



Dense zig-zag microstructures in YSZ thin films by pulsed laser deposition

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(Received 6 October 2014; accepted 25 December 2014; published online 13 January 2015)

The very brittle oxygen ion conductor yttria stabilized zirconia (YSZ) is a typical solid electrolyte for miniaturized thin film fuel cells. In order to decrease the fuel cell operating temperature, the thickness of yttria stabilized zirconia thin films is reduced. Often, these thin membranes suffer from mechanical failure and gas permeability. To improve these mechanical issues, a glancing angle deposition approach is used to grow yttria stabilized zirconia thin films with tilted columnar structures. Changes of the material flux direction during the deposition result in a dense, zigzag-like structure with columnar crystallites. This structure reduces the elastic modulus of these membranes as compared to columnar yttria stabilized zirconia thin films as monitored by nano-indentation which makes them more adaptable to applied stress. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4905578>]

The ionic conductivity and mechanical stability of the electrolyte membrane of solid oxide fuel cells (SOFC) and hence the final working temperature are important issues when operating a fuel cell, in particular thin film based miniaturized SOFCs (μ SOFC). The electrolyte yttria stabilized zirconia (YSZ) is the standard ionic conductor¹ used in fuel cell, being a brittle material due to its high hardness.² This point can become a concern for an early malfunction of devices due to cracking of electrolyte membranes when implemented in μ SOFCs as a result of the combination of a very high hardness, high operating temperatures, film morphology, and growth induced strain.^{3–6} One way to circumvent this problem is to modify the membrane's morphology. YSZ thin films grown by pulsed laser deposition (PLD) are known to exhibit a columnar morphology with diameters around 20 nm.^{7–9} This morphology is expected to follow the structure zone model of Thornton¹⁰ and could be overcome by an increase of the deposition temperature. However, with the very high melting point of YSZ above 2900 K,¹¹ deposition temperatures of at least 1500 K would be required for a significant change of the microstructure on technically relevant substrates. In addition, such a high deposition temperature poses serious limitations on any available heating systems, in particular, for a larger area deposition.

An alternative to modify the thin film morphology is to change the incident angle of the materials flux which can result in a change of the crystallographic growth orientation as well as materials' density. This approach is commonly known as glancing angle deposition (GLAD) or

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sculptured thin films.^{12,13} Structuring is thereby achieved by varying the angle between the material flux and the surface of the substrate. The microstructure of the growing thin film may then follow the orientation of the material flux typically realized for directional deposition techniques such as physical vapor deposition. For PLD, only a few attempts have been reported to prepare porous carbon or perovskite thin films with a tilted columnar structure.^{14–16}

Here, we present the sculpturing of YSZ thin films using PLD under variable angles with respect to the substrate surface normal. We will show that the influence of the deposition angle changes the microstructure and correspondingly the mechanical stability of these films. To achieve a glancing angle deposition, the geometry of a conventional PLD setup was modified (see Fig. S1 supplementary material¹⁷) similar to studies reported by others.^{14–16} Instead of the typical orthogonal alignment between the plasma plume expansion direction and the substrate surface (0° inclination), an arbitrary angle can be set. For the presented experiments, the deposition angle of the substrate was fixed at 45° but the angular range from 0 to 90° has also been explored.¹⁸ Additionally, in-plane rotations of 180° were performed to obtain a zigzag like growth morphology with the deposition stopped until the rotation was completed. Other deposition parameters were fixed for the deposition of 3 and 8 wt. % YSZ films: $\lambda = 248$ nm laser wavelength, 3 J/cm^2 laser fluence, pulse length 25 ns, 1.4 mm^2 laser spot size, 1 Pa oxygen background pressure, c-cut sapphire substrates,¹⁹ a substrate temperature $T_S = 600^\circ\text{C}$, and 4 cm distance between the revolving cylindrical target and the center of the substrate.

