On the influence of strain on ion transport: microstructure and ionic conductivity of nanoscale YSZ|Sc₂O₃ multilayers

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Multilayer samples of the type (YSZ|Sc₂O₃) × n with layer thicknesses between 8 nm (n = 100) and 250 nm (n = 5) were prepared on (0001) sapphire substrates by pulsed laser deposition (PLD). The samples were characterised using X-ray diffraction (XRD), scanning electron microscopy (HRSEM) and transmission electron microscopy (TEM/HRTEM, SAED (selected-area electron diffraction) and quantitative EELS (electron energy-loss spectroscopy)). The polycrystalline layers show a columnar microstructure, which is typical for the used preparation technique. The layers are highly textured and only one axial orientation relation is found between yttria-stabilised zirconia (YSZ), scandium oxide and the substrate:

(0001) Al₂O₃||(111) Sc₂O₃||(111) YSZ

A preferred orientation relationship also exists for the azimuthal rotation of the crystallites, which was demonstrated by SAED, XRD pole figure measurements and fast Fourier transformation (FFT) of HRTEM micrographs. The interfaces between YSZ, Sc₂O₃ and the substrate are sharp and do not contain diffuse transition regions. Dislocations appear not to be arranged in regular arrays. With increasing interface density (thinner individual layers in the multilayer), the conductivity of the multilayers decreases. We relate this to the negative nominal misfit present at the YSZ|Sc₂O₃ interfaces (compressive stress in YSZ at the phase boundaries). This observation agrees well with the previously investigated case of YSZ|Y₂O₃ (A. Peters et al., Phys. Chem. Chem. Phys., 2008, 10, 4623), where tensile misfit strain was present in YSZ at the phase boundaries, leading to a conductivity increase.

1. Introduction

The contribution of internal interfaces, either homophase boundaries (grain boundaries) or heterophase boundaries, to ionic transport in solid electrolytes is subject of strong interest for several reasons: Firstly, solid electrolytes are usually polycrystalline, and grain boundaries control the microstructure—in particular in thin films. Secondly, the dispersion of a second phase and the generation of heterophase boundaries have been proposed as a possible way to increase the conductivity (“heterogeneous doping”, see ref. 1–4). An increased conductivity may be caused either by an increased concentration of mobile charge carriers, by an increased carrier mobility or by a combination of both—as long as no new phases form at the interface. Within the “space charge concept” (see e.g. ref. 5–7), mainly a concentration effect is considered, caused by the shift of internal defect equilibria within boundary regions.

In order to understand the influence of a heterophase boundary on ionic transport in a typical solid electrolyte system with very small Debye length and negligible space charge regions, Korte et al. used a model system on the basis of YSZ (9.5 mol% yttria-stabilised zirconia) as solid electrolyte and rare earth oxides (RE₂O₃) with bixbyite structure as an insulating second phase.8,9 The lattice parameter of the RE₂O₃ phases can be varied by the choice of the rare earth metal, and thus, heterophase boundaries with a well defined positive or negative mismatch can be constructed. A quasi two-dimensional thin film geometry of the two phases has been chosen in order to obtain a most simple geometry. By decreasing the film thickness, the contribution of the heterophase boundaries to the total resistance (measured along the film) can be increased. From the practical point of view, the study of a single electrolyte film, sandwiched between two symmetric insulating layers should be sufficient, and a number of single layer studies have been published.10–13 Unfortunately, these measurements are hampered by the finite resistance of the substrate, which is usually much thicker than the thin electrolyte film. As the conductivity of the standard substrates like fused silica glass or sapphire is often unexpectedly high at elevated temperatures due to impurities, single layer measurements are easily spoiled by a parallel substrate conduction path.

In order to reduce the influence of a finite substrate resistance, Korte et al. used a multilayer arrangement. In multilayers, the total electrolyte resistance (along the film) is always significantly smaller than the substrate resistance once a sufficient number of thin films is stacked. The contribution of interfaces can be varied by varying the number of individual layers but keeping the total film thickness constant. In a previous paper, Peters et al. reported on the model system...
YSZ/Y_2O_3. They found an increasing ionic conductivity with increasing interface density, i.e., with increasing number of layers. Korte and Schichtel reported in ref. 9 and 14 on the influence of strain on ionic conductivity and presented a theoretical model based on elasticity theory. Some results of the conductivity measurements on different multilayer systems were already presented in these papers. The present paper focuses on the system YSZ/Sc_2O_3 and presents detailed investigations of the microstructure, which are then related to the results of the conductivity measurements.

2. Formal considerations

2.1 Structural considerations between YSZ and Sc_2O_3

Yttria-stabilised zirconia (YSZ) with 9.5 mol% Y_2O_3 is known to form the cubic CaF_2 structure (fluorite type). Sc_2O_3 crystallises in the z-Mn_2O_3 structure (bixbyite type), which is related to the cubic fluorite structure. Structural data for both materials are listed in Table 1.

The z-Mn_2O_3 structure is derived from the CaF_2 structure by doubling the lattice parameters, thereby combining eight unit cells of the fluorite phase and removing 16 O^2− ions from the new unit cell. The fcc cation sublattice and a primitive cubic anion sublattice is found in both structures. Thus, the z-Mn_2O_3 structure contains structural oxygen vacancies. Small deviations from the ideal fcc cation and primitive cubic anion sublattices in the z-Mn_2O_3 are caused by the relaxation of anion and cation positions. Because of the given structural relation and commensurable lattice spacings, we expect coherent or semicoherent interfaces for the combination of YSZ and the rare earth oxides of bixbyite structure. Furthermore, it is reasonable to expect a distinct orientation relationship between both phases.

If the orientation relationship between the rare earth oxide and YSZ layers is known, the nominal misfit at the interface can be calculated. The orientation of the layers is influenced by the substrate due to differences in nucleation rate and growth rate for the variously orientated crystallites. For sapphire as a substrate material with a trigonal R-centred z-corundum structure the structural data are also listed in Table 1.

