and (111) orientation by pulsed laser deposition to study both their crystalline structure and interfacial stability. The films were characterized by high-energy grazing incidence x-ray diffraction, x-ray reflectivity and x-ray photoelectron spectroscopy before and after annealing to 1400 K under ultra-high vacuum (UHV) conditions. The films were found to be epitaxial to the YSZ substrates, exhibiting good crystalline quality without defects like twinning, and low surface roughness. Upon reduction due to the annealing in ultrahigh vacuum (UHV), both samples showed an increase in lattice parameter while maintaining their original crystalline quality. The x-ray reflectivity measurements gave evidence for interdiffusion after annealing by the presence of an additional interfacial layer with reduced electron density. X-ray photoelectron spectroscopy revealed an increase in the concentration of Ce³⁺ and also yttrium at the surface upon annealing, indicating a slight reduction of the surface as well as diffusion of yttrium to the surface.

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1. Introduction

Cerium oxide is commonly used in automotive catalytic converters due to its ability to easily generate oxygen vacancies under reducing conditions up to a reversible phase transition. It is therefore able to store, release and transport oxygen as well as enhance the catalytic properties of metal particles deposited on its surface [1]. It is also a candidate for application in catalysts for the water-gas shift reaction as well as an anode or electrolyte material in solid oxide fuel cells [2,3]. Since cerium is 4-valent in stoichiometric CeO₂, the intrinsic concentration of oxygen vacancies can be varied by doping with 3-valent (e.g. Gadolinium) or 5-valent rare earth metals, further enhancing its versatility, especially its oxygen ion conductivity. Yttria-stabilized zirconia is commonly used as an electrolyte material in solid oxide fuel cells (SOFCs) because of its high oxygen ion conductance at higher temperatures. To get insight into the behavior of ceria as an electrode material on YSZ the growth and stability of ceria thin films on YSZ under different reducing conditions are of interest because they influence the ion conductivity and stability of the whole system.

Stoichiometric CeO₂ crystallizes in the face-centered cubic fluorite-type structure with a lattice parameter of 5.41 Å, expanding upon doping with gadolinium [4] as well as upon reduction [5]. Yttria-stabilized zirconia (YSZ) with a doping of 9.5 mol% yttria crystallizes in the same structure with a lattice parameter of 5.13 Å [6]. Despite this large lattice mismatch of around 5%, ceria thin films were reported to grow epitaxially on YSZ [7]. This makes them an interesting model system for new studies of the surface of ceria as a replacement for single crystals, which are difficult to obtain and often lack crystalline quality and purity. Interdiffusion between the YSZ substrate and Gd doped ceria thin films was reported to take place at temperatures above 1273 K [8] and XPS (x-ray photoelectron spectroscopy) and LEED (low energy electron diffraction) for films grown on Rhenium(0001) [10]. This is somewhat surprising considering the fact that the experiments were carried out at conditions where bulk CeO₂ shows no phase transition (see [11]). On the other hand, reduction at the surface was reported to start at much lower temperatures for single crystals as well as for thin films [12–16], and vacancies are also reported to be more stable at the surface as compared to in the bulk [17].

Here we present results on the crystalline structure, interfacial stability and surface composition of 25 nm thick 10% Gd doped ceria (GDC) thin films grown on YSZ-substrates by pulsed laser deposition.
(PLD). We employed a fast characterization method using high-energy grazing incidence x-ray diffraction in combination with a large 2D detector to determine the thin film structure and phase purity [18]. We show that the GDC films in (110) and (111) surface orientation are single crystalline and that the CeO$_2$ fluorite structure is stable upon annealing at 1400 K. From the expansion of the lattice after annealing we determined the amount of oxygen vacancies. X-ray reflectivity data before and after annealing of the films give evidence for interdiffusion at the CeO$_2$/YSZ interfaces. Complementary information is provided by X-ray photo emission (XPS), giving evidence for Y surface segregation after annealing and Ce$^{3+}$ formation at the surface, inline with oxygen vacancy creation.

