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NONSTOICHIOMETRIC COMPOUNDS

Preparation of nitrogen-doped YSZ thin films by pulsed laser deposition and their characterization

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Abstract The pulsed laser deposition technique was applied to deposit nitrogen-doped yttria stabilized zirconia (YSZ) thin films. The working parameters were varied in order to achieve a maximal nitrogen content. The films were characterized by SIMS, XPS, X-ray diffraction and optical spectroscopy. The surface topography was studied by AFM and HRSEM. The influence of the deposition parameters on the film properties is discussed.

Introduction

The development of new materials for solid state ionic devices is a subject of continuous studies, e.g., in order to meet the requirements for SOFC working at lower temperatures or to increase the specific selectivity and sensitivity of gas sensors and the efficiency of ceramic membranes. More recent activities in the field of electrochemically promoted catalysis emphasize the link between ionic materials and catalysis. Yttria stabilized zirconia (YSZ) is a well known material that has found wide applications as a oxygen ion conductor with a transference number of oxygen anions near to one in many of these applications. It is probably the most important solid electrolyte model system, and thus, subject to many fundamental studies on principles of solid ion conductors.

In this respect the nitrogen (anion) doping of ZrO_2 or YSZ has been reported by Lerch [1–4] as a less conventional alternative to the cation (e.g., yttria) doping. In nitrogen doped zirconia oxygen vacancies are created to compensate the negative charge introduced by the N^{3-} incorporation. Using the Kroeger–Vink notation the complete chemical reaction of oxygen substitution by nitrogen in YSZ can be written as:

$$N_2(\mathrm{gas}) + 3O_O^{\times}(\mathrm{YSZ}) \rightleftharpoons 2N_O'(\mathrm{YSZ}) + V_O^{\bullet\bullet} + 3/2O_2(\mathrm{gas}) \qquad (1)$$

The doping with nitrogen also stabilizes the cubic fluorite-type structure and modifies the electric properties of the material. Thus nitrogen doped YSZ (YSZ:N) in both cubic and tetragonal structure was found to be an excellent ionic conductor showing even nitrogen ion conductivity at high temperatures [5–9]. To date, the nitridation of single crystals or powders of YSZ is performed in gas tight furnaces at extremely reducing conditions and high temperatures (up to 2000 °C) [2].

In this paper we report our results of a systematic study on the preparation of thin films of nitrogen-doped YSZ by pulsed laser deposition (PLD) at much

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lower temperatures. PLD is one of the most flexible thin film deposition technique and allows the preparation of thin films of a large variety of materials absorbing in the UV range and with a precise control of the film thickness. Most important is the fact, that many compounds with sufficient UV absorption can be ablated and deposited virtually without loss of the metal components and that doping can easily be achieved by supplying another component from the gas phase.

In order to study the deposition of YSZ:N by PLD systematically we investigated the influence of the temperature, the background gas pressure and the yttria content on the amount of incorporated nitrogen. The resulting films have been analyzed with SIMS, XPS, XRD and optical spectroscopy in order to determine their chemical composition and their crystallographic and electronic structure.

Experimental

The YSZ:N films were prepared via pulsed laser deposition (PLD). A KrF excimer laser (Lambda Physik, Germany, wavelength $\lambda = 248$ nm, puls duration $\tau = 25$ ns) with an energy of 200 mJ was used for the ablation process in a high vacuum chamber. For a general introduction into the PLD technique see refs. [10, 11]. After a deposition time of 60 min (36,000 pulses at 10 Hz), the thickness of a single film was approximately 1.0 μm (determined by the cross-section in the HRSEM image), and thus, an average growth rate of 1 μm/h can be assumed for the PLD deposition process.

As target materials were used either pure ZrO_2 or ZrO_2 doped with 7, 9.5 or 13 mol% Y_2O_3 with a purity of 99.99% excluding Hf (the hafnium content corresponds to max. 1 mol%) produced by HTM Reetz (Germany). In the following text we denote them as 7YSZ, 9.5YSZ and 13YSZ, respectively. The nitrogen doped YSZ films are denoted as 7YSZ:N, 9.5YSZ:N and 13YSZ:N. As substrate material we used sapphire crystals with (0001) orientation of the surface[1]. The size of the substrates was typically 10 mm × 10 mm and the thickness of the films was homogenous over this area. The background gases (Messer, Germany) supplied to the PLD chamber had a purity of 99.5% (O_2), of 99.99% (N_2) and of 99.996% (Argon), respectively.

The following parameters were controlled: (a) The influence of the substrate temperature on the nitrogen concentration was studied at three temperatures in the temperature range from 500 to 700 °C. We found this temperature range to be optimal for the PLD deposition process of YSZ:N in nitrogen gas. As target material for this experiment we used 9.5YSZ. The cubic lattice of this material is fully stabilized and it has found the largest application in practice. We deposited films in nitrogen atmosphere with a constant pressure of 4 Pa and 4 cm distance between the target and the substrate. (b) The nitrogen gas pressure in the deposition chamber was varied in four steps in the range from 2 Pa to 8 Pa. Lower pressures led to a deposition of strongly reduced films and were not sufficient to achieve nitrogen concentrations higher than 0.5 at.%. Higher pressures resulted in a poor film quality. (c) The distance d between the target and the substrate was adjusted between 4 and 5 cm. (d) Finally we investigated the influence of the yttria concentration in YSZ on the nitrogen concentration in thin films at constant substrate temperature, constant d and p (N_2). We applied two extreme dopant concentrations, i.e., 0 mol% (pure ZrO_2) and 13 mol% Y_2O_3 which is the practical upper limit of yttria doping in most applications. As intermediate points we choose 7YSZ and 9.5YSZ as these concentrations are widely used in practical applications.

