

# Evolution of yttria-stabilized zirconia (100) surface morphology with temperature

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## Abstract

The evolution with temperature of the morphology of yttria-stabilized zirconia (100) stepped surfaces has been studied by AFM in a non-contact dynamic mode in air. The characteristics of the surface structure as the average step heights and terrace widths are determined as a function of the annealing temperature. Step formation begins around  $0.43 T_M$  (1000 °C). Step coalescence is observed above  $0.50 T_M$  (1200 °C) and leads to a stable stepped structure at  $0.60 T_M$  (1500 °C). The processes responsible for the structural evolution observed on the sample surfaces are discussed and a comparison with results obtained on  $Al_2O_3$  (0001) single crystal surfaces under similar experimental conditions is presented.

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## 1. Introduction

Yttria-stabilized zirconia (YSZ) has been extensively studied in many technological fields. Because of its high ionic conductivity, it is quite often used as an electrolyte material for devices, such as the solid oxide fuel cell and oxygen separators.<sup>1,2</sup> It may also be used as a substrate for film deposition or epitaxial growth of oxides.<sup>3</sup> Moreover, YSZ is a potential candidate as an inert matrix for actinide immobilization or transmutation<sup>4</sup> due to its high melting point and its strong resistance against irradiation. It is well known that the physico-chemical properties of YSZ surfaces are involved in all these applications. For instance, the initial surface structure affects drastically the physical properties of grown films.<sup>5</sup> Thus, a detailed knowledge of the surface morphology of YSZ single crystals is of great interest for future uses. It is also important to study the kinetics of formation of characteristic features on the surface, as

steps and associated terraces. Furthermore, the evolution of the surface topography with temperature at a nanometer scale is useful to understand rather complex diffusion mechanisms at the surface.

Conventional methods, such as scanning (SEM) or transmission (TEM) electron microscopy, are limited by the insulating character of YSZ.<sup>6</sup> Thus, the most appropriate technique to study the surface structure of YSZ at the nanometric scale is atomic force microscopy (AFM). A lot of surfaces of oxide single crystals as sapphire ( $Al_2O_3$ ) or magnesia (MgO), have been investigated with this technique.<sup>8–10</sup> The MgO (100) surface has been found to roughen and its step structure to disappear at high temperature ( $T \geq 1500$  °C), whereas a faceting process has been observed on the  $Al_2O_3$  (0001) surface. Nevertheless, only a few studies have been carried out on YSZ surfaces and their morphology evolution has not been yet investigated.<sup>5,7</sup>

This paper presents a study by AFM in air of the evolution at medium and high temperature (up to 1500 °C) of surfaces of (100)-oriented yttria-stabilized zirconia single crystals. Similarities with other oxide surfaces as  $Al_2O_3$  are subsequently discussed. To make the comparisons possible, we use both the temperature and the normalized temperature with the melting point  $T_M$  of YSZ ( $T_M = 2700$  °C) when we refer to annealings.

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## 2. Experimental

The samples consist of cubic (100)-oriented zirconia single crystals fully stabilized with 9.5 mol% yttria. They are mechanically and chemically polished by the manufacturer (NEYCO). In order to eliminate any factor of dispersion in the initial surface state, the whole study is carried out on a unique sample. Before annealing, it is cleaned in acetone and isopropyl alcohol. It is then heated in air for 1 h successively at 1000, 1200, 1400 and 1500 °C in a pure alumina furnace tube. After each annealing, the sample surface is studied by AFM in air at room temperature. At high temperature ( $T > 1000$  °C), the cooling time of the furnace is very fast ( $> 100$  °C/min). Thus, the morphology of surfaces observed at room temperature reflects the one obtained immediately after the annealings performed in the (1000–1500 °C) range because of short range diffusion processes during the cooling. Topographical images of the YSZ surface are recorded using a home-made AFM setup in a non-contact dynamic mode (frequency modulation detection method). They are obtained in a constant frequency mode. This detection mode, using a custom demodulator, enables a better resolution with a higher speed compared to commercial systems.<sup>11</sup> The images are all unfiltered and the maximum probed size is  $5 \times 5$   $\mu\text{m}^2$ .