Microstructural investigations were performed using a scanning electron microscope (SEM; Zeiss Supra VP55 FE-SEM) and a transmission electron microscope (TEM; Jeol JEM 2000 FS). The cross sectional SEM images (Fig. 1) were obtained by cleaving the samples parallel to the grown zigzag structure after the sputter deposition of a 5 nm chromium layer to avoid charge accumulation during the measurements. A cross-sectional SEM image of a 3YSZ thin film grown with the conventional PLD geometry is shown as a reference in Fig. 1(a). The film has a columnar structure parallel to the surface normal with an average column width of ~ 20 nm as reported in literature.^{7–9} By applying an inclination of 45° between the plasma plume and the surface normal, the microstructure depicted in Fig. 1(b) was obtained. The columnar structure is preserved but tilted towards the direction of the plasma plume with a column width similar to the reference sample. Remarkably, the angle between the columns and the surface normal is found to be $36^\circ \pm 3^\circ$ which also holds for inclination angles $>45^\circ$ (see Fig. S2 supplementary material¹⁷). For other materials, often an increase in the tilting angle of the sculptured structure can be observed with increasing inclination.^{12,13} By turning the sample by 180° after half of the deposition, the column growth direction was also turned in-plane by 180° (Fig. 1(c)). This zigzag structure can be repeated without any degradation of the well aligned columnar structure, as can be seen in Fig. 1(d).

A closer inspection of Fig. 1(d) suggests that at least some columns continue to grow at the kinks as single crystallites without any grain boundary and the grown structure has no or a very reduced porosity as compared to conventionally grown YSZ. To examine this further, TEM images of focused ion beam (FIB) cut lamella of an 8YSZ thin film were recorded for further clarification. Lamellae were cut from the samples in a dual beam FIB/SEM (Zeiss NVision 40), a gas injection system, and a micromanipulator MM3A from Kleindiek. Amorphous carbon was deposited by e-beam and ion-beam to protect the thin film during cutting. The lamellae were polished to electron transparency with currents from 13 nA down to 10 pA at 30 kV. An overview image of a double layer zigzag structure is shown in Fig. 2(a). The arrow shows the growth direction of the thin film with the numbers indicating (1) sapphire substrate, (2) YSZ thin film, (3) the chromium layer with a small region of amorphous YSZ due to the FIB cutting, and (4) the amorphous carbon protection layer. No pores were observed between the different columns or at the grain boundaries studied, neither in the low nor in the high magnification analysis showing that the film has a dense structure. This has been confirmed by samples cut at 90° to the zigzag structure showing no holes or pores, nor grain boundaries at the kink. A high resolution TEM image of the region around the kink (dashed line) of the zigzag structure is shown in Fig. 2(b). Apparently, all columns continue to grow through the kink without any evidence of a discontinuous crystal structure. This is demonstrated in addition in Figs. 2(c)–2(h) corresponding to the labeled white squares in Fig. 2(b). A comparison of the 2D Fourier transformed images of the same column before and after the kink ((e) and (g) as well as (f) and (h)) demonstrates the continuation of the same crystallographic orientation. As for the