The samples were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS IV, ION-ToF, Muenster, Germany), in the following abbreviated simply as SIMS, with the following typical parameters: a beam of 25 keV Ga^+, rastered over 100 μm × 100 μm, was used to generate secondary ions for analysis ($I_{Ga} = 1$pA); sputter etching of the surface was carried out with a beam of 2 keV Cs^+ rastered over 300 μm × 300 μm ($I_{Cs} = 150$ nA); charge compensation was achieved by flooding the surface with electrons ($I_e > 1$A) of energy less than 20 eV. We quantified the nitrogen concentrations in our thin films by comparing the intensity ratios $I(^{90}Zr^{14}N^-)/I(^{96}Zr^{16}O^-)$ with the ratio determined from an N-implanted sample, i.e., YSZ:N with known nitrogen content.

X-ray photoelectron spectroscopy (XPS) was carried out with a VG Instruments equipment. The measurements were performed with the Mg K_α line at 1253.6 eV with a line width of 0.7 eV. A hemispherical CLAM-type electron energy analyzer was used. The analysis chamber was equipped with an ion pump and a liquid nitrogen-cooled titanium sublimation pump, thus enabling a residual gas pressure of less than 10^{-8}Pa. To account for the charging effects of the

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[1] Some of the films for the optical absorption experiments were deposited on silica glass substrates.

insulating YSZ:N films at room temperature all spectra are calibrated with respect to the carbon C1s peak. The concentrations of the elements are evaluated as relative concentrations in at.%.

The atomic force microscope used for the surface imaging was a Q-scope 250 (Quesant, USA) with a head designed for a scan area from 200 nm × 200 nm up to 80 μm × 80 μm. The digital lateral resolution is approximately 1 nm, and the resolution of the z-axis is approximately in the same range. The measurements were performed in the non-contact mode with the following typical scan parameters: a scan rate of 0.5–3 Hz, integral and proportional gain in the range 250–400 and image resolution 300–600 dpi.

We used a high resolution scanning electron microscope (LEO Gemini 982). The electron source is a Schottky field emitter with acceleration voltage in the range of 0.2 keV up to 30 keV. The maximal resolution achieved is approximately 2 nm.

The X-ray studies of the samples were performed with a θ–2θ diffractometer (Siemens D500) with Cu-K$_\alpha$ radiation at room temperature.

The optical measurements were performed with a spectrometer Lambda 900 (Perkin-Elmer) in the range of 200–860 nm with a resolution of 1 nm and a scan rate of 250 nm/min. As light sources we employed a deuterium lamp emitting in the UV range (below 320 nm) and a tungsten-halogen lamp in the Vis/NIR-range (above 320 nm). As detectors we used a PbS-cell (in the range of 860–3300 nm) and a photomultiplier (in the range of 200–860 nm).

Experimental results

AFM and HRSEM imaging of the film surfaces

All films deposited under the given conditions show a smooth surface with only a small number of pores or droplets. An AFM image of the surface of a 7YSZ:N film deposited on a sapphire substrate is shown in Fig. 1.

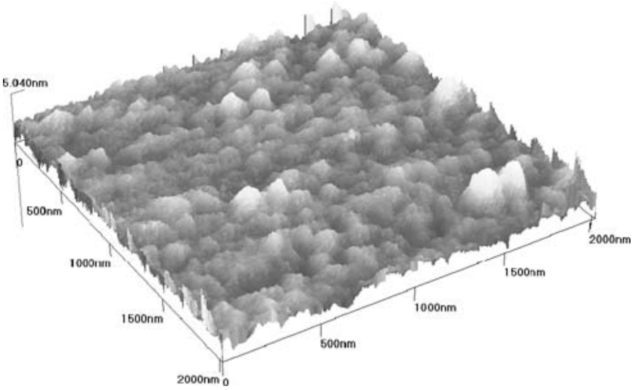

Fig. 1 AFM image of a 7YSZ:N film deposited on sapphire (0001). Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

The morphology of the film repeats on the large scale the morphology of the substrate. The grain size at the surface varies in the range of 30 nm up to approximately 90 nm, with an average hight of 4 nm. We found no difference in the surface morphology of the YSZ films deposited in nitrogen or in oxygen atmosphere. We also found no significant influence of the yttria content and the deposition parameters, i.e., temperature, pulse energy and gas pressure on the film surface morphology.

The films are virtually free of pores and perfectly dense, which is an important prerequisite for both the SIMS and optical experiments. The HRSEM image of a bilayer cross section consisting of one 9.5YSZ:N and one 9.5YSZ film (each with a thickness of approx. 1 μm) deposited on sapphire is shown in Fig. 2.

X-ray diffraction

We found that all films were crystalline as deposited, even without additional thermal post-treatment. The resulting diffraction patterns of three YSZ:N films and as well of the 7YSZ target material for comparison are shown in Fig. 3.

Apart from the intense (0006) Al_2O_3-peak at $2\theta = 41.68°$ and the peaks corresponding to Cu-K$_\beta$ and W-L$_\alpha$

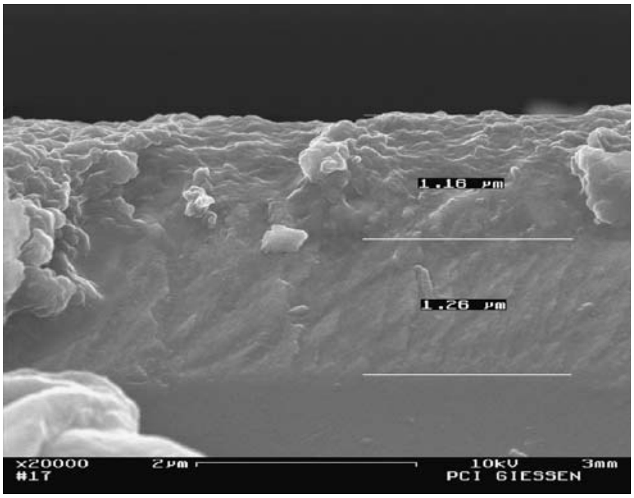

Fig. 2 HRSEM image of the cross-section of a 9.5YSZ:N/9.5YSZ sandwich film. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

