Thin Film Model Systems of ZrO₂ and Y₂O₃ as templates for potential industrial applications investigated by means of electron microscopy

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Abstract

An analytical high-resolution electron microscopy study of Y_2O_3 and ZrO_2 thin films, being relevant oxide model systems for a range of industrial applications, is reported. Both films were deposited on vacuum-cleaved $\text{NaCl}(001)$ single crystal planes at varying substrate temperatures. A transition from an amorphous to a well-defined and γ -ordered structure, exhibiting almost single-crystalline ordering of either body-centered cubic Y_2O_3 or tetragonal ZrO_2 , both with uniform electronic structure, has been observed upon raising the substrate temperature from 300 to 573 K. Pronounced crystallographic relationships between the face-centered cubic NaCl structure and the structures of the deposited oxides have been held responsible for the observed epitaxial growth. In summary, the chosen preparation pathway represents an easy and reproducible method to yield well-defined oxide structures at surprisingly low substrate temperatures being at the same time promising model candidates for materials-related (e.g. solid-oxide fuel cell) research. With respect to solid-oxide fuel cell technology, monitoring carbon deposition and reactivity following high-temperature treatments in hydrocarbon-containing gas feeds or the use as templates or supports for model systems of realistic anode materials on metallic or bimetallic basis are envisioned application areas.

1. Introduction

Among the transition metal oxides, both yttrium oxide/yttria (Y_2O_3) and zirconium oxide/zirconia (ZrO_2) exhibit a number of interesting and useful properties to render them appealing candidates to be used in variety of different technological applications. Both oxides are refractory materials with high chemical stability and are increasingly used in superconducting, microelectronics or ceramics industry [1-5]. One particular interesting application, which combines the strength of both materials, is the use of yttria-stabilized zirconia as ionic conductor in solid oxide fuel cells [6]. In this particular case, substitution of Zr^{4+} centres by Y^{3+} cations in the ZrO_2 structure, causing the formation of “yttria-stabilized zirconia (YSZ)”, leads to better ionic conductivity and at the same time partly or fully stabilizes metastable high-temperature ZrO_2 modifications (monoclinic ZrO_2 represents the stable modification at room temperature), depending on the yttria content [6]. In combination with a catalytically active metal, usually Ni, yttria-stabilized zirconia forms the anode of solid-oxide fuel cells and is responsible for the electro-oxidation of the combustion gas [7]. It is clear, that for a thorough understanding of the combination of both oxides, the performance of the single constituents have to be accurately known. This is especially important, as for yttria, its defect chemistry has been suspected to play a major role in influencing especially the chemical and mechanical properties [1] and particularly the polymorphism of ZrO_2 has been reported to crucially affect ceramic properties or catalytic performance [4]. Re-addressing SOFC applications again, especially ZrO_2 has been reported to catalyze the formation of carbon whiskers following carbon deposition [8], the latter being one of the main problems in fuel cell technology, eventually short-circuiting the entire cell or leading to stress-induced fracture of porous Ni cermet electrodes [7]. Given the importance and the problems faced if the presented oxides are used in research and application, the need for well-defined and-structured model oxide systems of Y_2O_3 and ZrO_2 , which can be used to study these properties in depth, is even more imperative. One particular promising pathway, which

has proven its strength already in a number of studies focusing on the preparation of well-defined metal [9], bimetallic [10] and oxide systems [11,12], is the use of well-structured vacuum-cleaved NaCl(001) single crystal facets as growth templates. This preparation exploits eventual crystallographic relationships and wetting phenomena at the oxide-NaCl interface to result in epitaxially grown, or at least very well-ordered particles, typically at much lower substrate temperatures (~ 573 K) than usually applied in various deposition processes [11-13]. The so-prepared systems are in turn especially suited for structural characterization by high-resolution electron microscopy (due to the presence of low-index zone axes) and the establishment of all kinds of structure-activity or –property relationships (e.g. catalytic activity/selectivity, mechanical or sensor properties) [9-14]. The chosen preparation pathway also offers the additional advantage of yielding free-standing, self-supported thin film model systems, i.e. no additional film/template interface is present after removal of NaCl, thereby excluding additional effects of this potential interface in subsequent treatments.