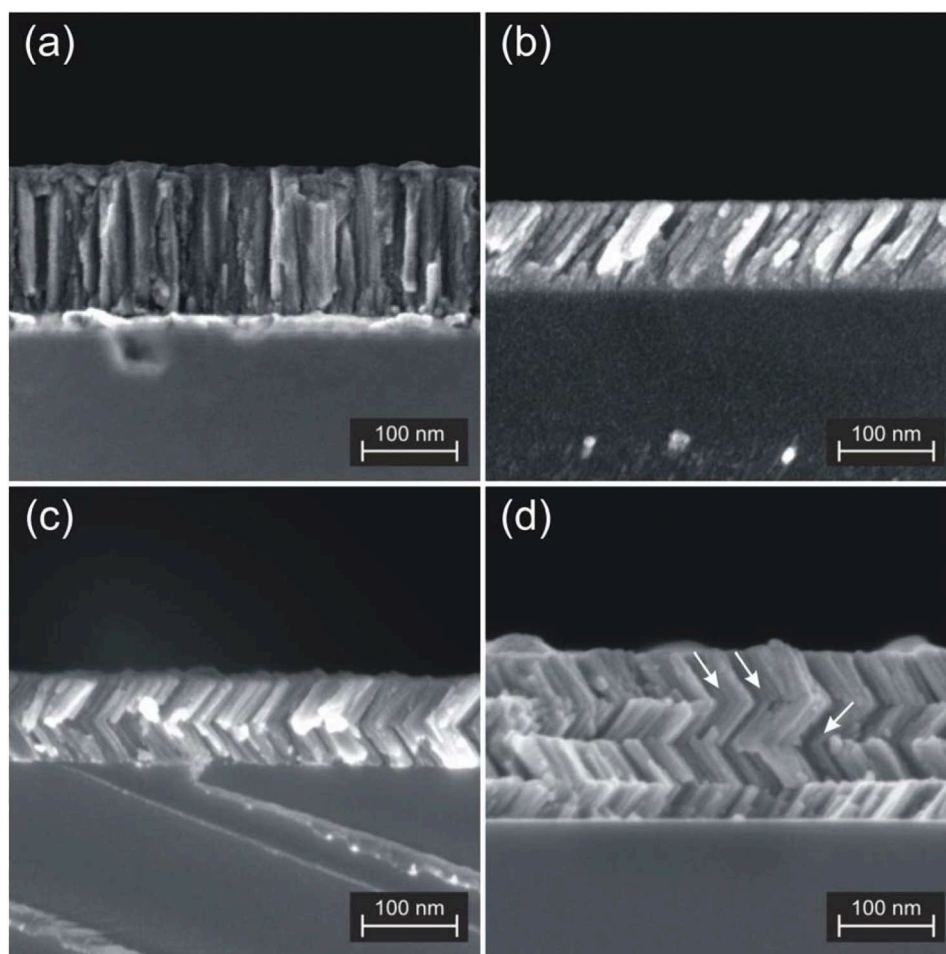


FIG. 1. SEM cross sectional views of YSZ thin films grown under (a) perpendicular incidence of the plasma on the substrate, (b)-(d) 45° of incidence with (b) no in-plane rotations, (c) one in-plane rotation by 180° after half of the deposition, and (d) three in-plane rotations by 180° after each quarter of the deposition time. The cleaving of the samples was done in the plane perpendicular to the plane spanned by the plasma propagation direction and the surface normal. Arrows indicate tilted columns with no visible change in crystallinity or a grain boundary at the kink.

crystallographic orientation, only two types were found in the acquired TEM images. They show a (100) out-of-plane orientation with in-plane orientations being either 8YSZ(001)||Al₂O₃ (11.0) or 8YSZ(011)||Al₂O₃ (11.0). Since the FIB cut lamella represents only a very small part of the whole sample, XRD measurements were performed for a macroscopic analysis of the crystalline structure which coincides well with the presented microscopic observation (see Fig. S3 supplementary material¹⁷).

Two observations are notable: (i) The zigzag structure appears to be dense and without obvious micro- or nanoporous structures in contrast to materials deposited either using PLD or other deposition techniques.^{12,13,15,16} The reason for this difference is most likely related to the relatively small inclination angle of 45° as compared to typically used angles >70°. In addition, the expected shadowing effect of the growing columns seems to be too weak to interfere with a dense growth due to an enhanced surface migration of species at the high deposition temperatures. The gas tightness of these films was verified by a successful implementation of zigzag structures as an electrolyte in μ SOFCs.¹⁸ (ii) The tilt angle of the columns is fixed at ~36° for any inclination of the material flux of $\geq 45^\circ$ while columns grow nearly perpendicular to the substrate at inclination angles <40° (see Fig. S2 supplementary material¹⁷). As reported by Pergolesi and co-workers, the free surface energies of the {001} and {111} facets of cubic YSZ are energetically closer than in doped ceria. As

