Using the macroscopic scale to predict the nano-scale behavior of YSZ thin films

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In this work, Yttria-stabilized zirconia (YSZ) thin films were deposited using dual reactive magnetron sputtering. By varying the deposition conditions, the film morphology and texture of the thin films are tuned and biaxial alignment is obtained. Studying the crystallographic and microstructural properties of the YSZ thin films, a tilted columnar growth was identified. This tilt is shown to be dependent on the compositional gradient of the sample. The variation of composition within a single YSZ column measured via STEM–EDX is demonstrated to be equal to the macroscopic variation on a full YSZ sample when deposited under the same deposition parameters. A simple stress model was developed to predict the tilt of the growing columns. The results indicate that this model not only determines the column bending of the growing film but also confirms that a macroscopic approach is sufficient to determine the compositional gradient in a single column of the YSZ thin films.

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1. Introduction

Due to its many interesting properties, Yttria-stabilized zirconia (YSZ) is a popular material used in several applications such as: buffer layers [1,2], oxygen sensors [3,4], nuclear applications [5] and thermal barriers coatings [6–8]. A typical example is the use of YSZ as electrolyte in solid oxide fuel cells [9–16]. Current studies aim to lower the process temperature of the electrolytes by reducing their thickness. However, a reduction in thickness might change the YSZ properties in comparison to the bulk properties. As a result, the fundamental aspects involved change due to the occurrence of nano-effects.

It is known that the deposition conditions play an important role on the microstructure and the crystallinity of the growing film [17,18], which consequently affects the properties of the film. Therefore, a good understanding of the microstructure and texture would open the possibility to manipulate the film properties by controlling the nanocrystalline microstructure of the thin film. As a first step, an investigation of the thin film morphology (and texture), as a function of both composition and deposition conditions, becomes necessary in order to understand the relationship between elemental composition, deposition conditions and properties.

In this work, YSZ thin films were deposited using reactive unbalanced magnetron sputtering [19–21]. In our previous work [22,23], the thin film morphology (and texture) of YSZ was studied as a function of both composition and target–substrate (T–S) distance. The preferential out-of-plane crystallographic orientation was shown to remain in zone T where the fastest growth direction [200] is dominant [24,25]. At higher Y contents, the addition of yttria in the zirconia lattice generates a strong tilt of the [200] preferential orientation. Pole figures and energy flux analyses yield an agreement with prior results. The deposition geometry was shown to have a great influence on the final tilt of the [200] orientation at low levels of Y. However, a quantitative approach was not developed.

This paper first discusses the grain and columnar tilt, the composition and the geometrical dependence on a macroscopic level, i.e. for the whole size of the sample. Scanning electron microscopy (SEM) cross sections and x-ray diffraction (XRD) pole figures will help us to elucidate this dependence. Then, a quantitative analysis was performed by the combination of annular dark field scanning transmission electron microscopy (ADF–STEM) and energy dispersive X-ray analysis (STEM–EDX), to obtain a quantitative compositional gradient map within a single YSZ column (nanometer scale). Based on these results, a simple stress model predicts the columnar tilt as a function of the gradient of composition along the YSZ samples. The developed model indicates that the nano-scale behavior (formation of the tilt) can be predicted from the macroscopic scale experimental data.

2. Experimental setup

YSZ thin films were deposited both on amorphous glass (76 mm × 22 mm) and on silicon (100) substrates (20 mm × 20 mm, for STEM sample preparation) using dual DC reactive unbalanced magnetron sputtering. Metallic Y and Zr targets were mounted on magnetrons and positioned 45° to the substrate holder in a stainless steel vacuum chamber. The substrate holder was grounded and was neither...
heated nor cooled during the deposition. The reactive deposition is performed with an inlet of oxygen oriented directly to the substrate surface. In this way, completely oxidized and optically transparent thin films can be grown while avoiding target poisoning. The vacuum chamber was pumped via a combination of a turbo-molecular and a rotary pump, reaching a base pressure of $10^{-4}$ Pa. Prior to the beginning of the deposition, experimental conditions were stabilized by protecting the substrate with a shutter. The magnetrons are operated in constant current mode ($I_v = 0.2$ A, $I_{cz} = 0.5$ A), using DC power supplies (Hüttinger Elektronik). A compositional gradient in the YSZ samples was achieved by changing the Y target–substrate ($T$–$S$) distance. Other deposition conditions such as $T_S$, $T$–$S$ distance, deposition time and gas pressure remained constant and equal to 90 mm, 20 min and 0.5 Pa, respectively. Further experimental details can be found in Lamas et al. [22,23].