The aim of the present study therefore is to easily and reproducibly prepare thin film model systems of both Y_2O_3 and ZrO_2 and to provide a thorough structural, morphological and electronic characterization of the eventually well-ordered films that can in turn be used as an initial reference state for subsequent characterization of the material's properties. Method-wise, the analysis will be based on analytical high-resolution electron microscopy, with special emphasis on structural and crystallographic analysis by selected-area electron diffraction (SAED) and high-resolution imaging, on chemical composition analysis by Z-contrast (i.e. HAADF - (high-angle annular dark-field)) imaging and on investigating of the electronic structure by electron-energy loss spectroscopy (EELS).

2. Experimental

Thin film model systems of Y_2O_3 and ZrO_2 were prepared in a dedicated high-vacuum chamber operating at a base pressure of $1 \cdot 10^{-6}$ mbar [10]. Both oxides were thermally deposited on vacuum-cleaved NaCl (001) single crystal facets, either by reactive deposition of metallic Y in $1 \cdot 10^{-4}$ mbar O_2 or by reactive deposition of ZrO_2 under reducing conditions in $1 \cdot 10^{-5}$ mbar H_2 . The latter was found to be necessary to suppress the evaporation of volatile W oxides during the deposition process. This is one of the most crucial steps in the entire preparation process and a significant word of caution should be added at this stage. Preparation of ZrO_2 and Y_2O_3 films by simple thermal evaporation is by no means a trivial business due to the low vapor pressure of both oxides. Both exhibit a vapor pressure of $\sim 10^{-4}$ mbar at roughly 2500 K and 2300 K, which among the oxides are comparably very high temperatures for a given and meaningful vapor pressure. This in turns puts serious demands on the crucibles that are used and basically only tungsten and tantalum fulfill the stability requirements. Tungsten appears to be the recommended choice [15]. However, both materials offer the serious drawback of forming volatile sub-stoichiometric oxides that are prone to evaporate if an oxygen background is established in the HV chamber to suppress the formation of oxygen-deficient Y_2O_3 or ZrO_2 structures. Adjusting the preparation conditions to suppress tungsten or tantalum oxides almost completely has been a serious task and the above-discussed conditions are the most promising. For ZrO_2 , even a moderate hydrogen background pressure deemed necessary. As outlined in the forthcoming section, this nevertheless causes the formation of stoichiometric ZrO_2 .

For both oxides, such a preparation led to mechanically stable films of about 25 nm thickness (as deduced from quartz crystal microbalance), which were detached from the NaCl template by dissolving the latter in distilled water and finally mounting the so-obtained free-standing films on gold grids for electron microscopy. Structural and morphological analysis of the so-prepared samples were performed either using a Zeiss 10 EM 10C or a 200 kV FEI TECNAI F20 STWIN Analytical (Scanning-) Transmission Electron Microscope (S)TEM equipped

with a Tridiem energy filter. Prior to imaging, the samples were sputter-cleaned to remove surface carbon impurities. The film composition was checked by Energy-dispersive X-ray Spectroscopy (EDXS). Basically only peaks due to the evaporated elemental thin film constituents (Y, Zr and O) and the gold grid (Au) were detected. Different amounts of Na (but always less than about 3%) were sometimes detected, too. However, Cl was never observed. The purity of the substrate was ensured by freshly cleaving the NaCl(001) crystals immediately before deposition of the oxide. The SAED patterns were externally calibrated with respect to the Pd (111), (200) and (220) spots in a separately prepared thin film, investigated under identical conditions. Structural modeling and simulation of the electron diffraction patterns was performed using the JEMS program [16].