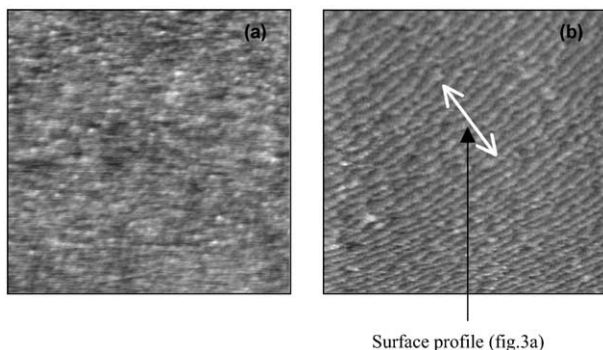


Fig. 1. (a) Surface morphology of a (100)-oriented YSZ sample ( $5 \times 5$   $\mu\text{m}^2$ ) before and (b) after annealing in air during 1 h at 1000 °C— $0.43 T_M$ .

## 3. Results

Figs. 1 and 2 present a series of typical images of a YSZ single crystal after annealings at various temperatures. The surface of the as-received and cleaned sample prior to annealing (Fig. 1a) is very smooth, with a mean roughness below 0.5 nm as determined by AFM. The image shows similarities with those obtained for magnesia (100) surfaces.<sup>10</sup> Unlike sapphire (0001) surfaces, YSZ ones do not display an arrangement of parallel steps.<sup>12</sup>

Only few changes in the surface morphology are observed before  $0.43 T_M$  (1000 °C). At this temperature, the  $5 \times 5$   $\mu\text{m}^2$  AFM images clearly show regularly spaced and roughly parallel steps (Fig. 1b). The step direction is almost the same in all the probed areas. Fig. 3 shows line profiles perpendicular to the step edges which are calculated from the AFM images presented in Figs. 1 and 2 at 1000 and 1500 °C. These analyses allow the determination of characteristic dimensions as step height and terrace width. At  $0.43 T_M$ , the average terrace width is 160 nm and the average step height is 0.5 nm (Fig. 3a), which corresponds to the dimension of one YSZ unit cell. Hereafter, 0.5 nm-high steps will be called monosteps. It is worth noting the greater resolution of the YSZ surface images compared to the ones of sapphire and magnesia surfaces. The lower chemical reactivity of YSZ surfaces to contaminants in air may be responsible for such a result.

Further annealings at higher temperatures lead to drastic modifications of the YSZ surface morphology. Steps of different heights and larger terraces form as the temperature increases. However, the annealing temperatures do not influence the initial step direction observed at 1000 °C. Fig. 4 shows histograms of the step heights calculated from numerous AFM images ( $\approx 20$ ), at different annealing temperatures. The results obtained at  $0.50 T_M$  (1200 °C) and  $0.56 T_M$  (1400 °C) show that the number of monosteps decreases. Consequently, steps with 1 nm in height and flatter terraces reaching widths up to 350 nm appear (Fig. 2a and b).

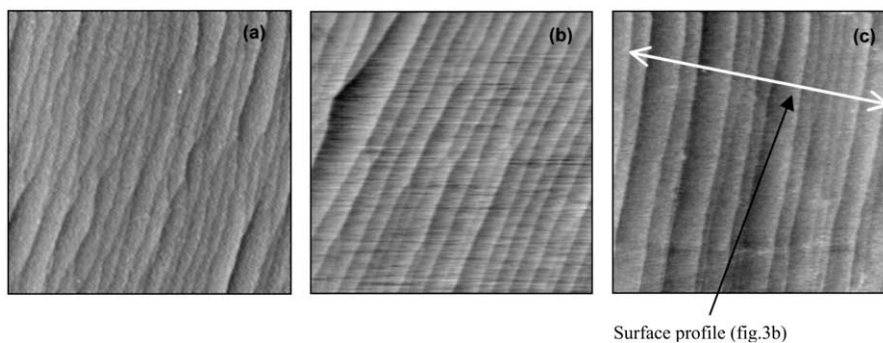


Fig. 2. Surface morphology of a (100)-oriented YSZ sample ( $5 \times 5$   $\mu\text{m}^2$ ) after annealing in air during 1 h at (a) 1200 °C— $0.50 T_M$ , (b) 1400 °C— $0.56 T_M$  and (c) 1500 °C— $0.60 T_M$ .