2. Experimental

10% Gd-doped ceria (GDC) thin films were prepared on 10 × 10 × 1 mm$^2$ single crystalline YSZ substrates with (111) and (110) orientation and a miscut below 0.1°. Both samples were grown by pulsed laser deposition (PLD) in O$_2$ at a pressure of 0.04 mbar and a substrate temperature of 925 K at a rate of 15 nm/min, resulting in 25 nm thick CeO$_2$ films as confirmed by x-ray reflectivity. Afterwards, both samples were introduced into a UHV-system with a base pressure of 3 × 10$^{-12}$ mbar and heated up to 1400 K for 100 min.

The samples were characterized by x-ray reflectivity as well as high energy GIXRD in combination with a large 2D detector. The second technique allows one to obtain full 3D reciprocal space maps in a few minutes only [19]. To get more detailed information about the oxidation states as well as the surface composition of different ceria thin films, XPS measurements were carried out before and after UHV annealing and compared to results from ceria single crystal surfaces.

The (110)-oriented sample was characterized at the ID03 beamline at the European Synchrotron Radiation Facility (ESRF) by means of x-ray reflectivity as well as grazing incidence x-ray diffraction. The (111)-oriented sample was characterized by x-ray reflectivity with a Cu K$_\alpha$ lab source equipped with parabolic multilayer optics; all x-ray diffraction measurements were performed at room temperature in air.

The high energy GIXRD measurements were conducted after annealing at the P07 high-energy beamline at PETRA III, Physics Hutch on a grazing incidence diffractometer [20] in air at a photon energy of 78 keV. Reflectivity measurements were carried out by using a point detector, while images of larger sections of reciprocal space were taken with a Perkin-Elmer area detector at an incident angle of 0.03° close to the critical angle for total external reflection for YSZ. To attenuate the intense Bragg peaks from the substrate and therefore allow measurement of the Bragg peaks from the film, small tungsten blocks were locally placed in front of the detector. By rotating around the surface normal theta axis with a step size of 0.1°, collecting 2D diffraction patterns after each step and summing up pictures in a certain angular range, diffraction patterns were recorded. In this way, one obtains an image of a reciprocal plane with fixed azimuthal angle, similar to transmission electron microscopy (TEM) diffraction patterns.

XPS measurements were carried out using a high-resolution 2D delay line detector. A monochromatic Al K$_\alpha$ x-ray source (photon energy 1486.6 eV; anode operating at 15 kV) was used as incident radiation. XPS spectra were recorded in fixed transmission mode. A pass energy of 20 eV was chosen, resulting in an overall energy resolution better than 0.4 eV. Charging effects were compensated by using a flood gun. The binding energies were calibrated based on the graphitic carbon 1s peak at 284.8 eV.

3. Results and discussion

3.1. Crystalline structure

3.1.1. Pre-characterization

From the pre-characterization of the (110)-oriented as grown ceria film on YSZ, the in-plane lattice parameters of the tetragonal (110) oriented unit cell were determined to $a = 3.81 \pm 0.01$ Å and $b = 5.44 \pm 0.03$ Å along the bulk (110) and (001) directions, respectively. The out-of-plane lattice parameter along the (110) surface normal was found to be $c = 3.73 \pm 0.01$ Å. This corresponds to an anisotropic compression in $a$ and $c$ of 0.52% and 2.61%, and an expansion in $b$-direction of 0.37% compared to the bulk values of $b = 5.42$ Å and $a = c = 3.83$ Å for 10% Gd-doped ceria [4]. From a simple misfit argument, one would expect an in-plane compression in both directions, since the substrate lattice constant (5.13 Å) is smaller than the film. This observation points to an anisotropic misfit dislocation driven relaxation behavior [21], which might be induced by surface defects like steps. The bulk reciprocal lattice is shown for two high symmetry planes in Fig. 1. The crystalline coherence length calculated with the Debye–Scherrer equation is 13.2 nm in $a$-, 20.5 nm in $b$- and 12.4–15.2 nm in $c$-direction, which is smaller than the total film thickness of 25 nm, likely due to defects such as dislocations induced by the 5% lattice mismatch to the substrate. The in-plane mosaicity of the film was around 1.8°, which is much larger than the substrate mosaicity, in line with the above mentioned defects.