2.2 Conductivity properties of the different phases

Stabilised zirconia is an extrinsic oxygen ion conductor. Its transport properties have already well been characterised (see for example ref. 18–20). The electronic transference number is negligible for ambient oxygen partial pressures.

Scandium oxide can be regarded as an electric insulator. Measurements of the total conductivity revealed it to be in the order of 10^{-7} S/cm at 750 °C. The major charge carriers under ambient oxygen partial pressures are p-type electronic defects.

3. Experimental

3.1 Sample preparation

We prepared multilayers of the type

Al_2O_3/Sc_2O_3/(YSZ/Sc_2O_3) × n

with a thickness d of the individual layers (measured for the ion-conducting YSZ phase) between ca. 8 nm (n = 100) and 250 nm (n = 5). The thickness of the Sc_2O_3 layers is similar to that of the YSZ layers. Details for every prepared sample are listed in Table 2.

Polished single crystalline sapphire substrates with a (0001) surface orientation were purchased from CrysTec GmbH. The size of the substrates was (10 × 10) mm^2.

The polycrystalline, sintered targets of YSZ were supplied by HTM Reetz GmbH. Targets of Sc_2O_3 were prepared from Sc_2O_3 powder by ball milling, pressing and sintering for 48 h at 1400 °C in air. 99.99% pure Sc_2O_3 powder was obtained from Chempur Feinchemikalien und Forschungsbedarf GmbH.

The YSZ/Sc_2O_3 multilayer specimens were prepared by pulsed laser deposition (PLD). During the deposition, the temperature of the sapphire substrates was kept at 1073 K (800 °C) while the background pressure of oxygen in the deposition chamber was adjusted to 6 × 10^{-2} mbar. For the ablation, an excimer laser was used (Lambda-Physik).

Table 2 List of the investigated multilayer samples. d is the thickness of the YSZ layers, d_{tot} is the mean total thickness of the multilayer.

<table>
<thead>
<tr>
<th>n</th>
<th>d [nm]</th>
<th>d_{tot} [nm]</th>
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<td>270</td>
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<td>5</td>
<td>252</td>
<td>2165</td>
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<td>150</td>
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Samples deposited with 2 Hz, 99 h annealed

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of the (0006) Al₂O₃ peak originating from the sapphire were typically taken from 20° and after annealing for 48 h, respectively 99 h. Measurements of the crystal structure of the samples directly after preparation and after annealing for 48 h, respectively 99 h. Measurements were typically taken from 20° to 90° (2θ) with a step width of 0.03° and an integration time of 2 s per step. The range between 41.5° and 42.5° was omitted due to the high intensity of the (0006) Al₂O₃ peak originating from the sapphire substrate.

With the same setup, rocking curves were recorded. X-ray source, sample and detector were aligned so that the reflection conditions were fulfilled for the YSZ (111) or the Sc₂O₃ (222) signal. Then the sample was tilted from \( \omega = -10° \) to \( \omega = +10° \) and the intensity was recorded.

For extended characterisation, pole figures were recorded from \( \psi = 0° \) to \( \psi = +80° \) and from \( \phi = 0° \) to \( \phi = 360° \) (Bruker D8 Discover, Cu-K\(_{α}\) radiation).

### 3.2 Structural characterisation by XRD

X-ray diffraction (SIEMENS Kristalloflex D500, Bragg Brentano, Cu-K\(_{α}\) radiation) was used to characterise the crystal structure of the samples directly after preparation and after annealing for 48 h, respectively 99 h. Measurements were typically taken from 20° to 90° (2θ) with a step width of 0.03° and an integration time of 2 s per step. The range between 41.5° and 42.5° was omitted due to the high intensity of the (0006) Al₂O₃ peak originating from the sapphire substrate.

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### 3.3 Microstructural characterisation by HRSEM/(HR)TEM/SAED and EELs

The structure, microstructure and chemistry of the samples were investigated by scanning electron microscopy (LEO Gemini 982, HRSEM) and by transmission electron microscopy (Philips CM20T, JEOL 4010 and an aberration-corrected FEI Titan 80-300).

HRSEM was used to determine the thickness of the individual layers in the multilayer samples. For this purpose, the samples were cross-sectioned and polished. The final polish was improved by the use of an Ar\(^+\) ion polishing system (Leica Microsystems/BALTeC RES 101). Micrographs were recorded in secondary electron (SE) and backscattered electron (BSE) mode at 10 kV accelerating voltage.

For (HR)TEM and SAED, the samples were first mechanically thinned and then processed with an ion beam down to electron transparency (grinding and dimple grinding, Ar\(^+\) ion thinning). To remove damaged surface layers (amorphous material), the samples were additionally cleaned by Ar\(^+\) ion milling at low energies (Linda Techoorg Ltd. Co., Budapest, Hungary).

High resolution images were recorded with an accelerating voltage of 400 kV (Jeol 4010), respectively 300 kV (FEI Titan 80-300).

Quantitative electron energy-loss spectroscopy (EELS) measurements (FEI Titan 80-300) were performed to determine the local composition of the samples. By quantitative energy-dispersive X-ray spectroscopy (EDXS), the stoichiometry of the individual materials was verified within the detection limits of the applied method. The microscope was operated in the scanning TEM (STEM) mode with a probe size smaller than 5 Å. A high-resolution post-column energy filter from Gatan GmbH (Germany) was used. Analytical line scans (step size 0.5–1 nm) were performed across the interfaces of the multilayers. To observe element-specific ionisation edges of all elements simultaneously within a single spectrum of each line scan the dispersion was set to 0.5 eV/channel. The element-specific net intensities of the O–K (532 eV), Y–M\(_{4,5}\) (160 eV), Zr–M\(_{4,5}\) (180 eV) and Sc–L\(_{2,3}\) (395 eV) ionisation edges (energy range in spectra 110–1100 eV) were quantitatively evaluated using theoretical ionisation cross-sections (for more details see also ref. 23 and references therein).