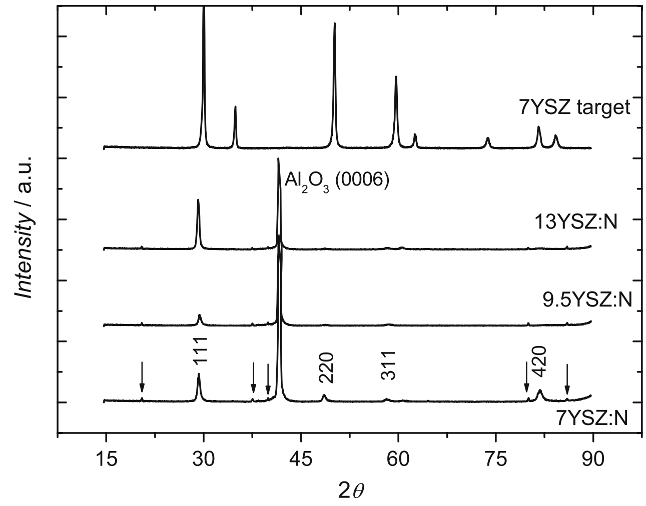

Fig. 3 X-ray diffraction pattern of 7YSZ:N, 9.5YSZ:N, 13YSZ:N thin films (1 μm thickness) deposited via PLD on sapphire (0001) and 7YSZ target. Deposition conditions: $p(N_2)$ = 4 Pa, T = 500 °C, d = 4 cm

radiation marked by arrows the main reflections were assigned to the cubic fluorite-type structure of YSZ. The orientation of the films is preferably in the (111) direction as this peak is much more intense than the others. Additional (220), (331) and (420) reflections are found with much lower intensity, but being more pronounced for the 7YSZ:N sample.

In Fig. 4 we also see the (200) reflection of the nitrogen-free YSZ film. This reflection is almost absent in the YSZ:N films, indicating different texture of YSZ and YSZ:N films.

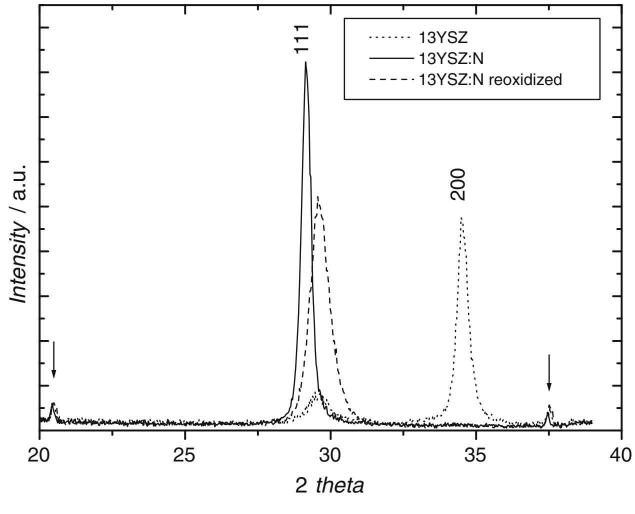

Fig. 4 X-ray diffraction patterns of a 13YSZ, a 13YSZ:N, and a re-oxidized 13YSZ:N (30 min at 700 °C) film at room temperature. Deposition conditions: $p(N_2)$ = 4 Pa, T = 500 °C, d = 4 cm

To demonstrate the effect of nitrogen doping we compare in Fig. 4 the positions of the (111) reflection of YSZ, of YSZ:N and of a nitrogen-doped sample which was subsequently re-oxidized in air at 700 °C for 30 min. The (111) reflection of 13YSZ:N is shifted towards a smaller 2θ value by 0.45° compared to 13YSZ. The reflection of the re-oxidized film has again the same 2θ value as the nitrogen free film.

SIMS analysis

The nitrogen content in the samples deposited at different substrate temperatures was subsequently analyzed by SIMS. The results are presented in Fig. 5.

At both temperatures 500 °C and 600 °C the nitrogen concentration is virtually equal and lies in the range between 5 and 6 at.%. At 700 °C the nitrogen content amounts to approximately 2.5 at.%.

The influence of the nitrogen pressure on the concentration of the incorporated nitrogen into the YSZ films is presented in Fig. 6. A maximum in the nitrogen content was obtained at $p(N_2)$ = 6 Pa.

The influence of the cation dopant (Y_2O_3) is also pronounced. The results of the SIMS analysis are presented in Fig. 7, showing that the highest nitrogen concentration is obtained in the 7YSZ:N sample.

XPS analysis of N-doped YSZ films

In order to collect an integral information from a larger area and additionally to understand more about the chemical nature of the bonds in the YSZ:N films we investigated our films by XPS.

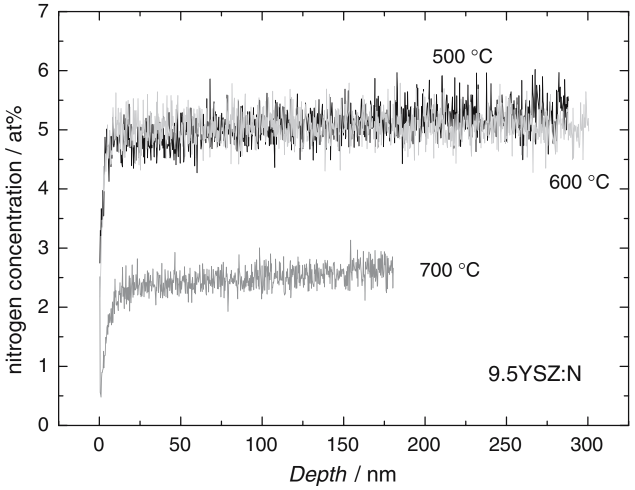

Fig. 5 Nitrogen depth profiles (determined by SIMS) of 9.5YSZ:N thin films deposited at different temperatures. ($p(N_2)$ = 4 Pa, d = 4 cm)