The composition is determined using the metal ratio of the film, calculated as $Y/(Y + Zr)$ and it was measured using energy-dispersive X-ray spectroscopy analysis (EDX) with a beam current of 208 $\mu$A and an acceleration voltage of 10 kV. The cross section images of these films were obtained via scanning electron microscopy (SEM), spot size 3 and acceleration voltage of 20 kV. Pole figure measurements, using a Sol-X energy dispersive detector, were used to evaluate the crystallinity and the biaxial alignment of the YSZ thin films. The pole angle ($\chi$) varied from 0° to 60° and the azimuthal angle ($\psi$) from 0° to 360°, in steps of 5°. Also, X-ray diffraction (XRD) was performed, using CuKα radiation in Bragg–Brentano configuration with a LynxEye Silicon Strip detector mounted into a D8 discover apparatus (Bruker AXS). The obtained data were converted to a polar plot graph. More information about the use of these plots can be found in Lamas et al. [22].

The electron transparent TEM samples were prepared in cross-section using a FEI Nanolab 200 DualBeam focused ion beam (FIB) instrument. A Pt protection layer was deposited onto the sample surface prior to milling. The total FIB lamella length is approximately 5 $\mu$m. ADF–STEM and STEM–EDX experiments were performed in a FEI Tecnai G2 transmission electron microscope operated at 200 kV, equipped with an energy dispersive X-ray analysis attachment. The EDX data were acquired in a 0–20 keV range and drift compensation was activated through the microscope control software. The elemental map and quantitative compositional results were generated using the Zr K-line (15.770 keV) and the Y K-line (14.958 keV) using the FEI TIA software. The summary of the samples used in this work is given in Table 1.

3. Results and discussion

3.1. Grain and columnar tilt in YSZ films

YSZ thin films with different compositional gradients were obtained by changing the Y $T$–$S$ distance and keeping the other deposition parameters constant. In Fig. 1, five different samples (see Table 1) are represented in a polar graph. This representation shows the transition from [200] to [111] out-of-plane preferential orientation based on XRD measurements in Bragg–Brentano configuration. As shown in our previous work [22], we concluded that this is actually a fictional transition due to the tilting of the columns, which differs depending on the amount of Y in the film, and hence there is no transition of the preferential orientation. When this information is correlated with the results of a pole figure, we can easily identify the grain tilt by considering the tilt of the [200] direction in the (100) plane, i.e., the value of the azimuthal angle in the polar graph.

Samples of Fig. 1 correspond to Y $T$–$S$ distance $= 240$ to $80$ mm with intervals of 40 mm. The corresponding compositions are 12, 17, 24, 29 and 39 at.% Y, respectively, corresponding to the average composition of the YSZ layer, which reflects the composition of the center of the sample. As can be seen in Fig. 1, the sample A at low content of Y has a mainly [200] out-of-plane preferential orientation, meaning that its pole figure will have a main peak in the center of the (100) pole and four peaks at 55° in the (111) pole. As the content of Y increases, the [200] direction tilts. Already for sample A, for instance, a small tilt of 8° of the [200] orientation is present. Samples C and E indicate a further tilt of the [200] direction. In the case of samples G and J, the [200] tilt is strong and almost corresponds to the [111] orientation. Furthermore, the crystals also rotate, which can be observed by the increase in intensity of one [111] peak in the (111) pole. Note that this rotation already starts from pole figure E.

SEM images of these samples are represented in Fig. 2. These images show a change in the columnar tilt. Sample A (240 mm) presents a very well defined zone T microstructure with sharp V facetted columns [25]. As the Y $T$–$S$ distance decreases, the columns tilt more and at very low distances the columns even become curved, as seen in sample G (120 mm) and sample J (80 mm). Nevertheless zone T growth is still present, easily identified by the overgrowth at the bottom of the columns and the V facetted columns [25]. The surface structure can also be explained from the columnar tilt. The crystallite habitus is a squared based pyramid showing the (111) facets, or stated differently a [111] crystal form. At low Y content (sample A) a clear “roof-like” surface structure is noticed which is defined by this crystal. As the crystallites tilt at higher Y contents, a flatter surface structure is noticed, since the surface is defined by the (111) facets which are parallel to the substrate.

It is possible to quantitatively determine the tilt generated in these films. The grain tilt, for example, was obtained via the value of the azimuthal angle, derived from the XRD analysis. The columnar tilt, on the other hand, was obtained via the geometric angle, i.e., the angle seen in the columns of the SEM images (samples A–J, except for sample I). Both vary as a function of the content of Y, the latter determined by a fixed position in the center of the glass substrate for different Y $T$–$S$ distances (240–80 with intervals of 20 mm). The results for these samples are shown in Fig. 3.

The variation of the grain and columnar tilt is equivalent until a certain composition, in this case approximately 20 at.% Y. This equivalence can be understood since the grains are the building blocks of the columns. However, above this value there is a discrepancy in the tilt value, which can be attributed to the 3D growth of the film which cannot be observed by a (2D) SEM image. This conclusion is strongly
supported by the rotation on the [111] peak in the pole figure at contents of Y higher than 20 at.%, as indicated in pole figure Fig. 1b, pole E.