3.1.2. Annealed samples

Maps of the reciprocal space of the h- and k-plane of the (110) oriented sample after annealing are shown in Fig. 2a and b. In both maps, sharp reflexes are visible, indicating a single preferential orientation without misoriented domains or a polycrystalline component also after annealing. They match the pattern and the momentum transfer Q-values expected for the face-centered cubic CeO$_2$ lattice (see Fig. 1), showing no signs of a different phase nor defects like twinning. In addition, the lattices of the film and the substrate are found to be rotationally aligned with respect to each other, showing that the film is epitaxial. The corresponding lattice parameters after annealing were determined

![Fig. 1. Schematic view of the measured planes in reciprocal space of a sample with cubic (110) orientation. (a): (h0l)-plane, (b): (0d0)-plane. Allowed reflections are marked with red dots and they are indexed in bulk reciprocal lattice coordinates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
as $a = 3.86 \pm 0.03 \, \text{Å}$, $b = 5.46 \pm 0.03 \, \text{Å}$ and $c = 3.81 \pm 0.03 \, \text{Å}$, corresponding to an expansion of 1.45% in $a$, 0.44% in $b$ and 2.17% in $c$ compared to the values before annealing, likely due to the reduction of the film [22]. The Debye–Schererrer crystallite size is $15 \pm 4 \, \text{nm}$ in $a$, $11 \pm 3 \, \text{nm}$ in $b$ and $11 \pm 3 \, \text{nm}$ in $c$ direction, getting worse along $b$, but showing no significant change along the other directions. The mosaicity corresponds to $2.1 \pm 0.3 ^\circ$, showing a slight increase upon annealing. Overall, the crystalline quality is comparable before and after annealing with some lattice expansion. The average increase of the lattice parameter of 0.3% with respect to the literature value for 10% Gd-doped CeO$_2$ may be used to estimate a change of the vacancy concentration. In this case about 3% oxygen vacancies result [22] in addition to the 2.5% from Gd doping, and lead to nominal stoichiometry of Gd$_{0.1}$Ce$_{0.9}$O$_{1.89}$.

Maps of the reciprocal space centered around theta values for the (h0l) and (0kl) plane of the (111)-oriented sample obtained after annealing are shown in Fig. 3a and b. Both show sharp Bragg reflections expected from the face-centered cubic lattice of CeO$_2$ with no indications of any Debye–Schererrer powder rings or phase transition to the hexagonal Ce$_2$O$_3$ phase. They also show no indications for twinning along the (111) direction, indicating a uniform ABC stacking of the closed packed (111) planes, as inferred from the comparison with the theoretical reciprocal lattice in Fig. 4. Despite the large mismatch to the substrate, the film follows the ABC stacking of the closed packed planes of the substrate. The reciprocal space maps also give evidence for a good rotational alignment of the lattice of the film with regard to that of the substrate, indicating that the films grew crystalline and epitaxial. From the positions of the peaks, the lattice constant was determined to $3.87 \pm 0.03 \, \text{Å}$ in the $a$- and $b$-direction, and $9.34 \pm 0.04 \, \text{Å}$ in the $c$-direction (employing hexagonal coordinates with $\alpha = \beta = 90 ^\circ$, $\gamma = 120 ^\circ$), leading to an in-plane lattice expansion of 1.04% compared to the bulk value of 10% Gd-doped ceria, while the lattice parameter in $c$-direction matches the literature value of 9.38 Å within the error bars.

The average expansion of the lattice parameter of ~0.5% leads to an estimated additional oxygen vacancy concentration of around 4% [22], similar to the (111) oriented sample. The Debye–Schererrer crystallite size is $12 \pm 5 \, \text{nm}$ in the surface plane and $10 \pm 2 \, \text{nm}$ perpendicular to the surface, and stays below the film thickness also for the (111) oriented films. The mosaicity of the film was determined to $1.7 \pm 0.6 ^\circ$. Overall, both samples show a good crystalline quality with a mosaicity slightly higher than the values reported in [7] for pure ceria films on YSZ prepared under similar conditions. The structure of both samples was stable upon annealing, as would be expected from the bulk phase diagram of ceria. No signs of either the cubic or the hexagonal Ce$_2$O$_3$ phase could be observed, in contrast to studies in [10] on ceria thin films grown on rhenium. Both samples show a similar expansion of the unit cell volume due to reduction and oxygen vacancy formation.