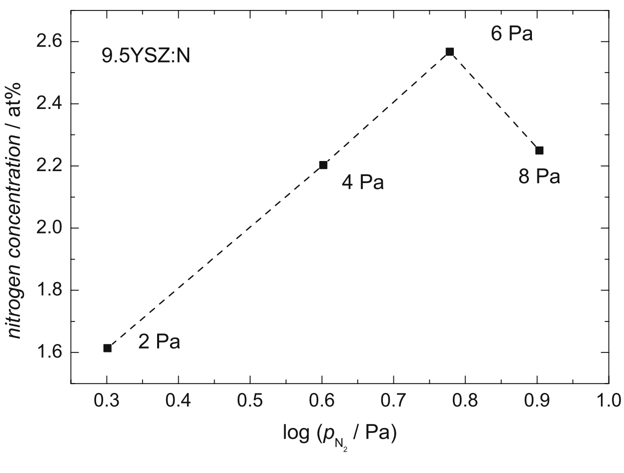

Fig. 6 Nitrogen concentration (determined by SIMS) in 9.5YSZ:N films deposited at different $p(N_2)$ on sapphire (0001). Deposition parameters: $T = 500$ °C, $d = 5$ cm

Yttrium (Y 3d spectra): In Fig. 8 the Y 3d spectra of different nitrogen-doped zirconia films are shown. The Y $3d_{3/2}$ peak appears at a binding energy of 158.9 eV (E_b for pure Y_2O_3 is 158.4 eV) irrespective of the yttria content. The peak intensity increases with increasing yttria concentration.

Zirconium (Zr 3d spectra): The position of the $Zr3d_{3/2}$ peak in ZrO_2:N (Fig. 9) is found at 182.4 eV in exact agreement with the literature [12], and the peak is shifted to higher binding energies in YSZ:N—respectively to 183.4 eV in 7YSZ:N; to 183.8 eV in 9.5YSZ:N and to 183.9 eV in 13YSZ:N. This shift of more than 1 eV relative to yttria free zirconia was confirmed to be reproducible.

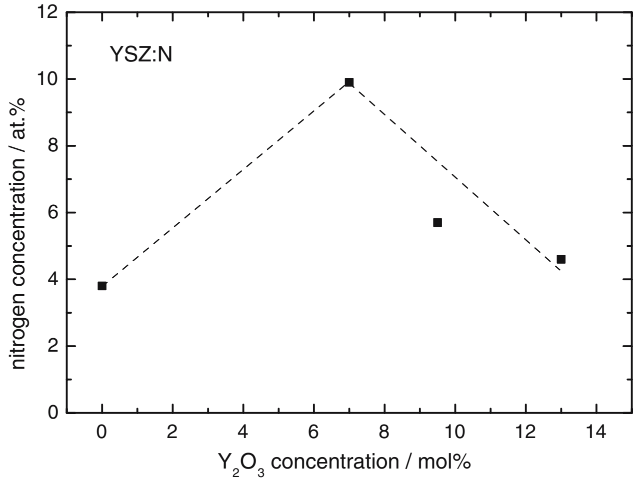

Fig. 7 Nitrogen concentration in YSZ:N films with different Y_2O_3 content deposited on sapphire (0001). Deposition conditions: $T = 500$ °C; $p(N_2) = 4$ Pa, $d = 4$ cm

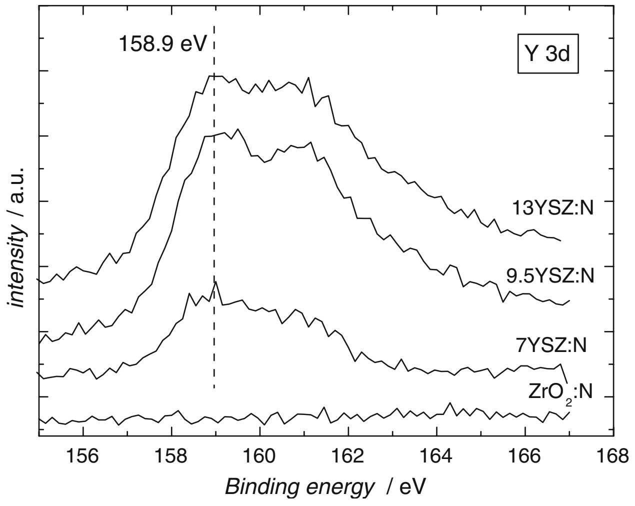

Fig. 8 XPS spectra of the Y 3d doublet in YSZ:N films with different yttria content deposited on sapphire (0001) after 2h Ar^+ sputtering. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

Oxygen (O 1s spectra): The O 1s peak of ZrO_2:N is found at a binding energy of 530.4 eV. In 7YSZ:N and 9.5YSZ:N, the signal lies at about 531.2 eV and in 13YSZ the peak is found at 531.4 eV (Fig. 10). These values are in a good agreement with those suggested in the literature (see discussion).

Nitrogen (N 1s spectra): All XPS spectra of films deposited in nitrogen (Fig. 11) shows clearly the N 1s peak. In 9.5YSZ:N and 13YSZ:N the nitrogen peak is detected at 398.7 eV on the film surface and shifts towards a lower binding energy of 397.8 eV after 1h

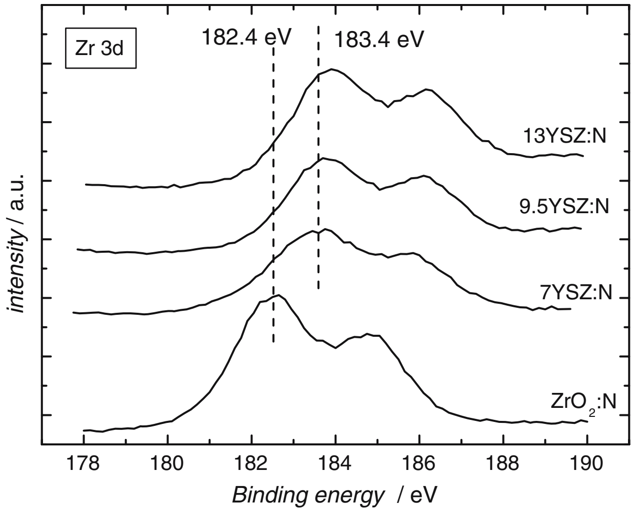

Fig. 9 XPS spectra of the Zr 3d doublet in YSZ:N films of different yttria content deposited on sapphire (0001) after 2h Ar^+ sputtering. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