### 3.4 Electrochemical measurements

To determine the total conductivity of the samples, AC impedance measurements were performed (PARSTAT Model 2273 potentiostat/galvanostat, Princeton Applied Research) under environmental pressure (air) in a temperature interval from 420°C to 780°C. A type S thermocouple close to the sample was used for the temperature measurements. The frequency range for the AC measurements was 1 MHz–1 Hz. DC measurements were performed with the same setup for comparison.

The samples were prepared for the electrochemical measurements by cutting stripes of about 8 mm length and 2 mm width and polishing the lateral surfaces down to a roughness of 9 micrometres. Silver paste was applied to the lateral surfaces and sintered for 10 h at 800°C in air. Afterwards, the sample was clamped between two silver net electrodes in a ceramic sample holder equipped with shielded platinum feed lines, which was placed in a high temperature furnace. Thus, the conductivity was measured parallel to the layers.

### 4. Results

#### 4.1 X-Ray diffraction

The high signal-to-noise ratio in the X-ray diffraction patterns of all samples (apart from two exceptions which were of lower quality: \( n = 5 \) and \( n = 100 \), \( d = 16 \) nm, deposited at 10 Hz) indicates that the layers were crystalline directly after deposition. In addition, the measurements clearly show a strong texture within the multilayers. A well-defined axial orientation relationship between YSZ and Sc₂O₃ was observed. Annealing the samples for 48 h at 800°C in air led to narrowing and higher intensities of the XRD signals, but not to a change in the preferred orientation of each sample. These findings apply to samples deposited at 10 Hz as well as to those deposited at 2 Hz. Fig. 1 contains normalised diffractograms (θ-2θ measurements) of all specimens with differing numbers of layers and for various thicknesses of the individual layers.

The mean (out of plane) lattice spacings of both YSZ and Sc₂O₃ after annealing were calculated by determining the exact peak positions of the (111) YSZ and (222) Sc₂O₃ reflections in the X-ray diffractograms and comparing them to literature values (see Table 1). We found that the lattice parameter of YSZ is dilated at an average of about 0.8% after heat treatment for 10 Hz pulse frequency and \( ca. \) 0.6% for a pulse frequency of 2 Hz. The Sc₂O₃ layers were also slightly dilated: the mean dilation was \( ca. \) 0.5% for samples deposited at 10 Hz and \( ca. \) 0.1% for those deposited at 2 Hz.
In the \(\theta-2\theta\) XRD measurements, the (111) YSZ and respectively the (222) Sc\(_2\)O\(_3\) reflection dominates for both phases. The preferred axial orientation relationship is thus:

\[
(0001) \text{Al}_2\text{O}_3 \parallel (111) \text{Sc}_2\text{O}_3 \parallel (111) \text{YSZ}
\]

Only two samples \((n = 5, d \approx 250 \text{ nm and } n = 100, d = 16 \text{ nm})\), both deposited at 10 Hz, show larger contributions of alternative orientations, namely

\[
(0001) \text{Al}_2\text{O}_3 \parallel (100) \text{Sc}_2\text{O}_3 \parallel (100) \text{YSZ}
\]

\[
(0001) \text{Al}_2\text{O}_3 \parallel (311) \text{Sc}_2\text{O}_3 \parallel (311) \text{YSZ}
\]

\[
(0001) \text{Al}_2\text{O}_3 \parallel (110) \text{Sc}_2\text{O}_3 \parallel (110) \text{YSZ}
\]

The signal intensity in the XRD patterns of these two samples was low, despite the fact that the total layer thickness was comparable to other samples. This indicates a much higher misorientation of these multilayers.

\(\theta-2\theta\) XRD measurements of samples deposited at 2 Hz (Fig. 1(b)) were similar to the measurements from samples deposited at 10 Hz. Only small contributions of alternative axial orientations were found in two samples.

For samples with \(d\) below 20 nm, shoulders are visible at the YSZ (111) and the Sc\(_2\)O\(_3\) (222) peak. For the sample with \(n = 100, d = 8 \text{ nm}\), a clear splitting of the peaks occurs. This is caused by a convolution with superlattice peaks, which appear when the superlattice period (one double layer YSZ/Sc\(_2\)O\(_3\)) gets sufficiently small to be resolved in the XRD pattern.

### 4.2 Texture analysis

Rocking curves of the (111) reflection of YSZ and the (222) reflection of Sc\(_2\)O\(_3\), respectively, reveal the degree of tilt misorientation present in the samples (see Fig. 2). For the YSZ signal in a sample with about 80 nm thick individual layers, a FWHM (full width at half maximum)-value of 1.93° was found, corresponding to a minor tilt misorientation. A sample with thin individual layers (about 16 nm) showed a broad YSZ signal with a FWHM-value of 14.69°. The FWHM values of the Sc\(_2\)O\(_3\) signals were similar to those of YSZ.
4.3 Microstructural characterisation by HRSEM, (HR)TEM/SAED

The thickness of the individual layers in all samples was measured by HRSEM on cross sections. In samples with very thin individual layers, the thickness was also determined by TEM measurements.

The columnar structure of the multilayer samples was visualised by bright-field TEM. In Fig. 4, a cross section of a sample with \( n = 100, d \approx 8 \text{ nm} \) and a deposition rate of 10 Hz is shown. For this sample, a columnar grain structure is found with individual columns being ca. 40–60 nm wide, extending through several individual layers or even through the whole multilayer. The columnar structure is characteristic for all samples. In samples deposited at 2 Hz, the columns are more uniform and the mean column size is larger (ca. 80–100 nm) than in the samples deposited at 10 Hz (see Fig. 4(d) for an example). The columnar structure of a sample deposited at 2 Hz is visible in Fig. 4(d).