Only a few percent of steps higher than twice the YSZ unit cell are detected.

The analysis of the AFM images obtained at higher temperatures reveals how the surface morphology develops. At  $0.50 T_M$  (1200 °C), a coalescence process mainly involving monosteps starts (Fig. 5a). At  $0.56 T_M$  (1400 °C) (Fig. 5b), the coalescence of monosteps and double steps leads to the formation of higher steps (i.e. steps of 2 nm in height). The step meandering disappears and the step edges become straighter.

At  $0.60 T_M$  (1500 °C), a higher number of multisteps (i.e. steps with different heights) reaching heights up to 2 nm and associated terraces 650 nm wide are detected on the surface (Fig. 4). The line profiles (Fig. 3b) reveal that monosteps and multiple steps coexist. After the coalescence process, the multiple steps remain parallel to the monosteps and tend to become straighter (Fig. 5c). Here, the monosteps exhibit terraces larger than initial monosteps (at 1000 °C). Unlike in MgO and Al<sub>2</sub>O<sub>3</sub>, faceting is not detected.<sup>13,14</sup> The quantity of steps present on the surface is inversely proportional to their height and steps of height above four times the YSZ unit cell dimension do not form. Finally, the absence of the characteristic coalescence pattern after the annealing at  $0.6 T_M$  seems to indicate that the morphology of the surface has reached a stable structure.

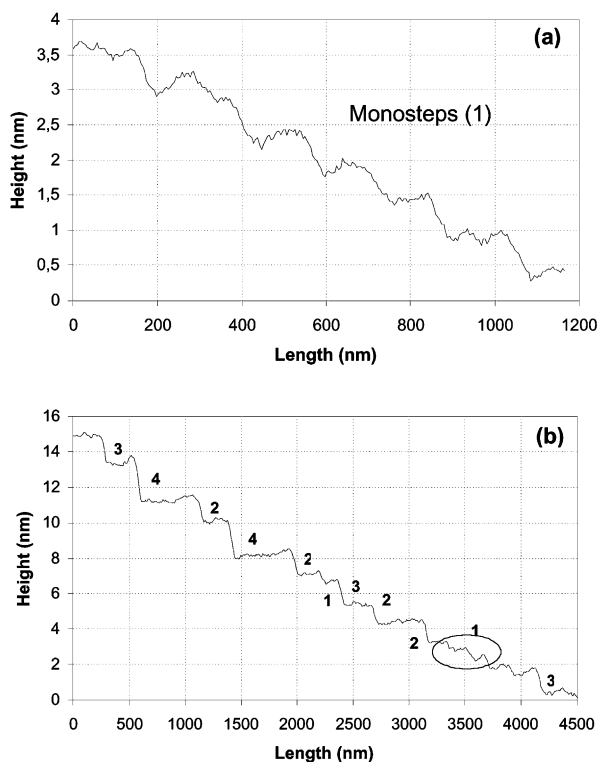


Fig. 3. Surface profiles of a (100)-oriented YSZ sample annealed in air during 1 h at (a) 1000 °C and (b) 1500 °C. Numbers close to the steps represent their heights normalized to the one of a monostep (e.g. 1 corresponds to a height of 0.5 nm).