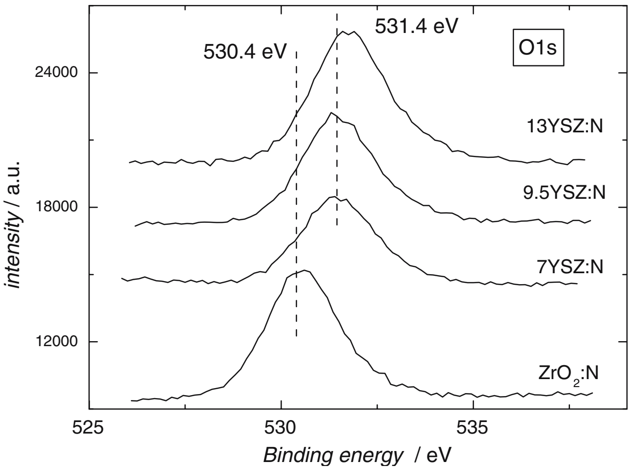

Fig. 10 XPS spectra of the O 1s peak in YSZ:N films of different yttria content deposited on sapphire (0001) after 2h Ar$^+$ sputtering. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

sputtering with Ar$^+$ and towards 397.3 eV after 2h sputtering. Thus, the binding energy gets the smaller the deeper in the film the spectra are taken. The N 1s peak for ZrO$_2$:N is found at a binding energy of 396.4 eV. Again 7YSZ:N shows quite different spectra: In contrast to the other films we found a broad signal at a binding energy of approximately 402.6 eV. At the position of the nitrogen N 1s peak in 9.5YSZ:N and 13YSZ:N (397.3 eV) we found no pronounced signal.

The quantification of the XPS spectra, i.e., the integration of the area beneath the peaks, allows to calculate the relative element concentrations within the different films. The results are presented in table 1.

The highest nitrogen content was found in 7YSZ:N, followed by 9.5YSZ:N, 13YSZ:N and ZrO$_2$:N.

Optical spectroscopy of N-doped YSZ films

All nitrogen-containing samples were transparent but of violet or dark violet color. We measured absorption spectra of YSZ:N films containing different amounts of yttria, deposited either on silica glass or on sapphire substrates. For the calibration we measured the absorption of the pure substrates as well as the absorption of YSZ deposited in oxygen and in argon atmosphere, i.e., without any nitrogen content. All spectra were collected at room temperature and at 300 °C, but no influence of the temperature on the absorption spectra was observed. In Fig. 12 the absorption spectra of YSZ, YSZ:N and ZrO$_2$:N films are shown.

The absorption spectra of all nitrogen-doped films show a broad absorption band in the range of the visible light, with a maximum at a wavelength of

Table 1 Relative concentrations of components in YSZ:N thin films as a function of the Y$_2$O$_3$ content as evaluated from XPS deposition conditions: $p(N_2) = 4 \times 10^{-4}$ Pa, $T = 500$ °C, $d = 4$ cm

Composition	N/at%	O/at%	Zr/at%	Y/at%
ZrO$_2$:N	1.6	63.5	34.8	–
7YSZ:N	12.1	63.7	19.7	4.6
9.5YSZ:N	7.1	58.3	23.6	10.9
13YSZ:N	6.5	56.8	23.5	13.1

Table 2 N 1s binding energies of different nitrogen containing zirconium compounds

	N 1s (E_b/eV)	Compound	Bond	Reference
1	398.5	BN	Covalent	[12]
2	396.4	Zr$_3$N$_4$	Zr–N	[14]
3	397.6	ZrN	Zr–N	[15]
4	397.3	ZrN	Zr–N	[16, 17]
5	396.3, 400.05	ZrON	Oxinitride	[16, 17]
6	403.2	N$_2$	Covalent	[16, 17]
7	402.8	ZrON/TiON	(Dinitrogen) M–N ≡ N–M	[18, 19]
8	395.8	ZrN$_2$	Zr–N	[20]
9	396.4	ZrO$_2$:N	Oxinitride	This paper
10	397.3	9.5YSZ:N, 13YSZ:N	Zr–N	This paper
11	402.6	7YSZ:N	(Dinitrogen) M–N ≡ N–M	This paper

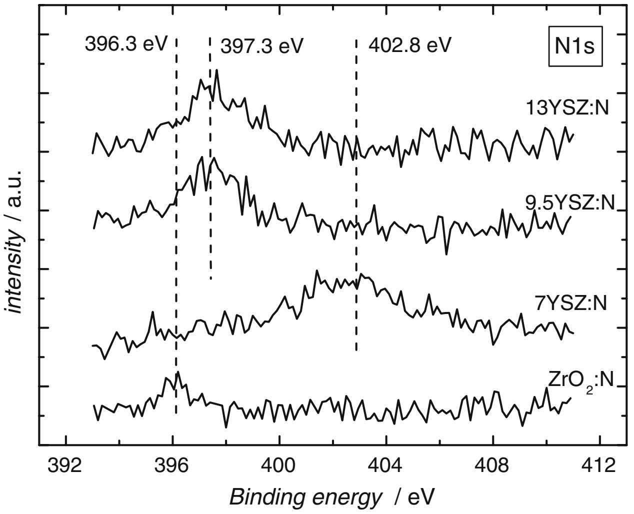

Fig. 11 XPS spectra of the N 1s peak in YSZ:N films of different yttria content deposited on sapphire (0001) after 2h Ar$^+$ sputtering. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