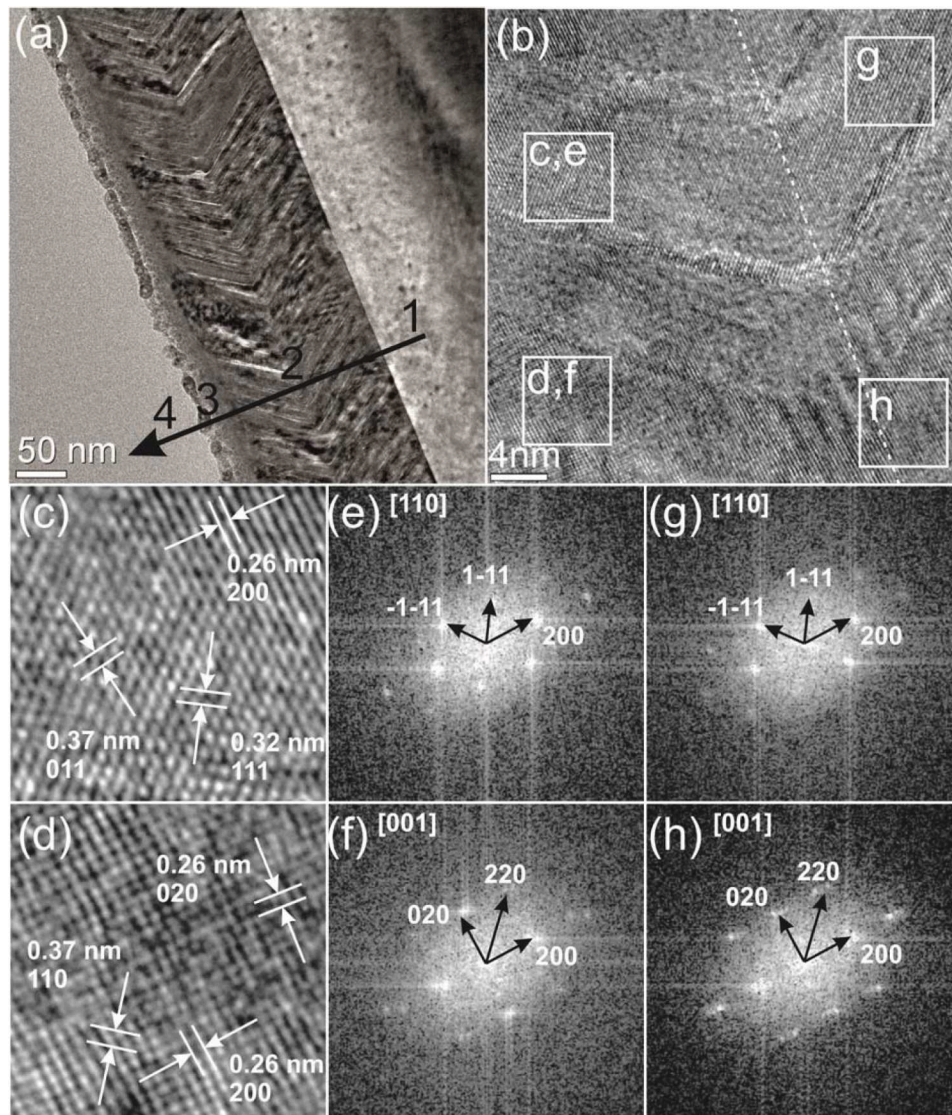


FIG. 2. TEM analysis of FIB cut lamella of a zigzag structured YSZ thin film (a) bright field-TEM overview image where the growth direction is indicated by an arrow. (b) High resolution TEM image of the region around the kink indicated by a dashed line. The labeling of the white squares corresponds to the following sub-figures. (c) and (d) High resolution TEM analysis of two small regions, where crystallographic orientations are indicated. (e)-(h) 2D Fourier transformed images for further illustration of the crystallographic orientations in the different regions of (b).

a consequence, nanocrystallites can exhibit both surfaces in thermodynamic equilibrium.²⁰ In any cubic lattice, the angle between these two surfaces is 54.7° and corresponds to the complementary angle of the columns inclination. It is, therefore, expected that a crystal facet when grown as a thin film orients itself according to one of the two possible orientations. Keeping the (001) growth orientation fixed when growing columnar films, a {001}-plane in the crystalline structure is the only solution for columns growing perpendicular to the surface. If tilted columns with a (001) out-of-plane orientation are grown, the remaining crystal planes for the columns' faces are the {111} facets irrespective of the inclination. Thus, the possible angles of the columns are fixed at either 0° or $\sim 36^\circ$ to the surface normal, as verified by other deposition angles.^{17,18}

The mechanical stability of YSZ thin films as free-standing membranes is very important. To investigate the mechanical properties of zigzag structures, nano-indentation measurements were