3. Results and Discussion

3.1. Characterization of the Y_2O_3 structure

Figure 1A highlights the structure and morphology of the Y_2O_3 films, prepared at 300 K substrate temperature. A fine-crystalline, quite regular and structurally homogeneous structure is obtained. The SAED pattern (shown as inset) reveals only broad halos, typical for almost amorphous structures. One particular problem being encountered upon investigating Y_2O_3 films by TEM is shown in Figure 1B. Prolonged exposure to the electron beam (~ 10 minutes) induces crystallization of the amorphous structure, leading to enhanced Bragg contrast in the images as well as the appearance of Debye-Scherrer-type reflections in the diffraction patterns. The most intense reflections can be addressed to the (222), (400), (125) and (145) lattice spacings of the bcc Y_2O_3 structure, measured at 3.05, 2.63, 1.90 and 1.63 Å ($d_{\text{theor}}(222) = 3.058$ Å, $d_{\text{theor}}(400) = 2.648$ Å, $d_{\text{theor}}(125) = 1.934$ Å and $d_{\text{theor}}(145) = 1.634$ Å) [17]. Since the evolution of the structure at high substrate or annealing temperatures is of particular importance for the subsequent preparation of metal-containing catalyst systems, Figure 2

reveals the structure of Y_2O_3 films prepared at 373 and 573 K, respectively. Already after deposition at 373 K, the structure of the film drastically changes and a significantly higher contrast is observed in the overview TEM image. Alongside these changes, the SAED patterns indicate formation of a polycrystalline structure, somewhat similar to the one observed after deposition at 300 K and subsequent irradiation. However, a careful analysis of the diffractograms already reveal faint spots superimposed on the Debye-Scherrer-type ring reflections, implying the presence of grains oriented along distinct orientations and zone axes. This trend is amplified at even higher substrate temperatures. Raising the temperature to 573 K, a characteristic structure consisting of elongated crystals, oriented only in-parallel or perpendicular to each other, is obtained. The sizes of the longer side of the crystals varies between 5 and 15 nm, the corresponding shorter outlines of the grains amount to a specific size of around 5 nm. Contrast variations are frequently observed and, as revealed by the SAED patterns of Figure 2C, mainly due to Bragg contrast. The SAED pattern itself is typical of an almost single-crystalline ordering of the grains. Only spot reflections, sometimes broadened indicating a lower degree of orientational ordering, are encountered. Table 1 summarizes and compares the experimentally determined distances of the SAED pattern to the ones of the bixbyite-type structure of body-centered cubic Y_2O_3 (lattice constant $a=10.596$ Å, PDF pattern number of the ICDD data base 01-071-0049), revealing a high degree of matching between theoretical and experimental lattice spacings [17]. The SAED pattern can in turn also be used to determine the orientation of the grains with respect to the electron beam. Using the marked spots in the diffraction pattern, a crystallographic analysis yields an orientation of [001], i.e. the epitaxial relationship between bcc Y_2O_3 and fcc NaCl(001) is mostly