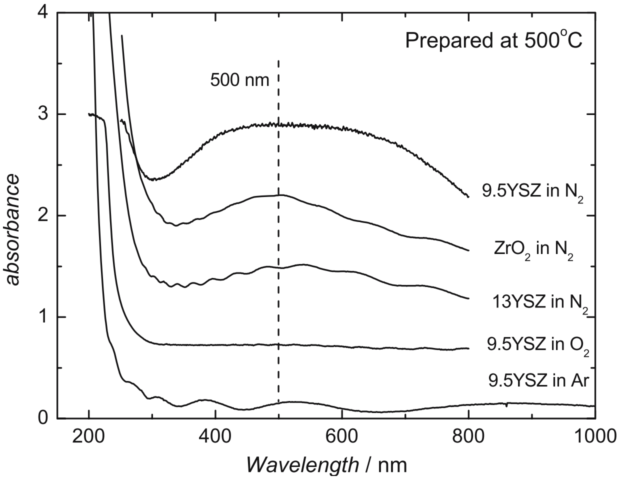

Fig. 12 Optical absorption spectra of ZrO_2, YSZ and YSZ:N films of variable yttria content (deposited on silica glass) at room temperature. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm, film thickness: 2 μm, an offset of approx. 0.5 absorption units was used)

approximately 500 nm. Additionally, a shift of the absorption edge towards larger wavelengths compared to samples prepared in oxygen or in argon is detected. The edge of the 9.5YSZ film deposited in argon is found deep in the UV range at about 200 nm. In 9.5YSZ deposited in oxygen it shifts to approximately 220 nm. The nitrogen doping shifts the absorption edge to about 250 nm. In the spectra of the other samples doped with different amounts of Y_2O_3, this shift is also observed—but as in these experiments two parameters were changed (both nitrogen and yttria concentrations), we cannot relate this effect only to the nitrogen content. The ‘‘oscillations’’ in the absorption spectra of 9YSZ prepared in Ar and 13YSZ:N deposited in nitrogen (see Fig. 12) can be attributed to interference effects of the films.

A significantly different spectrum was recorded with the 7YSZ:N film, see Fig. 13. The optical band edge is determined as 201 nm. An absorption peak at 263 nm is registered, which is not observed in films with other yttria concentrations. In 7YSZ:N, the typical broad absorption maximum is shifted to lower wavelengths and is centered at 455 nm.

Discussion

Before we summarize the essential observations we discuss the main results of the different analytical studies.

AFM and HRSEM imaging of the surface: The AFM images prove that both nitrogen-free and nitrogen-doped films have the same microstructure at the surface. The roughness of the films lies in the nm range, and thus, is very small compared to the thickness of the films in the micron range. The concentration of pores and droplets is small, and we interpret the surface topology as the result of a typical grain size in the range between 20 and 50 nm. From the AFM images we can conclude that PLD is a suitable method for the preparation of YSZ:N films of high surface quality. HRSEM proves that the films are virtually pore-free and adhere well to the substrate.

XRD analysis: The films deposited in different gas atmospheres were always crystalline. Using the Sherrer equation we calculate from the FWHM of the reflections an average grain size comparable to the grain size measured by AFM (in average 40 nm). Both types of films show significant orientation effects. When the deposition process was carried out in nitrogen, the YSZ:N films grew preferably in (111) orientation. The deposition in oxygen increased pronouncedly the intensity of the (200) and (220) peaks, but the (111) reflection was still present. The position of the reflections in the YSZ:N films is shifted towards lower 2θ values compared to the films prepared in oxygen.

The re-oxidation process and loss of nitrogen of the YSZ:N films does not seem to influence the original (111) orientation. The (111) reflection shifts back to the position measured for YSZ films grown in oxygen, indicating that the nitrogen content influences the lattice parameter. As the (200) and as well the other reflection does not appear upon re-oxidation, the orientation is maintained. Thus, we can preferably grow (111) oriented YSZ films doped with nitrogen and we can subsequently oxidize the sample (removing nitrogen) retaining its orientation.

In Fig. 3 the position of the main (111) peak for the nitrogen doped films is found at smaller 2θ values than those calculated for cubic YSZ free of nitrogen. This result differs from those reported by Lerch [4] on YSZ:N powders, where a shift of the reflections was towards higher 2θ. However, an exact calculation of the lattice constant and the symmetry of our YSZ:N films was not possible, because of a distortion of the cubic fluorite type structure (and/or thermal stress) and the strong texturing. For the YSZ prepared in oxygen atmosphere this deviation is noticeable but smaller compared to the YSZ:N films.

Summarizing, two main results are obtained: (a) A distortion of the cubic symmetry in the YSZ and YSZ:N films can be observed. This might be due to the incorporated nitrogen and/or due to strain fields caused by the nano-crystalline film structures. The distortion is highly reduced after the re-oxidation/heat treatment.

(b) The deposition of films in different background gas led to different orientations of the crystalline films.

These observations require more intensive and systematic measurements in order to understand the underlying crystallographic details.

SIMS analysis—Influence of the deposition temperature: We find that an intermediate substrate temperature around 500 °C and 600 °C leads to the highest nitrogen content of YSZ deposited in nitrogen gas. At higher temperatures the nitrogen content is smaller and at lower temperatures the film quality is poor. At higher temperatures, the oxinitride is probably partially re-oxidized by oxygen impurities in the nitrogen atmosphere. In order to check this hypothesis, one ought to deposit YSZ in ultra-pure nitrogen atmospheres which is technically difficult. However, the intermediate temperature range appears to be a reasonable compromise between a declining film microstructure with decreasing substrate temperature and decreasing nitrogen incorporation with increasing substrate temperature.