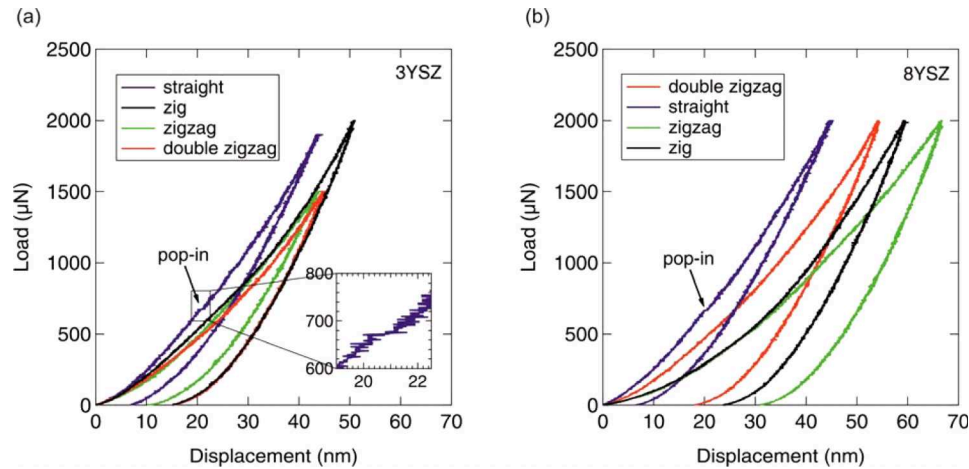


FIG. 3. Load-displacement curves of (a) 3YSZ and (b) 8YSZ thin films structured with different numbers of zig layers (0, 1, 2, and 4). The inset of part (a) shows the magnified part with a pop-in of the load-displacement curve of the conventionally grown sample. In the supplementary material, all acquired P - h curves are shown for completeness in Fig. S4.¹⁷

performed with a load-controlled Berkovich-type nano-indenter Ubi (Hysitron). Mechanical properties, such as hardness H and reduced modulus E_r , are extracted from the unloading part of the load-displacement (P - h) curve using the Oliver and Pharr method.²¹ In order to avoid the influence of the substrate in the measurement, the maximal penetration depth of the indenter was limited to 15% of the total thickness of the YSZ film with sample thicknesses ranging from 300 to 700 nm. For each sample, 36 P - h curves were acquired with typical indentation curves depicted in Figs. 3(a) and 3(b) for 3YSZ and 8YSZ thin films, respectively. Clearly visible is the larger indentation depth at maximum load for tilted structures compared to the conventionally grown samples. The hardness H is defined as the ratio between the maximum applied force P_{\max} over the projected contact area A_p .

The reduced elastic moduli E_r can then be calculated via Sneddon's equation $S = \frac{dP}{dh} = 2\beta E_r \sqrt{\frac{A_p}{\pi}}$, where S is the slope of the initial part of unloading elastic curve termed stiffness, and β is a shape correction factor set to 1.034 for a Berkovich indenter. Finally, if the Poisson's ratio ν of the thin film is known, the reduced elastic modulus E_r can be converted to Young's modulus E via

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}, \quad (1)$$

where the index i denotes the indenter's material parameters (diamond indenter: $E_i = 1140$ GPa, $\nu_i = 0.07$).

It is known that YSZ has a strong anisotropy with respect to its Poisson's ratio.² While it has a value of $\nu > 0.8$ for the [100] direction it is close to zero ($|\nu| < 0.1$) for the [111] and [110] directions. Since the presented thin films are highly oriented, an average Poisson's ratio for the calculation of the Young's modulus is in this case not very meaningful as it is commonly done for polycrystalline samples.²² Therefore, the derived reduced elastic moduli counting for indentation modulus and Poisson's ratio evolutions are plotted in Figure 4(a). Straight columns have a strongly preferential (100) out-of-plane orientation, whereas tilted structures show in addition a partial (111) orientation with a much higher degree of mosaicity, i.e., a structure with a slightly tilted (100) orientation. Since YSZ is a strongly anisotropic material, elastic properties are expected to be orientation dependent and thus exhibit different values for straight or tilted structures. For 3YSZ, a ratio $\frac{E}{1-\nu^2}$ of ~ 310 GPa is measured independent of the microstructure and thus of the orientation. For 8YSZ, a slightly increased value for $\frac{E}{1-\nu^2}$ has been determined for straight columns as compared to 3YSZ, whereas for the zigzag morphology the values are systematically lower. Compared with results obtained on bulk single crystals,² the microstructure of the samples described here reduces the influence of the anisotropy on the elastic modulus.