### 3.2. Interfacial stability

The reflectivity measurements of the (110)-oriented sample before and after annealing are shown in Fig. 5, together with a fit and the corresponding electron density profile. The fitting was performed with layer models using a program that implements the Parratt algorithm [23] together with a root mean square interfacial roughness $\sigma$ according to [24]. The parameters obtained from the fitting are shown in Table 1. For the reflectivity curve before heating, a 2-layer model was employed with a 25 nm GDC layer on a YSZ substrate and one layer on top of the ceria layer to take adsorbates on the surface like water or carbon into account. The electron density of the GDC layer was found to be slightly lower than the bulk value, possibly due to defects or islands not grown together completely. The density of the film on top is much lower, matching to the assumption of an adsorbate like water. The roughness $\sigma$ of the substrate is around 2 Å with no significant change.
compared to typical values of bare YSZ substrates. There is no indication of interdiffusion between the substrate and the film. After annealing, a clear oscillation at a Q-value much larger than that of the thickness oscillations from the film appears, indicating that a layer with a significantly different electron density and much smaller thickness has formed either at the surface of the ceria layer or at the interface between the ceria layer and the substrate.

To obtain a good fit of the reflectivity curve after annealing, an additional, 0.9 nm thick, diffuse layer with slightly reduced electron density had to be added at the interface between the film and the substrate. We attribute this layer to interdiffusion and metal vacancy accumulation at the interface during annealing. The electron density and also the thickness of the GDC layer did not change, whereas the density of the layer on top went up to 67% of bulk CeO$_2$ and the thickness increased to 1.4 nm. This additional layer at the surface may arise from material that segregated to the surface, which is also corroborated by the XPS results, see below.

The reflectivity measurements of the (111)-oriented sample before and after annealing and the corresponding electron density profile from the fit are shown in Fig. 6. The resulting fitting parameters are summarized in Table 2. For the data before annealing, a 3-layer model with one 25 nm thick GDC film between two very thin layers at the surface and the interface had to be used, indicating that a layer with a significantly different electron density and much smaller thickness has formed either at the surface of the ceria layer or at the interface between the ceria layer and the substrate.

To fit the data after annealing, the same 3-layer-model from before annealing was used. As a main effect, we observe an increase in the top most surface layer thickness and roughness, similar to the (110) oriented sample, in line with outward diffusion of material. The thickness of the GDC layer stays constant with the error bars, but the interface to the YSZ substrate got significantly roughened, pointing to an enhanced interdiffusion between the film and the substrate.

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**Table 1**

Parameters from the fitting of the GDC thin film on YSZ (110) before and after annealing. The difference in the substrate effective electron density is due to the inclusion of dispersion effects.

| Layer          | Thickness (Å) | σ (Å) | Electron density (Å$^{-3}$) |
|----------------|---------------|-------|----------------------------|
| Before annealing |               |       |                            |
| III            | 3.51          | 2.54  | 0.64                       |
| II (GDC)       | 250.31        | 6.97  | 1.76                       |
| YSZ-substrate  | –             | 2.36  | 1.59                       |
| After annealing |               |       |                            |
| III            | 14.03         | 4.97  | 1.27                       |
| II (GDC)       | 250.31        | 5.08  | 1.75                       |
| I              | 9.13          | 8.62  | 1.57                       |
| YSZ-substrate  | –             | 3.86  | 1.62                       |

Fig. 4. Schematic view of the measured planes in reciprocal space of (111)-oriented CeO$_2$. (a): (h0l)-plane, (b): (0kl)-plane. Allowed reflections are marked with red dots and are indexed in bulk reciprocal lattice coordinates. Twinning would lead to additional spots at positions marked by circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (a) X-ray reflectivity as a function of the momentum transfer Q = 4π/λ⋅sinα with α as glancing angle and (b) effective electron density profile perpendicular to the surface both of the (110)-oriented sample (1) before (12.4 keV photon energy) and (2) after annealing (78 keV photon energy). The red line (0) in (b) marks the bulk value of the electron density. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3.3. XPS