$$\text{Y}_2\text{O}_3 [001] // \text{NaCl}[001].$$

This orientational relationship is related to the cube/cube orientation, being typical for structural arrangement of similar cubic structures. In the present case, the epitaxial growth is based on the close relationship between some of the lattice planes of the bcc Y_2O_3 and fcc NaCl structure. For example, the (400) lattice plane of Y_2O_3 and the (200) lattice plane of NaCl (2.64 Å [17, 18] vs. 2.73 Å [19]) match to a degree of 98 %, corroborating previous results regarding the epitaxial growth of small metal and oxide particles on NaCl(001) [9-13] and further emphasizing the outstanding role of NaCl as a growth template. Figure 2D correlates the experimental SAED pattern to that of a simulated electron diffraction pattern for Y_2O_3 grains oriented along the [001] direction to the electron beam, confirming the assumed orientation relation. So far, only crystallographic arguments have been stressed for the observed contrast variations. To fully exclude contributions from chemical inhomogeneities, STEM imaging under Bragg- and Z-contrast conditions has been performed. Since the observed Z-(or HAADF-) intensity is strongly dominated by variations in the average atomic number Z (proportional to $Z^{1.5-2}$ depending on the effective collection angle of the detector, which is dialed by the choice of the camera length of the microscope), constant thickness and density assumed, differences in the chemical compositions should be visible under Z-contrast conditions. This comparison is shown in Figure 3. Figure 3A highlights the contrast of the sample under Bragg contrast conditions (camera length 300 mm), Figure 3B under Z-contrast conditions (camera length 30 mm). In the latter case, only thermally-diffuse scattered and electrons from high scattering angles contribute to the image. In Figure 3A, the contrast from the different orientations of the grains is still visible. However, the corresponding Z-contrast image reveals only a homogeneous structure with no contrast variations. It is therefore safe to assume, that no chemical inhomogeneities in the film exist and the contrast variations are purely caused by Bragg contrast. High-resolution images, as exemplified in Figure 4, show a variety of lattice fringes. The ones that are most frequently encountered are the (211), (125), (222) and (400) lattice spacings. The first two, probably arising from overlapping Y_2O_3

grains, are shown in the respective HRTEM image, alongside a Fourier transform of a part of the image. We note at this stage, that the presented preparation of well-defined almost single-crystalline films allows to overcome one of the most serious drawbacks outlined in the previous studies on the growth and use of Y_2O_3 films-the fact that many applications of Y_2O_3 were and are limited by the presence of different crystallographic orientations if as usually grown on polycrystalline deposits (e.g Si wafers) [3]. A further advantage that becomes evident at this stage is related to the suppressed occurrence of possible phase transformation between different polymorphic forms of Y_2O_3 at very high substrate temperatures. In this respect, Pailloux et al. detected the simultaneous presence of monoclinic Y_2O_3 after deposition at 973 K at the interface $\text{Y}_2\text{O}_3/\text{MgO}$ [3], which could in the present case be basically circumvented by the use of much lower substrate temperatures.

As for a full characterization of the sample also information about the electronic structure has to be provided, Figure 5 focuses on the development of the electronic structure upon changing deposition parameters, as measured by EELS. Figure 5A and B highlight the stripped edge as well as the high energy-loss region. In general, the energy-loss near-edge structure does not change very much with substrate temperature and still exhibit very similar features in both regions. As a judgment of the oxidation state of Y in Y_2O_3 , usually the intensity ratio of the two peaks of the O-K edge is used [3]. For stoichiometric bulk Y_2O_3 , the peak at the lower energy loss is smaller, which can also be anticipated in the O-K edge displayed in Figure 5A. We can therefore conclude, that the overall stoichiometry of the film is close to Y_2O_3 and a substantially defective structure is absent at both temperatures.

3.2. Characterization of the ZrO_2 structure

The structural evolution of the ZrO_2 film is highlighted in Figure 6A (300 K) and 6B (573 K). Similar to Y_2O_3 , the film structure at low substrate temperatures is of amorphous nature. Hardly any contrast variations are seen in the overview TEM images and also the SAED