Near the substrate, the individual layers are completely flat. With increasing distance to the substrate, a slightly wavy morphology develops, especially in samples with thin layers. This effect is stronger in samples deposited at 2 Hz. A comparison of the layer morphology near the substrate and at some distance is shown in Fig. 4(d) and (e).

Details on the local microstructure are obtained by high-resolution (HR)TEM. In the following, HRTEM investigations of a multilayer sample deposited at 2 Hz and with 50 YSZ and 50 Sc\(_2\)O\(_3\) layers (\( n = 50 \)) and of a sample with \( n = 150 \), deposited at 10 Hz, are shown as examples. As all samples deposited at the same pulse frequency were treated in exactly the same way, the findings for these two samples can be regarded as representative for all prepared multilayers.

The interfaces between YSZ and Sc\(_2\)O\(_3\) are well ordered and sharp. No additional phase between the individual layers is found. The closed packed lattice planes in both phases are interconnected 1:1 without any disordered regions. This was also observed for the system YSZ/Y\(_2\)O\(_3\). In contrast to the system YSZ/Y\(_2\)O\(_3\), the interface between the sapphire substrate and the first Sc\(_2\)O\(_3\) layer does not contain any visible transition region.

4.3.1 Orientation relationships. Selected-area electron diffraction (SAED) confirms the results obtained by XRD. The clear reflections in the SAED prove the well-developed crystallinity of the investigated multilayers. For the multilayer sample shown in Fig. 4(a), the associated SAED pattern is shown in Fig. 4(b). It was recorded from an area approximately 15 YSZ/Sc\(_2\)O\(_3\) double layers wide. It can easily be seen from the positions of the (111) YSZ reflections that the [111] direction is perpendicular to the layers, indicating that the crystallites in the layers are orientated accordingly. In this SAED pattern, reflections of two azimuthal orientation variants are superimposed. They can be identified as:

1) \([1\overline{1}0] \text{Sc}_2\text{O}_3\|[1\overline{1}0] \text{YSZ}\||\overline{B}\)

2) \([112] \text{Sc}_2\text{O}_3\|[112] \text{YSZ}\||\overline{B}\)

Fig. 3 (a), (b) Pole figure for the YSZ (220) and Sc\(_2\)O\(_3\) (440) reflections of the sample with \( n = 50, d = 34 \text{ nm}, 2 \text{ Hz} \). (a) shows the pole figure for the YSZ (220) reflections, (b) for the Sc\(_2\)O\(_3\) (440) reflections.

Pole figure measurements agree with the results from XRD by indicating the orientation along the [111] direction as the preferred one for both phases in the multilayers.

The pole figures depicted in Fig. 3(a) and (b) show the signal intensities for the (220) and (440) reflections, obtained from a sample deposited at 2 Hz and 50 individual layers for each phase, being ca. 34 nm thick. Broadened maxima are visible at six positions of the azimuthal (in-plane) angle \( \phi \) with the tilt angle \( \Psi \) being ca. 35°. The \( \phi \) angles of the six maxima in the pole figures are the same for both YSZ and Sc\(_2\)O\(_3\). This indicates firstly that there is also a preference present for the azimuthal orientation of the crystallites in the YSZ as well as in the Sc\(_2\)O\(_3\) layers and secondly that this preference is the same for both phases. According to the symmetry of the (110) YSZ and (220) Sc\(_2\)O\(_3\) planes, the six maxima represent two variants for the azimuthal orientation:

\([1\overline{1}0] \text{Sc}_2\text{O}_3\|[1\overline{1}0] \text{YSZ}\)

The second variant is rotated by 60° to the first one. This is the same as a mirror inversion.

From the pole figure measurements alone, it is in principle possible that a third variant (and its mirror image) exists:

\([1\overline{1}0] \text{Sc}_2\text{O}_3\|[1\overline{1}0] \text{YSZ}\)

\(\overline{B}\)
All (hkl) indices in the SAED refer to the YSZ. The vector $\vec{B}$ is the direction of the electron beam.

Another feature is also visible in the SAED pattern in Fig. 4(b): the corresponding reflections for YSZ and Sc$_2$O$_3$ (not indexed) are found at identical angular positions. At the peak positions labelled (222) and (222), the (444) and (444) peaks of Sc$_2$O$_3$ are clearly discernible from the YSZ peaks. This shows that the axial as well as the azimuthal orientation variants present are identical for the YSZ and Sc$_2$O$_3$ crystallites.

A more detailed insight into the local microstructure can be gained by Fast Fourier transformation (FFT) of selected areas.
in high resolution TEM images. An example is shown in Fig. 5(a). Regarding the preferred orientation of the crystallites in the multilayer, the FFT pictures agree well with the XRD and SAED measurements. The reflections of the (111) YSZ and (222) Sc$_2$O$_3$ lattice planes as well show that the [111] direction is perpendicular to the layers and parallel to the [0001] direction in the substrate. Concerning the azimuthal orientation within the YSZ and Sc$_2$O$_3$ layers, many FFT analyses from different positions in the multilayer samples showed two variants which are rotated by 60° towards each other:

1a) $[\bar{1}10] \text{Sc}_2\text{O}_3 || [\bar{1}10] \text{YSZ} \parallel B$

2a) $[110] \text{Sc}_2\text{O}_3 || [1\bar{1}0] \text{YSZ} \parallel B$

These results agree with the azimuthal orientation relationship between YSZ and Sc$_2$O$_3$ which was derived from the pole
figures. It is important to note that within individual columns, the azimuthal orientation was always the same for both phases. Therefore, the third variant which was possible judging from the pole figures alone could not be verified in the HRTEM images.

A different variant of the azimuthal orientation of the YSZ and Sc$_2$O$_3$ crystallites, which was found more rarely in HRTEM micrographs, was:

$$2) [112] \text{Sc}_2\text{O}_3/[112] \text{YSZ}/\bar{B}$$

This variant is also visible in the SAED pattern in Fig. 4(b).