#### 4. Discussion

The results obtained in this study are similar to recent ones obtained on films grown on YSZ stepped surfaces for annealings up to  $0.5 T_M$  (1000 °C)<sup>5</sup> (the highest temperature used in this latter work). The evolution of the morphology at these temperatures also corresponds to the one exhibited on the surface of Al<sub>2</sub>O<sub>3</sub>. Nevertheless, some

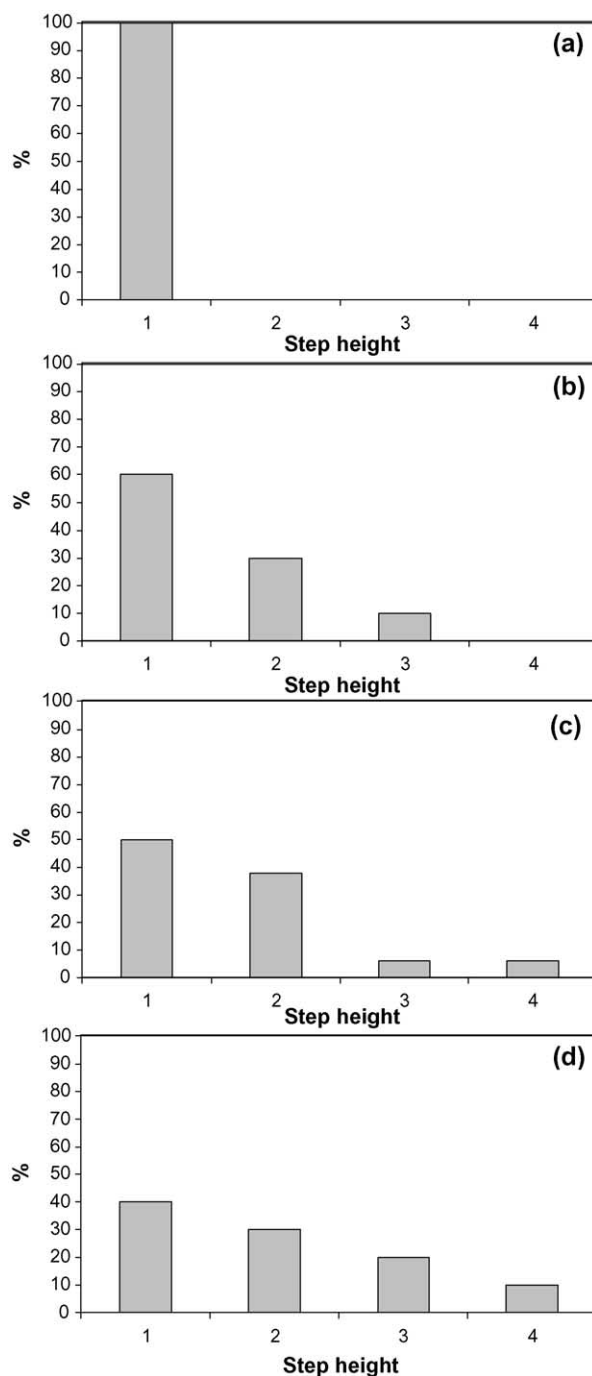


Fig. 4. Ratio of  $n$ -uple steps ( $n = 1, 2, 3, 4$ ) to the total number of steps after annealing in air during 1 h at (a) 1000 °C, (b) 1200 °C, (c) 1400 °C and (d) 1500 °C.  $n$  represents the step height normalized to the one of a monostep.

differences appear at high temperatures as the absence of a faceting process and the high stability of monosteps on the YSZ surfaces up to  $0.60 T_M$ .

Three temperature ranges can be distinguished to explain the evolution of the morphology of YSZ surfaces and to make a comparison with the one of  $Al_2O_3$  surfaces (Fig. 6).

Below  $0.50 T_M$ , the surface shows no sign of the coalescence process as on sapphire surfaces. At  $0.43 T_M$  ( $1000\text{ }^\circ\text{C}$ ), monosteps develop on the YSZ surface. In that temperature range, sapphire and YSZ stepped surfaces differ on their step edge morphology.  $Al_2O_3$  step edges are straighter than YSZ ones. This may be the direct result of the substrate elaboration since as received  $Al_2O_3$  surfaces present well aligned steps, which is not the case of YSZ ones.