pattern basically reveals diffuse halos. In contrast, at 573 K substrate temperature, the contrast is significantly enhanced and a structure consisting of elongated grains develops (Figure 6B). The corresponding SAED pattern (Figure 6C) reveals partial ordering of the grains, with broad elongated spots superimposed on a series of ring reflections. Comparing the SAED pattern to Y_2O_3 obtained after deposition at similar temperatures, we note general less ordering. However, some ordering exists, but a quasi-single-crystalline pattern as for Y_2O_3 has never been observed. This is easily understood on the basis of the crystallographic relationships of the prepared Zr-O compound with the underlying $\text{NaCl}(001)$ template. Phase analysis of the diffraction pattern (cf. Table 1) indicates the presence of well-ordered tetragonal ZrO_2 . The analysis is based on the experimental determination of a series of strong diffraction spots/rings at 2.98, 2.57, 2.11, 1.83, 1.56, 1.29, 1.17 and 1.05 Å, corresponding to the (101), (110), (102), (112), (211), (220), (213) and (312) lattice planes ($d_{\text{theor}}(101) = 2.96$ Å, $d_{\text{theor}}(110) = 2.540$ Å, $d_{\text{theor}}(102) = 2.104$ Å, $d_{\text{theor}}(112) = 1.815$ Å, $d_{\text{theor}}(211) = 1.536$ Å, $d_{\text{theor}}(220) = 1.271$ Å, $d_{\text{theor}}(213) = 1.177$ Å, $d_{\text{theor}}(312) = 1.041$ Å) of the tetragonal ZrO_2 compound (lattice constants $a = 3.596$ Å, $b = 5.185$ Å, PDF number 01-079-1768) [20]. We note at this stage, that we are aware of the fact that for ZrO_2 cubic and tetragonal structures with very similar lattice parameters exist [4]. Cubic ZrO_2 exhibits a lattice constant of 5.11 Å [21]. Therefore discrimination between these two phases is not straightforward by SAED. However, the measured reflection at 2.11 Å exists only for tetragonal ZrO_2 and thus serves as a convenient tool to exclude the presence of the cubic modification in the present case. Formation of the tetragonal structure represents an interesting result, since generally the monoclinic phase is the thermodynamically stable phase at room temperature and tetragonal ZrO_2 is only metastable [4]. A variety of methods for stabilizing the tetragonal ZrO_2 phase exist, including Y-doping or stabilization by co-existence of monoclinic and tetragonal ZrO_2 [4]. Tetragonal ZrO_2 has also been prepared by chemical solution deposition processes at temperatures of 973 K [22]. In general, the polymorphism of ZrO_2 has already been

scrutinized in detail, specifically including the phase transformation between monoclinic and tetragonal and tetragonal to monoclinic, respectively [23]. Addressing the question, what specifically stabilizes the tetragonal ZrO_2 phase in the present case, two explanations are in principle at hand on the basis of available literature: Firstly, it has been reported that specifically, the similarity of tetragonal ZrO_2 to that of amorphous hydrous ZrO_2 has been held responsible for preferential formation of the tetragonal phase [23, 24]. In that respect, also a mechanism of topotactic growth of tetragonal ZrO_2 on nuclei of amorphous hydrous ZrO_2 has been discussed by Tani et. al. [24]. Secondly, focusing on the stability of nanoparticulate tetragonal ZrO_2 , a critical diameter below which the tetragonal phase is stable, has been determined theoretically and experimentally to between 5-40 nm. The experimentally-determined values were without exception higher than the theoretically determined ones. This discrepancy was in part explained by adsorption of different species (especially water), subsequently changing energetic stability considerations [23]. Various explanations have been given in order to account for the stability of the nanoparticulate metastable tetragonal phase at ambient conditions, including surface energy issues, presence of anionic vacancies or domain boundaries [23,26-29]. The ultimate reason for stabilization is, however, not entirely clear yet. Although we cannot exclude some of the reasons discussed above, one of the most promising arguments for explaining the stability of the tetragonal phase in the present case is related to the use of “crystallization aids”, i.e. the appearance of the tetragonal structure is related to crystallographic relationships with similar structure, thereby kinetically favoring the formation of this particular crystal structures [4,23]. This is a concept that has been verified in a number of previous investigations using NaCl as a growth substrate [9-14], hence we therefore tentatively relate the appearance of the tetragonal structure also to the above-mentioned crystallographic relationships of ZrO_2 with the NaCl template. This is evidenced by a comparison of the experimentally obtained SAED patterns with simulated electron diffraction patterns of tetragonal ZrO_2 samples in different

orientations. Hence, the spots in the SAED pattern shown in Figure 6C can be addressed to ZrO_2 grains oriented along the $[111]$ zone axis. We note that the SAED pattern can only be consistently interpreted by the presence of different domains, i.e. ZrO_2 grains oriented along the $[111]$ zone axis but along different azimuthal orientations. In addition, of course, several grains not specifically oriented contribute to the SAED pattern, too. Summarizing, although the crystallographic relationships are obviously not as pronounced as in the case of Y_2O_3 , the NaCl structure also acts as a rather efficient stabilization agent for the tetragonal ZrO_2 structure at comparably low substrate temperatures.