A SAED pattern from a region including the substrate and the first 3–4 layers is shown in Fig. 4(c). It is obtained from the multilayer sample with $n = 150$, $d \approx 11$ nm and a deposition rate of 10 Hz. Due to the overlap it is possible to obtain the azimuthal orientation relationship between the substrate and the layers. An analysis of the reflections shows it to be:

$$[1\bar{1}00] \text{Al}_2\text{O}_3/[1\bar{1}0] \text{Sc}_2\text{O}_3/[1\bar{1}0] \text{YSZ}/\bar{B}$$

The FFTs in Fig. 5(a) reveal a different variant for the azimuthal orientation relationship between the substrate and the layers:

$$[1000] \text{Al}_2\text{O}_3/[1\bar{1}0] \text{Sc}_2\text{O}_3/[1\bar{1}0] \text{YSZ}/\bar{B}$$

However, this variant was rarely found.

### 4.3.2 Dislocation density

In the sample deposited at 2 Hz with $n = 50$ YSZ layers, a high density of dislocations was found by FFT filtering and also in unfiltered micrographs. In the HRTEM micrographs of the sample deposited at 10 Hz ($n = 150$), the dislocation density was much lower. Two different types of dislocations are present: the first type with Burgers vectors having components parallel to the interface, the second type with Burgers vectors perpendicular to the interfaces (see Fig. 5(b) and (c), the dislocations are marked by dashed circles.). Especially dislocations of the first type were not restricted to the interface, but also often found in the layer volume or at the grain boundaries. Strain contrast is visible in the HRTEM images in regions with high dislocation densities. Rarely, the dislocations are arranged in ordered arrays with almost equal distances between individual dislocations. Fig. 5(c) shows an example of an ordered dislocation array at an interface near the substrate. No such array was found at interfaces farther from the substrate. Frequently, dislocations of the first type, appearing to have antiparallel Burgers vectors, were situated directly next to each other in FFT filtered micrographs.

In contrast to the interfaces between YSZ and Sc$_2$O$_3$, quite regular arrays of dislocations were found at the interface between the sapphire substrate and the first Sc$_2$O$_3$ layer. This can be seen in a FFT-filtered HRTEM micrograph of the sample with $n = 150$, deposited at 10 Hz, in Fig. 5(d). The dislocations are separated by a mean distance of about four (1123) planes in Al$_2$O$_3$ and about 3 (002) (left crystallite), respectively (222) (right crystallite) planes in Sc$_2$O$_3$.

### 4.3.3 Interdiffusion

Quantitative EELS measurements from the sample with $n = 50$, deposited at 2 Hz, revealed a relatively sharp chemical separation of the individual layers after heat treatment. This result is considered as representative for all YSZ:Sc$_2$O$_3$ multilayer samples. Fig. 6 shows the quantified composition across an YSZ layer in the investigated sample after 99 h annealing at 800 °C in air. The line scan over a distance of 50 nm was performed in a region near the substrate. The width of the boundary region estimated from this line scan is about 1.5 nm. Similar results were obtained from measurements on the sample with $n = 150$, deposited at 10 Hz. This means that interdiffusion or segregation can be excluded at temperatures up to 800 °C. It can be assumed that the interfaces between Sc$_2$O$_3$ and YSZ are narrower than the measured boundary regions in Fig. 6. A part of the broadening may arise from slightly tilted interfaces in the TEM sample.

### 4.4 Electrical conductivity

Impedance measurements of the multilayer samples between 420 °C and 780 °C resulted in one semicircle in the Nyquist plot (Fig. 7). From the x-axis intercept of the semicircle, the sample resistance $R$ and thus the conductivity $\sigma$ was determined. Sample resistances determined from DC measurements were comparable to the AC results. To calculate the conductivity of the multilayers, only the YSZ layers and their geometry were taken into account. The following equation was used:

$$\sigma = \frac{b}{R \cdot l \cdot n \cdot d}$$

where $l$ is the width of the multilayer samples, $d$ the thickness of the YSZ layers, $n$ the number of the YSZ layers and $b$ the distance between the electrodes. $\sigma$ therefore actually corresponds to the conductivity of the YSZ phase and includes the bulk as well as the grain boundary contribution since these could not be separated in the impedance plot.

The conductivity of an uncoated sapphire substrate, measured by impedance spectroscopy with the same electrode setup as described for the multilayer samples, was five orders of magnitude lower than the conductivities of the multilayers. A sample coated with a single layer of Sc$_2$O$_3$ revealed a two orders of magnitude lower conductivity (calculated for the Sc$_2$O$_3$ layer). This proves that those phases can indeed be neglected for the total sample conductivity.

![Fig. 6 Quantified EELS line scan of the multilayer sample with $n = 50, 2$ Hz. The sample was annealed at 800 °C for 99 h in air. The phase boundary was found to be relatively sharp.](image-url)
Compared to polycrystalline bulk YSZ samples, the conductivity of the YSZ phase in the thin film multilayers is decreased. Park and Blumenthal determined a conductivity of 3.14 $\times$ $10^{-3}$ S/cm at 800 °C for a sintered polycrystalline sample of 8 mol% YSZ. The values obtained for the YSZ phase in the multilayers investigated in this study are typically in the range of $10^{-4}$ S/cm, which is comparable to earlier studies by Peters et al.