Cerium-, oxygen-, gadolinium- and carbon-related peaks are detected in the XPS survey spectra of both CeO₂(110) and (111) thin films before annealing (not shown here). Fig. 7 shows the Ce 3d spectra obtained from the CeO₂ (110) thin film and reference scans from a CeO₂ (110) single crystal. The spin-orbit doublet with unprimed labels, v and u, corresponds to the primary Ce 3d⁵/₂ and Ce 3d³/₂ states, while the bands labeled v₀, v′, v″ and u₀, u′, u″ represent satellite features arising from the different Ce ionization states, as can be identified from the comparison with the spectrum of an undoped CeO₂(110) single crystal surface, spectrum A in Fig. 7 [25,26]. The dominating peaks labeled v, v″ and u, u″ are characteristic for the Ce⁴⁺ species, whereas the weak peaks for Ce³⁺ are indicated at positions labeled v₀, v′ and u₀, u′.

Annealing the Gd-doped ceria films in ultra-high vacuum up to 1400 K increases the amount of non-stoichiometric oxygen vacancies and therefore the amount of Ce³⁺ ions. The stability of these vacancies at the surface is in line with results from [17]. The increase in Ce³⁺ and correspondingly in oxygen vacancies at the surface is also consistent with the increased average lattice parameter of the films after annealing reported in the last section.

In Fig. 7, in addition to the gadolinium peak from the doping, there is also an yttrium peak appearing in the spectrum of the annealed sample, which shows that yttrium is actually diffusing from the substrate through the film to the surface. This confirms that the change in the electron density at the interface between film and substrate seen in the reflectivity measurements can be at least partially attributed to inter diffusion at the interface and subsequent Y surface diffusion.

| Table 2 |
| Parameters from the fitting of the Gd₀.₁Ce₀.₉O₁.₉₅ thin film on YSZ (111) before and after annealing. |

| Layer               | Thickness | σ     | Electron density |
|---------------------|-----------|-------|------------------|
| Before annealing    |           |       |                  |
| III                 | 6.93 Å    | 4.37 Å| 0.78 Å⁻³         |
| II (GDC)            | 249.61 Å  | 8.37 Å| 1.82 Å⁻³         |
| I                   | 12.74 Å   | 13.19 Å| 1.60 Å⁻³         |
| YSZ-substrate       | –         |       | –                |
| After annealing     |           |       |                  |
| III                 | 24.91 Å   | 19.93 Å| 0.82 Å⁻³         |
| II (GDC)            | 253.16 Å  | 11.55 Å| 1.78 Å⁻³         |
| I                   | 7.83 Å    | 30.67 Å| 1.67 Å⁻³         |
| YSZ-substrate       | –         | 3.03 Å| 1.62 Å⁻³         |

Fig. 6. X-ray reflectivity (a) and effective electron density profile (b) of the (111)-oriented sample (1) before (8048 eV photon energy) and (2) after (78 keV photon energy) annealing. The red line (0) in (b) marks the bulk value of the electron density for GDC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. XPS spectra of (a) of the Ce 3d region (b) of the Gd 4d region (A) single crystal, (B) as-prepared thin film and (C) thin film after annealing to 1400 K. The binding energies were calibrated to the C 1 s peak at 284.8 eV.
Only small amounts of yttrium can have diffused through, because otherwise there would be a notable decrease in the film lattice parameter, which was not observed in our study [8]. We made similar observations in terms of Ce\(^{3+}\) formation and Y segregation for the (111) oriented GDC thin film before and after annealing.

4. Summary and conclusion

To summarize, we have shown that Gd doped CeO\(_2\) films grow epitaxially on YSZ for both (110) and (111) substrate orientation without twinning despite of the large lattice mismatch of 5%. We find that their crystalline structure is stable upon annealing in vacuum with no indication of phase transformation in contrast to undoped ceria films on YSZ(100) [9]. We observe that the unit cell volume increased, which we attribute to the reduction of the films with 3–4% oxygen vacancy formation. The interface between the film and the substrate, however, was not stable under annealing and showed interdiffusion, with yttrium segregating to the surface of the ceria films on both samples as monitored by XPS. The structural quality of the films and their improved thermal stability under reducing conditions compared to undoped CeO\(_2\) films [9,10] make them suitable for detailed future in situ investigations of CeO\(_2\)/YSZ model anode/electrolyte systems under oxygen transport and hydrogen oxidation conditions.

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