Another contribution for this difference can be related to the error involved in the columnar tilt angles obtained via SEM images. At high concentrations the bending resembles a more curved shape rather than a straight tilt, which increases the error when quantifying the columnar tilt angle.

3.2. Determination of the compositional gradient on a nanometer scale

The dual magnetron configuration induces anisotropy in the flux of material towards the substrate. As demonstrated in the work of Radnóczi et al. [26] and Saraiva et al. [27] for AlInN and Mg(M)O systems, respectively, the deposition strategy will induce a compositional gradient over the constituting crystallites. The quantitative compositional gradient along the columns is obtained via TEM analysis in combination with ADF–STEM and STEM–EDX. Fig. 4a to d shows the color map representation of the STEM–EDX images for Y T–S distances equal to 240, 160, 120 and 90 mm, samples A, E, G and I, respectively. It is possible to distinguish the enrichment of Y on one side of the column. The Y concentration is indicated by the color bar. It is noticeable that when the T–S distance gets smaller, the amount of Y gets higher across the column, i.e. the gradient across the column increases. In order to obtain the composition coordinates on a column, the data

![Fig. 1. a) Representation of the grain tilt on a stereographic projection for 5 samples with different compositions and b) pole figures showing the orientation of the (111) and (100) crystallographic planes. The Y target–substrate distance are: A (240 mm), C (200 mm), E (160 mm), G (120 mm) and J (80 mm). The position of the Y magnetron is indicated on the pole figures.

![Fig. 2. Cross section SEM images of YSZ samples with Y T–S distance varying from 240 to 80 mm in intervals of 40 mm. The microstructure is characteristic for zone T growth. As the Y T–S distance decreases (A–N–J), the columns show a bigger tilt.](image-url)
collected via STEM–EDX is used. Each pixel in this mapping corresponds to a determined content of Y. Fig. 4e to h shows the ADF–STEM images of the investigated area of the four different samples. The V-shaped faceted columns are well defined and correspond to the microstructure exhibited in the SEM images shown above. The deformation of the V-shaped faceted columns, when the content of Y increases and the porosity formed between the columns, can be observed. The darker region beneath the columns is the silicon substrate and the top layer above the columns is the protective layer deposited while preparing the sample via FIB.

Using the information provided by the color map of Fig. 4a to d, two regions with different compositions are distinct along the columns, i.e. one region rich in yttrium and one rich in zirconium. An example of a composition profile in function of the distance within a column for sample A, E, G and I is shown in Fig. 5. Fig. 5a schematically represents how the composition varies within the column. Based on several analyses, it can be concluded that the composition changes over a distance much smaller than the corresponding columnar width. Moreover, these distances agree with the crystal size ($\kappa$) parallel to the substrate. The crystal size ($\kappa$) is the same as the one retrieved for the Debye–Scherrer equation [28–30]. The $\kappa$ is considered to have a symmetric shape since the results via grazing angle XRD [31] (at 1°) gives the same value for the crystal size. Hence, the compositional gradient along a column is considered to be the difference in composition between high ($C_1$) and low content ($C_2$) of yttrium divided by the correspondent average crystal size being equal to 25, 22.7, 12.1 and 11.5 nm for

Fig. 3. The grain tilt, evaluated from the azimuthal angle in pole figures, and the columnar tilt measured from the SEM images, as a function of the composition (at.% Y) measured by SEM–EDX.
samples A, E, G and I, respectively. In summary, the compositional gradient within a column is given by:

$$\frac{\partial C}{\partial x} = \frac{C_1 - C_2}{\kappa_\parallel}$$  

(1)

The analysis based on ADF–STEM and STEM–EDX shows two interesting points. The first point is related to the ratio between the maximum and minimum Y content on a column profile. The average ratio $R = C_1/C_2$ of samples A, E, G and I, repeating the analysis as shown in Fig. 5 for 12 different locations in the column, are $3.048 \pm 0.764$, $3.601 \pm 0.862$, $3.772 \pm 1.803$ and $2.708 \pm 0.511$, respectively. Hence, this ratio between both compositions is approximately 3/1 and seems to be independent of the T–S distance.

The second point is that the difference in composition in one column corresponds with the composition measured by SEM–EDX on the center of the sample, i.e. at the macroscopic level $C_{\text{mac}}$. These two results allow us to rewrite Eq. (1) as follows,

$$\frac{\partial C}{\partial x} = \frac{C_1 - C_2}{\kappa_\parallel} = \frac{C_{\text{mac}}}{\kappa_\parallel}(2(R-1)/R + 1)$$  

(2)

As the ratio seems to be independent of the T–S distance, Eq. (2) shows that the compositional gradient can be retrieved from measurements at the macroscopic level, facilitating the analysis because no TEM sample preparation is needed. As $R$ equals approximately 3/1, a 1:1 relationship between the determination of the compositional gradient at microscopic level (ADF–STEM and STEM–EDX measurements) and at the macroscopic level (SEM–EDX) is expected. This is confirmed in Fig. 6.