As can be seen in Fig. 8, the total conductivity of the multilayers decreases clearly with decreasing thickness $d$ of the individual YSZ layers, respectively with an increasing density of YSZ|Sc$_2$O$_3$ interfaces. This was observed for samples deposited at 10 Hz as well as for those deposited at 2 Hz, but the decrease was steeper for samples deposited at 2 Hz. The error bars in Fig. 8 were calculated from the uncertainty of $d$, estimated from HRSEM and TEM measurements at different sample positions, the accuracy measuring the sample dimension and from uncertainties of the resistance, estimated from the scatter in the impedance plots. Linear fitting of the experimental data results in an $y$-axis intercept of 8.15 $\times$ $10^{-4}$ S/cm and a slope of $-4.98 \times 10^{-10}$ S for the samples deposited at 10 Hz. For the samples deposited at 2 Hz, an $y$-axis intercept of 6.02 $\times$ $10^{-4}$ S/cm and a slope of $-6.25 \times 10^{-10}$ S was obtained. As was discussed in ref. 8, $\sigma_{\text{tot}}$ can be expressed by:

$$\sigma_{\text{tot}} = \sigma_{\text{vol}} + 2\delta(\sigma_{\text{int}} - \sigma_{\text{vol}}) \cdot \frac{1}{d}$$

According to this relation, the $y$-axis intercept corresponds to the bulk conductivity $\sigma_{\text{vol}}$ of the multilayers, which includes the grain boundary contribution. The bulk conductivity derived by the linear fit and the conductivities for the individual samples were lower for multilayers deposited at 2 Hz.

From the slope of the linear fit, which corresponds to $2\delta(\sigma_{\text{int}} - \sigma_{\text{vol}})$, the interfacial conductance $\delta(\sigma_{\text{int}} - \sigma_{\text{vol}})$ relative to the bulk conductivity ($y$-axis intercept) can be calculated. $\delta$ is the width of the strained interface regions. The value of $\delta$ can only be estimated since we did not measure the strain in the multilayers locally and only average values were obtained by X-ray diffraction. If we assume $\delta$ to be 10 nm, an interface conductivity of $\sigma_{\text{int}} = 3.42 \times 10^{-4}$ S/cm is calculated for samples deposited at 10 Hz. For samples deposited at 2 Hz, the calculation of $\sigma_{\text{vol}}$ for $\delta$ equal to 10 nm yields a negative value, indicating that the extent of the interface region may be larger.

From temperature dependent measurements, the activation energy for transport in the multilayers was determined. Examples for the obtained Arrhenius plots are shown in Fig. 9. For the error bars the accuracy of the temperature measurement was estimated to be $\pm 3$ K. A tendency to higher activation energies with decreasing thickness $d$ of the individual layers was found, but it was not strictly fulfilled by all samples. For samples deposited at 10 Hz, the lowest activation energy was 1.09 eV, measured for a sample with $n = 20$, $d = 43$ nm and the highest energy was 1.27 eV, measured for a sample with $n = 100$ and $d = 16$ nm. In Fig. 9, the results for four samples deposited at 10 Hz are shown as example. For the samples deposited at 2 Hz, the lowest activation energy was 1.10 eV, measured for a sample with $n = 30$ and...
5. Discussion

5.1 Orientation relationships and misfit

The preferred axial orientation relationship was confirmed by XRD, pole figure measurements, (HR)TEM and SAED investigations:

\[(0001) \text{Al}_2\text{O}_3 \|[111] \text{Sc}_2\text{O}_3 \|[111] \text{YSZ}\]

The two preferred, mirror inverted azimuthal orientations indicated by the pole figures can be linked to the SAED patterns and to the FFT analyses of the HRTEM micrographs (an example is shown in Fig. 5). As mentioned above, for the majority of the crystallites which could be analysed by FFT, one of the two mirror inverted variants (1a) and (1b) was found. The SAED pattern in Fig. 4(c) reveals the orientation relationship which was most often found between the substrate and the first layers. We assume that this orientation relationship is similar for all samples, so that the two mirror inverted variants of the azimuthal rotation found in the pole figures can be fully identified as:

1a) \([1\bar{1}00] \text{Al}_2\text{O}_3 \|[1\bar{1}0] \text{Sc}_2\text{O}_3 \|[1\bar{1}0] \text{YSZ}\]

1b) \([1\bar{1}00] \text{Al}_2\text{O}_3 \|[\bar{1}1\bar{0}] \text{Sc}_2\text{O}_3 \|[\bar{1}1\bar{0}] \text{YSZ}\]

Other azimuthal variants, found for example by comparing the FFTs in Fig. 5(a) and in the SAED in Fig. 4(b), could not be related to maxima in the pole figures. This indicates that these azimuthal variants are more rare.

Regardless of the orientation variant, the azimuthal orientation of the crystallites within one column in subsequent layers is always the same.

Considering the found orientation relationship, we can calculate the nominal misfit \(f\). In YSZ and \(\text{Sc}_2\text{O}_3\), the lattice planes \((\bar{1}1\bar{0})\) YSZ, \((112)\) YSZ, \((220)\) \(\text{Sc}_2\text{O}_3\) and \((224)\) \(\text{Sc}_2\text{O}_3\) are perpendicular to the interface plane. The lattice spacings \(d(\text{YSZ}(1\bar{1}\bar{0}))\) and \(d(\text{Sc}_2\text{O}_3(224))\) are equal to 3/2 of the interatomic spacings of close packed planes of oxygen anions in the interface plane. Assuming a 1:1 match between close packed planes of oxygen anions and scandium cations for the found azimuthal orientation, the nominal misfit \(f_{\text{YSZ}/\text{Sc}_2\text{O}_3}\) yields as:

\[
f_{\text{YSZ}/\text{Sc}_2\text{O}_3} = \frac{d(\text{Sc}_2\text{O}_3(224)) - d(\text{YSZ}(1\bar{1}\bar{0}))}{d(\text{YSZ}(1\bar{1}\bar{0}))}, \text{100\%}
\]

\[
f_{\text{YSZ}/\text{Sc}_2\text{O}_3} = -4.28\%
\]

The calculated misfit is negative because the lattice spacing of \(\text{Sc}_2\text{O}_3\) is somewhat smaller than that of YSZ. This results in a compressive strain in YSZ near the interfaces and a tensile strain in \(\text{Sc}_2\text{O}_3\).