Influence of the nitrogen partial pressure and the target-substrate distance: We found a maximum of the nitrogen content at a nitrogen gas pressure of 6 Pa, which can easily be rationalized. With decreasing pressure the interaction between the thermal plasma and the nitrogen background gas becomes weaker and the deposited films are subject to partial reduction. With increasing pressure the interaction becomes too strong and the plasma expansion is hampered, leading to a poor film quality in general. The same dependence of the nitrogen content on the nitrogen pressure with a maximum at a pressure of 6 Pa is found for the system Ga–O–N (reported in a forthcoming study).

During the experiments on the pressure variation, we also increased the distance between the target and the substrate from 4 to 5 cm. This led to a significantly lower nitrogen concentration. We assume that this weaker doping effect is caused by a kind of size selection. The larger the distance the less molecular species arrive at the substrate. Larger clusters and droplets arrive at the substrate even at large distances without severe scattering on their way. And these larger clusters and particles will react less with the background gas, thus reducing the doping effect in the growing film.

In essence, also the distance between target and substrate has an optimum value. Too small distances do not allow a sufficient interaction of plasma and background gas, too large distances favor the deposition of larger clusters and droplets. In our experiments we found a distance of 4 cm as best suited for a significant nitrogen doping.

Influence of the Y_2O_3 concentration: The maximum in the nitrogen content in 7YSZ:N thin films (Fig. 7) that the total defect concentration determined by the sum of cation and anion dopant is an important parameter. The fluorite-type lattice does only accommodate a limited number of anion vacancies, and a too high defect concentration leads to a saturation effect. Practically we reach an optimum which in our study is 7YSZ.

The doping of pure ZrO_2 or partially stabilized YSZ bulk material (powders and single crystals) with nitrogen by thermochemical methods has already been studied extensively by Lerch [4] and Lerch et al. [1–3, 5, 13] and it has been found that nitrogen alone (i.e., anion doping) cannot fully replace the cation doping. But as in our case, Lerch et al. report an upper limit of anion vacancies in the YSZ:N compound. However, a systematic study on the nitrogen doping as a function of the cation dopant concentration has not been performed.

XPS analysis—N 1s spectra: The reference value for the N 1s binding energy of the N^{3-} state in XPS is suggested in the literature [12] as 398.5 eV for the compound boron nitride. As BN is a covalent rather than an ionic compound this value can only serve as a rough guide line. In other XPS studies on nitrogen containing zirconia binding energies of 396.4 or 396.6 eV have been reported and assigned to N^{3-} in Zr_3N_4 [14]. Soto et al. [15] suggested the value of 397.6 eV for the N^{3-} state in ZrN, whereas Milosev et al. [16, 17], who investigated in situ the oxidation of ZrN to ZrO_2, have assigned the value of 397.3 eV. The same authors have suggested values of 396.3 and 400.05 eV for the nitrogen peaks of the oxinitride ZrO_2:N. A higher binding energy of 403.2 eV is attributed to adsorbed N_2 species. Other authors [18, 19] have registered a peak at 402.8 eV and suggested that this peak represents dinitrogen species in the solid. Finally Del Re [20] even attributed (after peak deconvolution) the value of the N 1s peak at 395.8 eV to a ZrN_2 compound. In general, the increase of the valence state of N^{3-} towards less negative values (oxidation) is always related to an increasing binding energy.

The N 1s peak positions in our spectra of thin YSZ:N films appear roughly at the same positions as reported by the other authors. However, we have to keep in mind that all data available from the literature describe pure (undoped) ZrO_2 and ZrN or Zr_3N_4. As it can be seen, the addition of Y_2O_3 to zirconia causes a shift in the Zr 3d and O 1s peaks of about 1 eV towards higher binding energies. So we can also expect a shift for the N 1s peak in YSZ. We suggest that the binding energies of 397.3 eV measured on 9.5YSZ and 13YSZ represent the oxinitride coordination in YSZ:N but not the Zr–N coordination as in the ZrN compound. At this stage we exclude the possibility of Zr_3N_4 formation as it would cause a large shift of the Zr 3d peak which has not been observed.

N 1s spectra of 7YSZ:N:The nitrogen N 1s peak position (Fig. 11) deviates from those recorded for ZrO_2, 9.5YSZ and 13YSZ. It is detected at 402.6 eV—a value very close to 402.8 eV reported by [19] for dinitrogen species. The results suggests that the high nitrogen concentration in 7YSZ:N is correlated with the presence of nitrogen species in a valence state more positive than 3–. At this stage it is still too early to conclude whether nitrogen is present as N^{3-}, N^{2-} or as already reported dinitrogen—N_2^{x-}. There are no systematic studies concerning this system and our results cannot be compared with known standards, but the existence of nitrates (i.e., N^{x+}) can be excluded because the binding energies of the nitrates are much higher (up to 10 eV) than those recorded for our films.

The main question we cannot answer unequivocally on the basis of the present results concerns the valence state of nitrogen in zirconia. Usually it is accepted that N^{3-} is incorporated in the anion sublattice and our results do not disagree with this hypothesis. But the N 1s peak at a high binding energy in 7YSZ:N is not in agreement with the simple picture of N^{3-} ions. Rather this observation suggests the existence of nitrogen molecular ions in the YSZ lattice. We cannot exclude this possiblity, as nitrogen dianions are stable in other ionic compounds. To confirm such suggestions more detailed studies with a monochromatic X-ray source with much higher intensity and better energy resolution (synchrotron radiation) are required in order to investigate in situ the changes of the nitrogen either during its incorporation (reduction) or upon oxidation. Combined with quantum mechnical calculations these experiments might clarify the valence state of nitrogen in YSZ. However, these findings should be taken as first hints and a systematic XPS study on YSZ and YSZ:N is clearly missing.

Zr 3d spectra

In YSZ:N (Fig. 9) the binding energies of the Zr 3d doublet are not shifted towards the values typical for the ZrN bond (about 180 eV) as suggested by [16, 17, 19, 21], but are closer to those assigned to the oxinitride coordination (182.2 eV), but is almost equal to the value for a nitrogen free YSZ.