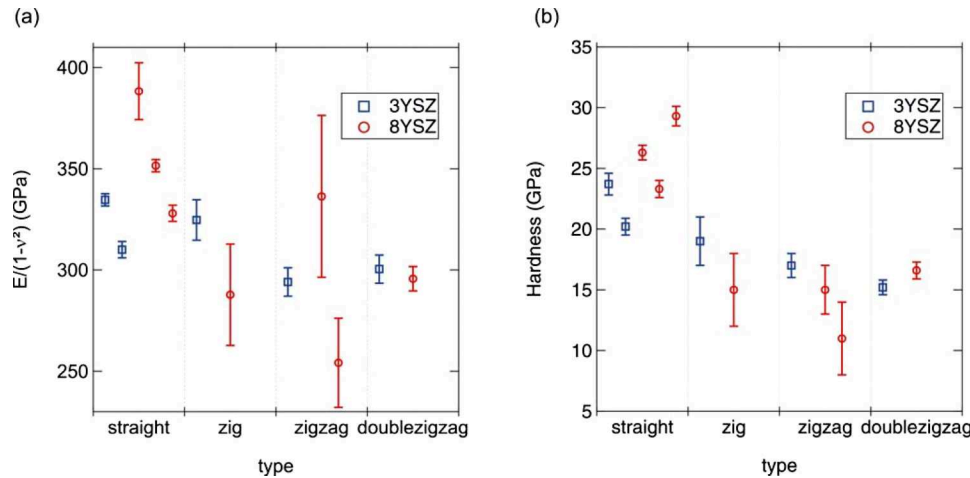


FIG. 4. (a) Hardness and (b) the ratio $\frac{E}{1-\nu^2}$ of 3YSZ and 8YSZ thin films with different numbers of zig layers (0, 1, 2, and 4). The error bars indicate the 2-sigma region of the 36 single measurements as extracted from the measurements shown in Figure S4.¹⁷

Looking now at the measured hardness for samples with a preferential (100) and (111) orientation, the hardness is homogeneous for straight columns for both 3 and 8YSZ thin films (Fig. 4(b)).² When introducing the tilted structures, the hardness decreases significantly which strongly suggests that tilted interfaces and/or grain boundaries seem to act as less efficient obstacles to plastic deformation. The analysis of whether this is, e.g., related to the nature of the grain boundary or simply related to the inclination of the boundaries with respect to the loading axis is beyond the scope of this paper.

For YSZ P - h curves, a typical feature of a so-called pop-in was found (see inset of Fig. 3(a)). The pop-in was present in most of the P - h curves of films with straight columns and appeared within a range of 500-900 μ N. This corresponds to a very high von Mises stress, estimated to be about 17 GPa, and is considered to be in the order of the theoretical stress values for YSZ. For films with tilted columns, no pop-in appeared in any P - h measurement. Usually, the appearance of a pop-in in a P - h measurement is associated with a low dislocation density in monocrystals.² For straight columns, they appear at a penetration depth of ~ 20 nm which corresponds to a contact area of approximately 60×60 nm² which is larger than the average width of a single column (see Figs. 1 and 2). Therefore, it is not obvious how this reoccurring feature correlates with the film microstructure. However, with the larger mosaicity and hence a higher degree of disorder for zigzag structures, the absence of a pop-in structure in P - h curves seems to be consistent.

In summary, it is demonstrated that the orientation of columnar grains of PLD grown YSZ layers can be modified by changing the angle between the material flux and the substrate. The maximum average angle of these tilted columns is, however, limited to $\sim 36^\circ$, the angle between the crystallographic orientations of (111)_c and (001)_c which shows the lowest free surface energies among the low index surfaces of YSZ. The transition from vertically aligned columns to the tilted columns occurs in a narrow range around 40° - 45° between material flux and substrate normal. Layers of tilted columns with opposite tilt (rotated in-plane by 180°) can be grown on top of each other without any loss of crystalline order. The columnar grains do not show a discontinuity at the kink even on an atomic scale. Furthermore, the PLD grown thin films are found to be highly dense and gastight¹⁸ with an ionic conductivity like conventionally grown YSZ, an important prerequisite for μ SOFC applications. 3 and 8YSZ films with tilted columns result in a lower hardness ($\sim 35\%$) and a lowering of the ratio $\frac{E}{1-\nu^2}$ by $\sim 10\%$ as compared to conventionally grown YSZ films. The number of tilted layers (up to 4) was found to play only a minor role, in particular, for 3YSZ. This study demonstrates that mechanical properties of YSZ films can be tuned and optimized in a simple approach which could be beneficial for free standing membranes for an improved adaptability to thermally induced strain.

This project is financed by the Paul Scherrer Institute and the Swiss National Science Foundation (SNF Project No. 200021 126783). The FIB cutting was performed at EMEZ, ETH Zürich within the Project No. 0936. The assistance of Julia Martynczuk (ETHZ) and Gerhard Bürki (EMPA, Thun) is greatly acknowledged.

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