The misfit between the \((0001)\) Al\(_2\)O\(_3\) substrate and the first \(\text{Sc}_2\text{O}_3\) layer is expected to be high due to the differences in crystallographic structure. The best match is realised with the \((111)\) \(\text{Sc}_2\text{O}_3\) planes, because these planes have a threefold symmetry which coincides with the threefold symmetry of the \((0001)\) Al\(_2\)O\(_3\) plane (see Fig. 10):

\[(0001) \text{Al}_2\text{O}_3 \|[111] \text{Sc}_2\text{O}_3\]

This gives an explanation for the experimentally found axial orientation relationship between the substrate and the first \(\text{Sc}_2\text{O}_3\) layer.

In case of a \((0001)\) oriented \(\text{Al}_2\text{O}_3\) substrate, the lattice planes perpendicular to the substrate surface are \((1\bar{1}00)\) \(\text{Al}_2\text{O}_3\) and \((1120)\) \(\text{Al}_2\text{O}_3\). The lattice spacing \(d(\text{Al}_2\text{O}_3(1120))\) is equal to the interatomic spacings of close packed planes of oxygen anions in the interface plane. Assuming a 1:1 match between close packed planes of oxygen anions and scandium cations for the found azimuthal orientation, the nominal misfit \(f_{\text{Sc}_2\text{O}_3/\text{Al}_2\text{O}_3}\) yields as:

\[
f_{\text{Sc}_2\text{O}_3/\text{Al}_2\text{O}_3} = \frac{d(\text{Al}_2\text{O}_3(1\bar{1}2\bar{0})) - \frac{2}{3}d(\text{Sc}_2\text{O}_3(224))}{\frac{2}{3}d(\text{Sc}_2\text{O}_3(224))}, \text{100\%}
\]

\[
f_{\text{Sc}_2\text{O}_3/\text{Al}_2\text{O}_3} = 18.3\%
\]

If we assume a 4:3 match (as has been found earlier for the system YSZ/\(\text{Y}_2\text{O}_3\)) and is indicated by the distance of the dislocations in the \(\text{Al}_2\text{O}_3/\text{Sc}_2\text{O}_3\) interface visible in Fig. 5(c), the nominal misfit reduces to 5.13%.

5.2 Texture analysis

The pole figures in Fig. 3 confirm the well developed texture of the samples and the favoured orientation of both phases along the \((111)\) axis.

The rocking curves obtained for two different samples provide information on the tilt misorientation of the individual layers. The FWHM values show that the tilt misorientation of the
crystallites in the sample with thinner individual layers is much greater (ca. 14.7°) compared to the sample with thick layers (ca. 1.9°). Comparing this result with findings from the TEM micrographs, we conclude that the high misorientation in thinner layers is connected to the increasing undulation of those layers with increasing distance to the substrate. The origin of the undulations may be irregularities developed during the PLD preparation, e.g., an island-like growth process most effective in thin layers. The effects sum up when more and more layers are stacked. An alternative interpretation of the wavy morphology is that it is caused by the misfit strain between the layers. Jin-Phillipp and Sata found similar undulations in CaF$_2$/BaF$_2$ multilayers. They interpreted the development of this wavy structure as a mechanism of stress release between the two phases. As an extreme case of this wavy structure, they reported a columnar structure with discontinuous, 1 nm individual thick layers.

5.3 Dislocation density

The relatively large misfit of 5.13% between the Al$_2$O$_3$ substrate and the first Sc$_2$O$_3$ layer is not expected to be compensated by strain only. Instead, a high defect density is anticipated in the interface. A disordered transition region was not found in the HRTEM measurements as it was the case for YSZ/Y$_2$O$_3$ multilayers. Instead, a regular network of dislocations is formed, as can be seen in Fig. 5(c).

At the interfaces between YSZ and Sc$_2$O$_3$, two different types of dislocations were found: the first type having Burgers vectors with components parallel to the layers, the second type with Burgers vectors perpendicular to the layers. Dislocations of the first type were seldom found in regular arrays. The example shown in Fig. 5(c) therefore illustrates a rare case. In most cases, dislocations of the first type were found in strained regions inside the layers and often in seemingly antiparallel arrangements. Their density is not uniform in different crystallites, but seems to be much higher in small columns. Because of the often found antiparallel arrangement, the net effect of these dislocation pairs on the strain release between the layers is presumably small. It is also possible that antiparallel dislocations in FFT-filtered HRTEM micrographs are an artefact of the filtering. Because of a limited number of HRTEM measurements, we can not exclude this for sure. The dislocations of the second type do not contribute at all to a reduction of the misfit strain parallel to the layers.

Jin-Phillipp et al. also reported on dislocations having Burgers vectors perpendicular to the layers in BaF$_2$/CaF$_2$ heterostructures. As origin of these dislocations, the wavy morphology of the layers at the substrate from some distance in the substrate is discussed. Thus, dislocations of the second type release the additional strain perpendicular to the layers which is caused by this morphology. This is supported by the fact that near the substrate where the layers are flat, we only found very few dislocations of the second type. Based on the assumptions of Jin-Phillipp et al., indeed the development of the wavy layer morphology can be identified as a mechanism for the release of misfit strain. This is consistent with the observation that in samples deposited at 2 Hz the wavy morphology is even more pronounced.

An important effect of the release of misfit strain and the density of dislocations is caused by the grain boundaries. On the one hand, they impede the motion of dislocations through the sample during annealing. On the other hand, dislocations and other structural defects are accumulated in the grain boundaries. A part of the strain present in the multilayers will be released by this defect accumulation.