3.3. Prediction of the grain and columnar tilt

The model is based on the work of Timoshenko [32] used to predict the bending of a bimetallic thermostat. In the latter, two different metal strips are connected to each other. As the two metals have different thermal expansions, heating will result in the bending of the whole. The curvature radius $r$ in the work of Timoshenko is given by:

$$r = \frac{6(\alpha_1 - \alpha_2)(t_1 - t_2)(1 + m)^2}{w(3(1 + m)^2 + (1 + mn)(m^2 + \frac{1}{mn})}$$  

(3)

with $\alpha_1$ being the thermal coefficient of metals 1 and 2, $(t_1 - t_0)$ the variation of temperature, $w$ the total width of the bimetal strips, $m$ the ratio of the strip thicknesses, and $n$ the ratio between the elastic moduli of both metals. The product $(\alpha_1 - \alpha_2)(t_1 - t_0)$ corresponds to the difference in length $(L_1 - L_2)/L$.

A schematic drawing of the columnar growth is shown in Fig. 7. The Y source is located at the left hand side, while the Zr source is located on the right hand side, meaning that the increase of Y content leads to a tilt of the column towards the Zr side, as indicated in Fig. 7. In this drawing we can identify the compositional profile of each column (determined via STEM–EDX) and a straight line which corresponds to the macroscopic composition (determined via SEM–EDX). In the center of the columns there is a region limited by the crystal size which assembles the entire compositional gradient in the column. $L_2$ defines the region of smaller expansion of the lattice. $L_1$ defines the region of bigger expansion of the lattice due to the insertion of Y$_2$O$_3$ and $L$ is the length with no insertion of yttria. The variable $h$ corresponds to the total thickness of the film.

As stated before, the product in Eq. (3) $(\alpha_1 - \alpha_2)(t_1 - t_0)$ in the model of Timoshenko corresponds to a relative length difference between the two metal stripes $(L_1 - L_2)/L$, which is given, in our case, by the difference in lattice parameter between both sides of the column over the lattice parameter ($a$) of a pure ZrO$_2$. The lattice parameter of YSZ $a(C)$ depends on its composition and it was determined by XRD [23] and follows Vegard’s law [33]. Hence, the relative length difference in the case of YSZ can be written as follows.

$$\frac{L_1-L_2}{L} = \frac{a(C_1) - a(C_2)}{a} = \Delta C(r_y - r_{2y})$$  

(4)


Fig. 6. Compositional gradient of a single column (STEM–EDX) vs. the local compositional gradient of the full layer (SEM–EDX). The line shows the 1:1 relationship.

Fig. 7. Schematic drawing of the columnar growth on the substrate. The Y and Zr target are positioned on the left and right hand side, respectively. The compositional profile in the column is indicated. $L_1$ and $L_2$ represent the different expansions due to the insertion of Y$_2$O$_3$ in the ZrO$_2$ lattice and $h$ defines the thickness of the film.
gradient measured at the nanometer scale. Both results, in comparison, can be predicted on YSZ thin films on a macroscopic scale and these results can be used to determine the tilt on nanometer scale.

4. Conclusions

The tilt of the preferential orientation in YSZ thin films was demonstrated to be the consequence of the insertion of yttria in the zirconia lattice. The result of several deformed lattices stacked on top of each other is a distorted grain. Several distorted grains will lead to a bent column. By using pole figures we can quantitatively determine the grain tilt as a function of the compositional gradient. The columnar or ‘visible’ tilt at higher contents of yttrium was identified using scanning electron microscopy cross section images and it differs from the grain tilt. This was shown to be caused by the rotation of the lattice, as seen in the pole figures at Y contents above 20 at.%, likewise a contribution of the error when determining the angles of the bent columns.

Using ADF–STEM and STEM–EDX mapping in selected YSZ samples yielded a quantification of the compositional gradient as well as the coordinates of these values along the columnar structure. It was shown that the compositional gradient is equivalent on the nanometer (single column, STEM–EDX) and macroscopic level (total sample surface, SEM–EDX) of the sample.

Furthermore, a new model based on the known theory used for bimetal thermostats was developed to explain the grain and column tilt based on the yttria insertion in the zirconia lattice. It was shown to be in full agreement with former results in our group. Furthermore, this model allows combining both nanometer- and macroscopic-scale compositional gradients. As a result, the grain tilt can be predicted on YSZ thin films on a macroscopic scale and these results can be used to determine the tilt on nanometer scale.

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