To clarify the observed contrast structure, in a similar line of arguments as for Y_2O_3 , a combination of dark-field and Z-contrast imaging has been employed. Figure 7 highlights a comparison of STEM images taken under Bragg- (7A, camera length 300 mm) and Z-contrast (7B, camera length 30 mm) conditions. Whereas the film structure is still visible under Bragg-contrast conditions, a very homogeneous structure is obtained under Z-contrast conditions. Hence, we conclude that also in the case of tetragonal ZrO_2 , the contrast variations in bright field TEM images are basically due to Bragg contrast rather than chemical inhomogeneities. Corroborating these results, dark-field images taken using different diffraction spots clearly indicate the crystallographic variations of different ZrO_2 grains within the film (Figure 8A and B). A representative HRTEM image is shown in Figure 9, revealing a fair number of ZrO_2 grains in different orientations (as also shown in the Fourier transform). By far the most common lattice fringes observed, and also depicted in Figure 9, are related to the (101) spacings measured at 2.97 Å.

Focusing on the electronic structure of the samples, shown in Figure 10 (stripped edge 10 A, high-loss region 10 B), we note that some minor differences exist in the stripped edge, but the overall features are quite similar and specifically, the O-K energy-loss near-edge structure is comparable, indicating – in a similar line of argumentation as for Y_2O_3 – that the overall

stoichiometry is close to ZrO_2 . As mentioned in previous publications, it should in principle be possible to distinguish between the three polymorphic phases of ZrO_2 - cubic, tetragonal and monoclinic - using the splitting of either the Zr L2 white line or the Zr M3 edge [30]. Equally, the electron-loss near-edge structure of the O K-edge has been exploited for discrimination of the different polymorphs [30]. However, as several drawbacks in the analysis exist, namely, the long acquisition times of the spectrum at high energy losses due to the poor signal-to-noise ratio (to measure the Zr L2 edge), the difficulty to subtract the background under the Zr M2,3 edges and the generally only very small differences in the O K-edge structures [30], unambiguous addressing of the EEL spectra to either the amorphous ZrO_2 or the a single tetragonal ZrO_2 phase is not possible in the present case.

4. Conclusions

In conclusion, we have shown that the thin film model approach can be successfully exploited to reproducibly prepare films of two oxide systems with highly relevant applications in different industrial- and research-oriented areas, but specifically also in solid oxide fuel cell technology. Exploiting the outstanding properties of NaCl single crystal facets as growth templates, well-ordered and -defined Y_2O_3 and ZrO_2 films have been deposited by epitaxial growth. We also emphasize that part of the attractivity and superiority of the prepared model systems is related to the preparation at quite low substrate temperatures, basically limited by the vapor pressure of the NaCl template, in any way excluding substrate temperatures higher than 673 K. Hence, the very high preparation temperatures usually applied ($T > 773$ K) are efficiently circumvented. An essential feature of the so-prepared systems is furthermore related to the unique possibility to study structural changes eventually occurring upon treatments in different gas atmospheres or during catalytic reactions and to subsequently establish unambiguous structure-activity or structure-property relationships. Referring to a

current hot topic in SOFC-relevant applications, this e.g. might include monitoring the deposition and reactivity of different carbon-containing species being formed upon annealing treatments in hydrocarbon-containing gas mixtures. Moreover, as a next logical step, Y_2O_3 and ZrO_2 are promising candidates to be used as supporting oxides for small metal or bimetallic particles on Cu- or Ni-basis. This in turn would also open the possibility to easily obtain highly ordered model systems of SOFC-relevant anode materials.