5.4 Influence on ionic conduction

Two structural parameters are expected to influence the ionic transport in the interfaces between YSZ and the rare earth oxide: the lattice strain and the dislocations. Dislocations may act as fast transport paths and enhance the ionic conductivity. Lattice strain may either enhance or hinder transport, depending on whether it is tensile or compressive, respectively. A detailed theoretical treatment on the effect of strain on the ionic conductivity in multilayers has already been presented in. As the free enthalpy of migration $\Delta G^M$ of oxygen vacancies depends on pressure $p$, also the ionic conductivity $\sigma_\text{O}^-$ should be pressure dependent. Using a hopping model, the (bulk) ionic conductivity for an extrinsic oxygen ion conductor follows as:

$$\sigma_\text{O}^- = \frac{(2F)^2}{RT} \frac{c_0}{V} \beta \nu d_V \omega_{\text{O},V} \exp \left( \frac{-\Delta G^M}{RT} \right)$$

(5)

The jump distance of the vacancy is denoted with $d_V$ and its geometry factor with $\beta$. The prefactor $\omega_{\text{O},V}$ depends on the vibration frequency of the regular lattice atoms. The change of the ionic conductivity with pressure is described by the migration volume $\Delta V^M$ (volume of activation) for a vacancy jump:

$$\left( \frac{\partial \ln \sigma_\text{O}^-/\sigma_{\text{O},0}^-}{\partial p} \right)_T = -\frac{\Delta V^M}{RT}$$

(6)

For simplification all factors on the left side of the exponential expression in eqn (5) are assumed as (nearly) pressure independent and subsumed as $\sigma_{\text{O},0}^-$. For a vacancy mechanism $\Delta V^M$ is always positive, i.e., the surrounding lattice will be expanded in the transition state. In the case of YSZ/Sc$_2$O$_3$ multilayers, the YSZ phase is compressively strained near the interfaces due to the negative misfit between the layers ($\nu > 0$). Thus, the total conductivity of the multilayers should decrease with increasing interface (phase boundary) density, which is indeed observed for the investigated multilayer samples. As long as a linear dependence is observed between interface density and total conductivity one can assume that the conductivity of the bulk (plus grain boundaries) and the conductivity of the strained interface regions close to the phase boundaries is still independent on the layer thickness. For samples deposited at 2 Hz, the conductivity effect is somewhat stronger. This can be explained by the larger mean grain size in these multilayers and the therefore lower density of grain boundaries in the system. As part of the strain is presumably released at the grain boundaries, the net strain is larger in samples deposited at 2 Hz. However, due to the small number of investigated samples which were deposited at 2 Hz, the values obtained by linear fitting of the data should be treated as a coarse estimation.
Comparing the present results to the system YSZ/\textit{Y}_2\textit{O}_3, where tensile strain is acting in the YSZ phase ($\rho < 0$) and accordingly an increase in conductivity is found with increasing interface density, we find that our theoretical considerations on the influence of strain on conductivity are proven to be right. As the two systems are very similar with regard to the material properties, especially the charge carrier density, we can rule out space charges to be of major relevance for the observed phenomena. Also, the dislocation density in both systems is similar, so that we can also assume that dislocations do not play a significant role for ionic conductivity in the investigated multilayers. The observed change in conductivity in the investigated YSZ/Sc$_2$O$_3$ multilayer system can therefore be explained in terms of elastic strain in the YSZ phase and the increase in the free enthalpy of migration with increasing compressive strain (increasing local pressure), which was expected from the pressure dependence of the ionic conductivity.

It is important to note that the actual, local strain at the interfaces was not determined within this work. XRD delivered mean results for the whole multilayer, showing that an out of plane dilation is present in all samples (as observed before by Peters \textit{et al.}[$^8$]). This should correspond to an in plane compression of all layers. There are several contributions to the total strain state of the multilayers: thermal strain and microstrain generated during the crystallisation process. The misfit strain is superimposed to these strains. The thermal strain is expected to be small due to similar thermal expansion coefficients of the utilised materials, but further investigations are needed to clarify the role of microstrain. However, since the thermal strain and the microstrain depend on the sample preparation and the subsequent annealing, these contributions should be equal for samples deposited with the same pulse rate and as a first approximation independent from the interface density. The change of the ionic conductivity with increasing interface density can therefore safely be attributed to the misfit contribution.

6. Conclusions

We investigated the influence of structural parameters and especially misfit strain at phase boundaries on ionic conduction thin film systems. Our model systems were geometrically well defined YSZ/Sc$_2$O$_3$ multilayers, prepared by pulsed laser deposition.

Detailed structural characterisation of the polycrystalline samples proved that the interfaces were sharp without disordered regions or segregated phases. A distinct axial orientation relationship was found between the sapphire substrate, Sc$_2$O$_3$ and YSZ:

\[(0001) \text{Al}_2\text{O}_3||(111) \text{Sc}_2\text{O}_3||(111) \text{YSZ}\]

Two mirror inverted azimuthal orientation variants were found. However, within one column of crystallite, only one variant was present for both phases.

Almost no regular dislocation arrays were found at the interfaces. In addition to dislocations having a Burgers vector with components parallel to the layers, dislocations with a Burgers vector perpendicular to the layers were formed as a consequence of a wavy layer morphology. The development of this morphology itself was identified as an important mechanism for the release of misfit strain.

Regarding the conductivity of the YSZ phase in the multilayer samples, a clear decrease with increasing interface density could be observed. The origin of this decrease is the compressive strain acting near the interfaces in YSZ, which agrees with theoretical considerations on the pressure dependence of the ionic conductivity published earlier.[9,14] Dislocations or space charge regions are not considered to contribute to the change in conductivity. Our interpretation of the conductivity properties of the multilayers agrees well with the results of a former investigation on YSZ/\textit{Y}_2\textit{O}_3 multilayers,$^8$ where tensile strain in the YSZ phase led to an increase in conductivity with increasing interface density. The present work together with the work from Peters \textit{et al.} on the system YSZ/\textit{Y}_2\textit{O}_3 and also on the incoherent multilayer system CSZ/\textit{Al}_2\textit{O}_3,$^{26}$ is an important contribution to the understanding of strain and microstructure effects on ionic conductivity.

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