Between  $0.50 T_M$  and  $0.60 T_M$ , the coalescence process occurs and multiple steps appear (Fig. 5a,b). This process involves the interaction between monosteps or multiple steps and proceeds following the zipper-like scheme observed on sapphire samples.<sup>12</sup> Step edges on YSZ surfaces also smooth when the annealing temperature increases, which increases the minimum distance between two adjacent steps. The evolution of sapphire

and YSZ surfaces is quite identical in this range of temperature (coalescence of monosteps begins at  $0.55 T_M$  on  $Al_2O_3$  surfaces).

At  $0.60 T_M$  ( $1500\text{ }^\circ\text{C}$ ), the coalescence process seems to be finished. The surface morphologies of YSZ and  $Al_2O_3$  differ in their characteristic step heights and distribution. Only a few percent of steps with heights 3 or 4 times the YSZ unit cell exist (Fig. 4), and steps higher than 2 nm are not detected whereas steps with heights up to 10 times the one of a monostep are observed in  $Al_2O_3$ . Moreover, the monostep proportion is much lower on sapphire surfaces. Nevertheless, the step edges are straight in both these oxides. Further annealings at  $1500\text{ }^\circ\text{C}$  during 4 h confirm the stability of the YSZ surface morphology. The transport of matter, which occurs principally by surface diffusion along the step edges and across the associated terraces at temperatures lower than  $0.6 T_M$ ,<sup>15</sup> can still be considered as the dominant process at higher temperatures, since well-aligned steps remain on the sample surface. The evaporation–condensation mechanism, generally favored at high temperature<sup>15,16</sup> does not prevail in this case, as no planarization or roughening processes are detected at  $0.60 T_M$  unlike on MgO surfaces.<sup>10</sup> No faceting process

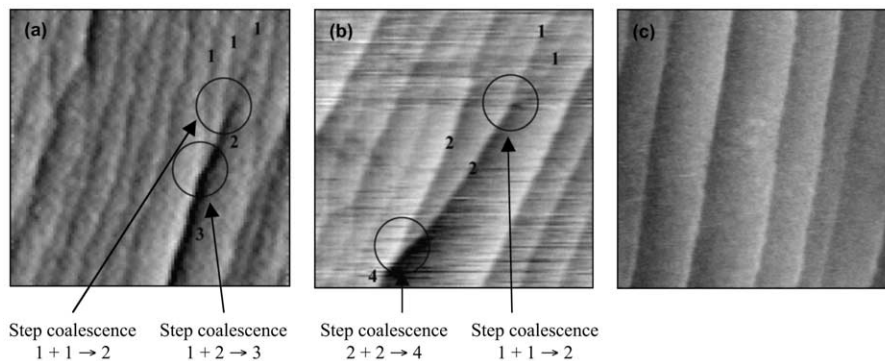


Fig. 5. Surface morphology ( $2.5 \times 2.5\ \mu\text{m}^2$ ) of a (100)-oriented YSZ sample annealed in air during 1 h at (a)  $1200\text{ }^\circ\text{C}$ , (b)  $1400\text{ }^\circ\text{C}$  and (c)  $1500\text{ }^\circ\text{C}$ . Numbers close to the steps represent their heights normalized to the one of a monostep.

Temperature ( $T/T_M$ )	$< 0.5$	$0.5 - 0.6$	$0.6 - 0.74$	$> 0.74$
YSZ	Formation of monosteps	Coalescence of steps	Stabilization of the stepped structure ?	
	Smoothing of step edges		Straight multiple steps	
$Al_2O_3$	Initial straight monosteps	Coalescence of steps		Faceting of high multisteps

Fig. 6. Scheme of the morphology evolution of YSZ and  $Al_2O_3$  with temperature.

is observed on YSZ surfaces but this could be attributed to the relatively low annealing temperature since that phenomenon appears on  $\text{Al}_2\text{O}_3$  surfaces at  $0.74 T_M$ , which translates into a temperature of  $1900^\circ\text{C}$  for YSZ.