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Figure Captions

Figure 1 TEM overview images of a Y_2O_3 film deposited at 300 K substrate temperature in the initial state (A) and after irradiation with the e-beam for 10 minutes (B). The corresponding electron diffraction patterns are shown as insets

Figure 2 TEM overview images of a Y_2O_3 film deposited at 373 K (A) and 573 K substrate temperature (B). The electron diffraction pattern of (A) is shown as inset, the corresponding pattern of film (B) in a separate panel C. Panel D depicts the simulated electron diffraction pattern of bcc Y_2O_3 oriented along the [001] zone axis

Figure 3 STEM images of the Y_2O_3 film deposited at 573 K under Bragg-contrast (A, camera length 300 mm) and under Z-contrast conditions (B, camera length 30 mm)

Figure 4 High-resolution electron micrograph of the Y_2O_3 film deposited at 573 K exhibiting (211) and (125) lattice fringes of the bcc Y_2O_3 structure

Figure 5 Electron-energy loss spectra of the stripped edge (A) and the high-loss region (B) collected on the Y_2O_3 film after deposition at different substrate temperatures, as indicated in the figure

Figure 6 TEM overview images of a ZrO₂ film deposited at 373 K (A) and 573 K substrate temperature (B). The electron diffraction pattern of (A) is shown as inset, the corresponding pattern of film (B) in a separate panel C. Panel D depicts the simulated electron diffraction pattern of tetragonal ZrO₂ oriented along the [111] zone axis

Figure 7 STEM images of the ZrO₂ film deposited at 573 K under Bragg-contrast (A, camera length 300 mm) and under Z-contrast conditions (B, camera length 30 mm)

Figure 8 Dark-field images of the ZrO₂ film prepared at 573 K substrate temperature taken with the (101) spot (A) and the (112) spot (B). The electron diffraction pattern is shown as insets. The relevant spot, which has been used for dark-field imaging, is marked by a circle

Figure 9 High-resolution electron micrograph of the ZrO₂ film deposited at 573 K exhibiting sets of (101) and (125) lattice fringes of the tetragonal ZrO₂ structure

Figure 10 Electron-energy loss spectra of the stripped edge (A) and the high-loss region (B) collected on the ZrO₂ film after deposition at different substrate temperatures, as indicated in the figure.

Table 1

Correlation of the experimentally determined lattice spacings d_{measured} [Å] to those of body-centered cubic Y_2O_3 and tetragonal ZrO_2 ($d_{\text{theoretical}}$ [Å]) alongside assignment to distinct theoretical lattice planes, characterized by $d(hkl)$

Y_2O_3 deposited at 573 K				
d_{measured} [Å]	$d_{\text{theoretical}}$ [Å]	Assignment $d(hkl)$		
5.264	5.297	2	0	0
4.322	4.325	2	1	1
3.767	3.746	2	2	0
3.064	3.058	2	2	2
2.649	2.648	4	0	0
2.504	2.497	4	1	1
2.374	2.369	4	2	0
2.256	2.259	3	3	2
2.173	2.162	4	2	2
2.084	2.077	1	3	4
1.937	1.934	1	2	5
1.778	1.765	6	0	0
1.733	1.718	6	1	1
1.683	1.675	0	2	6
1.636	1.634	1	4	5
1.598	1.597	6	2	2
1.561	1.562	1	3	6
1.504	1.498	5	4	3
1.472	1.469	0	4	6
1.320	1.324	8	0	0
1.215	1.215	6	6	2
ZrO_2 deposited at 573 K				
d_{measured} [Å]	$d_{\text{theoretical}}$ [Å]	Assignment $d(hkl)$		
2.957	2.954	1	0	1
2.604	2.592	0	0	2
2.112	2.104	1	0	2
1.832	1.815	1	1	2
1.556	1.557	1	0	3
1.517	1.535	2	1	1
1.294	1.296	0	0	4
1.204	1.177	2	1	3