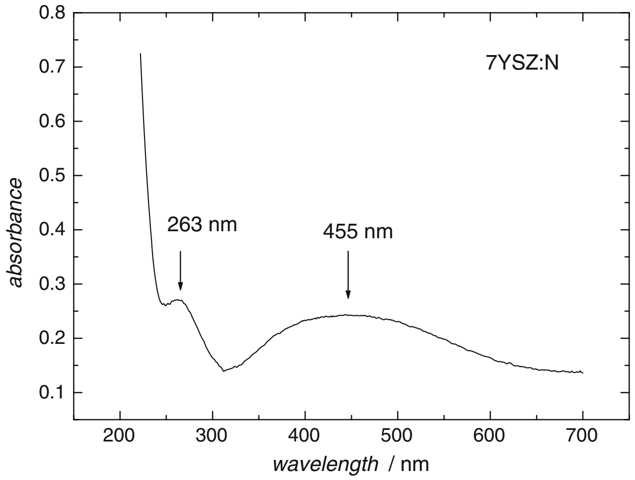

Fig. 13 Optical absorption spectrum of a 7YSZ:N film on sapphire (0001) at room temperature. Deposition conditions: $p(N_2) = 4$ Pa, $T = 500$ °C, $d = 4$ cm

The Zr $3d_{3/2}$ peak position is not shifted towards lower binding energies by the nitrogen incorporation, and thus, the reduction of Zr^{4+} can be excluded within the limit of detection. The depth profiling of different YSZ materials upon sputtering with argon ions (up to 2h) demonstrates that the Zr 3d peak remains unchanged for each YSZ composition. The recorded higher binding energies of Zr $3d_{3/2}$ in YSZ compared to ZrO_2 has to be explained by the changes of the crystalline structure of the films and the presence of yttrium.

O 1s spectra: No comprehensive study on the XPS spectra of pure and yttria doped zirconia can be found, and different opinions about the position of the O 1s peak in pure zirconia have been published. The reported binding energies for O 1s vary in the range from 529.7 to 530.9 eV [16, 17, 19, 21], whereas the value suggested in [12] is 531.3 eV. In our experiments, the addition of yttria to ZrO_2 shifts the O 1s peak towards higher binding energies by approximately 0.9 eV compared to those for the pure oxide.

Y 3d spectra: Y 3d spectra do not shift with increasing yttria content. We can definitely exclude a possible yttrium nitride formation from a further consideration because the suggested binding energies for the Y $3d_{3/2}$ peak in YN are much lower (156.6 eV) [22] than those recorded for our films (the standard for pure Y_2O_3 is $E_b =$ 158.4 eV).

Quantitative analysis of the XPS spectra: The nitrogen concentrations determined by XPS and SIMS do not agree exactly and differ by 20 up to 30%. As XPS collects the integral information from the whole surface of a sample and the concentrations given above are relative, and as SIMS data could also give an error of maximum 10%, this difference is acceptable. Nevertheless we can conclude that PLD is suitable for nitrogen doping and results in nitrogen concentrations of up to 10 at.%.

Additional information can be obtained from the relative concentration changes as determined by XPS (O 1s, Y 3d and Zr 3d). Obviously ZrO_2 dissolves only a small concentration of nitrogen under the given experimental conditions, and the metal/non metal ratio corresponds within the experimental error to a 1:2 stoichiometry. Roughly the same 1:2 ratio is obtained for the 9.5YSZ:N and 13YSZ:N films, but the yttrium/zirconium ratio is unreasonaby high. Clearly the 7YSZ:N film shows the highest nitrogen content, corresponding to approx. 16% of the anions. But the metal/non metal ratio is here unreasonably small (approx. 1:2.7). Even neglecting nitrogen, oxygen to metal ratio is still too high. Thus, at this point we can only conclude that nitrogen has definitely been incorporated with concentrations of several per cent. The exact content cannot be given. Whereas the integration of the XPS peaks leads to unreasonable results, the spectra themselves are reliable and give clear evidence for the homogeneous dissolution of atomic nitrogen in YSZ. Only in the case of 7YSZ:N there is additional evidence for molecular nitrogen species.

Optical spectroscopy: YSZ:N shows a broad absorption band around 500 nm, while the nitrogen free reference samples prepared in oxygen and argon atmospheres show practically no absorption in the UV and VIS range. Like in the SIMS and XPS studies, the nitrogen-doped 7YSZ:N sample exhibits a different behavior and shows an additional absorption maximum at 263 nm. This maximum might also be related to a second type of nitrogen differing in its charge or in its position in the lattice of zirconia. The broad absorption around 500 nm is typical for nitrogen doped and/or reduced material [23] and suggests that nitrogen energy levels are placed almost in the middle of the band gap in the non-stoichiometric zirconia. This finding is clearly supported by theoretical calculations [24].

Conclusions

Crystalline YSZ:N films of high quality and with relatively high concentrations of nitrogen (several at.%) can easily be prepared by PLD in molecular nitrogen background gas (electrochemical doping has been recently reported [25, 26]). The YSZ films deposited in oxygen and nitrogen atmosphere show a small distortion in the cubic symmetry, and the films grown on sapphire (0001) are preferably orientated in (111) direction. The highest nitrogen contents have been achieved at intermediate temperatures between 500 and 600 °C and a nitrogen gas pressure of 6 Pa. The effect of the yttria content in the targets is pronounced showing a maximum of the nitrogen concentration at 7 mol% Y_2O_3. Along with this maximum in the nitrogen content, 7YSZ:N shows specific features in the XPS analysis and optical absorption. A high binding energy of the N 1s state suggests either the existence of molecular nitrogen ions or of single ions with a valence state more positive than 3–. The nitrogen content does not influence both the binding energies of Y 3d and the Zr 3d peaks, and thus, we exclude any significant cationic reduction of the films.

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