Two factors may be responsible for the differences observed between sapphire and YSZ surface morphologies at high temperature (above  $0.60 T_M$ ).

The first factor resides in the structural difference between both oxides. The lattice structure of sapphire along the (0001) direction can be described by a succession of distorted hexagonal compact layers of oxygen atoms sandwiching two close layers of aluminum atoms. The hexagonal unit cell height comprises six layers of oxygen, and six such double layers of aluminum. The dimension of the unit cell of sapphire along the  $c$ -axis is  $1.3\text{ nm}$  and the height of a monostep measured ( $0.2\text{ nm}$ ) corresponds to  $c/6$ .<sup>12</sup> In YSZ, the lattice structure is cubic (fcc fluorine structure) and it can be described by a succession of layers of oxygen and zirconium atoms along the (100) direction. The dimension of the unit cell is  $0.5\text{ nm}$  and exactly corresponds to the height of one monostep. In the first case, a monostep refers only to a portion of the unit cell whereas in the second case, the monostep refers to an entire unit cell. This may account for the fact that monosteps on YSZ surfaces are more stable structures than on  $\text{Al}_2\text{O}_3$  and that coalescence is comparatively limited.

The second factor originates from the very high width of the terraces initially formed on YSZ surfaces. The average width of a terrace associated to monosteps ( $160\text{ nm}$ ) is 5 times the one observed on sapphire surfaces. Thus, the interactions between two steps are weaker and the YSZ coalescence process is not favored. The morphology of the YSZ surface at high temperature may be the result of a competition between two processes. The first one is the coalescence process which starts around  $0.50 T_M$ . It depends on the step-to-step attractive interaction and thus decreases with higher distances. The second one is the minimization of the energy of the surface structure by step edge smoothing, which straightens the step edges and increases the minimum distance between two steps. When the terraces become too wide, the coalescence process stops. Although all the step edges on sapphire surfaces are very straight, the initial average step to step distance is very small compared to the one of YSZ monosteps. That can explain that the coalescence process is maintained further in  $\text{Al}_2\text{O}_3$  and that the decrease with temperature of the number of monosteps on YSZ surfaces is less important.

## 5. Conclusion

The evolution upon annealing in air of the surface morphology of (100)-oriented yttria-stabilized zirconia single crystals has been studied up to  $0.60 T_M$  ( $1500^\circ\text{C}$ )

by AFM in a non-contact dynamic mode. At medium temperature ( $T \leq 0.56 T_M$ ), the surface morphologies are similar to the ones of other oxides like  $\text{Al}_2\text{O}_3$ . The monostep formation occurs at  $0.43 T_M$  ( $1000^\circ\text{C}$ ) with a mean direction which remains constant during all the annealings. The average step height is shown to increase with temperature. At  $0.50 T_M$  ( $1200^\circ\text{C}$ ), monosteps coalesce, as for  $\text{Al}_2\text{O}_3$ , and multiple steps form. Meanwhile, the step edges become straighter. As a consequence, the minimum distance between two steps increases, which lowers their mutual interactions. At higher temperature ( $T \geq 0.60 T_M$ ), the step to step interactions become too weak for the coalescence process to occur and no step heights above four times the YSZ unit cell dimension have been recorded. This behavior indicates that one of the most important parameters in the evolution of the surface structure is the initial step to step distance. The final morphology may be the result of the competition between two processes: step edge smoothing, which increases the minimum terrace widths, and step coalescence. The differences of structure between sapphire and YSZ single crystals may also account for this particular high temperature evolution.

Finally, the nanostructuring of YSZ is possible upon a large range of temperature. Furthermore, AFM observations showed that YSZ surfaces after annealing present a much more stable and uniformly distributed step structure than other ceramic oxides, such as  $\text{Al}_2\text{O}_3$ . In this work, we have demonstrated that the use of YSZ surfaces as substrates for epitaxial growth or film deposition should develop rapidly in a near future.

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