GROWTH MECHANISM AND SURFACE MODIFICATION OF NANOSTRUCTURED CeO_2 FILMS BY CHEMICAL SOLUTION DEPOSITION

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The growth mechanism of 7-80 nm thick CeO_2 nanometric epitaxial films, deposited on (001)-YSZ from 2,4-pentadionate solutions, has been investigated using x-ray diffraction (XRD), x-ray reflectivity (XRR), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and reflection high energy electron diffraction (RHEED). The film thickness was tuned according to its linear dependence on solution concentration (0.08M-0.7M). The synthesis was performed under Ar/5%H_2 at 750ºC for 4h. The grain size, microstructure and surface evolution of the films has been investigated between 650ºC and 1300ºC in Ar/5%H_2, air, and oxygen atmospheres.

XRD analysis ($\theta/2\theta$, ω and ϕ scans), of samples processed at 750ºC under Ar/5%H_2, reveal the occurrence of only the (00*l*) orientation and an excellent off-plane and in-plane epitaxial qualities, both being thickness dependent. $\Delta\omega$ lies between 0.1° and 0.28°. From a comparison of (111) ϕ-scans of film and substrate a cube-on-cube epitaxial relationship is deduced. Careful inspection of the (111) ϕ-scan peaks reveals that they consist of two contributions, one broad peak ($1.0°<\Delta\phi<1.8°$) and a superposed narrow one ($\Delta\phi=0.2°$), suggesting the coexistence of regions with different degree of texture. In both cases the width of the distribution increases with thickness. Diffraction averaged residual stresses, as determined using the $\sin^2\psi$ method, exhibit a clear decay with increasing thickness.

Cross section TEM observations (Fig. 1a) indicate also a nanometric granular structure which contrasts with the columnar microstructure typically reported for films deposited by vacuum techniques [1]. Grains are rounded and no significant through-thickness grain size (typically 10 to 20 nm in diameter) variations are observed. Analysis of AFM images (Fig. 1b) revealed typical rms roughness values between 2 and 4 nm. Strikingly, however, only those grains epitaxially nucleated on the substrate display a strict cube-on-cube orientation, as demonstrated by the selected area electron diffraction pattern taken across the interface (inset). Indeed, RHEED patterns which are sensitive to the top-most material at the surface, indicated a disordered structure (Fig. 1c). Such a texture variation perpendicular to the substrate is consistent with the bimodal ϕ-scan line shapes commented above.

In order to get insights into the growth mechanism of these nanostructured films, the temperature dependence of the in-plain grain size was investigated for nominally 40 nm thick films annealed for 4 h at 650°C, 700ºC, 750°C, 800°C, 850ºC and 900°C in Ar/5%H_2, by quantitative analysis of AFM images. It was noted that grain sizes derived from AFM images were artificially magnified as a consequence of the convolution of the tip and grain shapes. Accordingly, these results were used to analyse the evolution of the grain size but can not be taken as a realistic measure of the lateral size of the grains. The observed temperature dependence of the grain size obeys an Arrhenius type behaviour given by $\langle r\rangle^2-\langle r_o\rangle^2=a_o t\exp(-Q/kT)$, where $\langle r\rangle$ is the average grain radius after a time t, $\langle r_o\rangle$ is average initial grain radius, a_o is a constant, Q is an activation energy for grain boundary motion, and k and T have their

usual meanings [2]. From the slope of this plot, a value Q=1.04 eV is obtained. This behavior is typically observed in 3D systems undergoing a thermally activated coarsening process, as expected for the present films since they exhibit a grain size significantly smaller than the film thickness. Interestingly, it was observed that the surface roughness increases with temperature, thereof with grain size, up to rms values within 8-13 nm. This behaviour suggests that there is no grain boundary energy (or grain boundary grooving) contribution to surface roughening [3] and that the increase in roughness is dominated by the expected increase of height variations within individual grains as their size increases.

Post annealing at 1000ºC in air or oxygen produces a dramatic modification of the microstructure and surface features of the films (Fig. 2a-c). The granular structure evolves to an almost single crystalline fully epitaxial film with an ordered terraced surface dominated by the (001) planes with rms of ~ 3nm. Holes are identified both in the TEM and AFM images are likely generated as a result of the contraction of the film during the microstructural transformation.

Acknowledgements

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References:

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Figures:

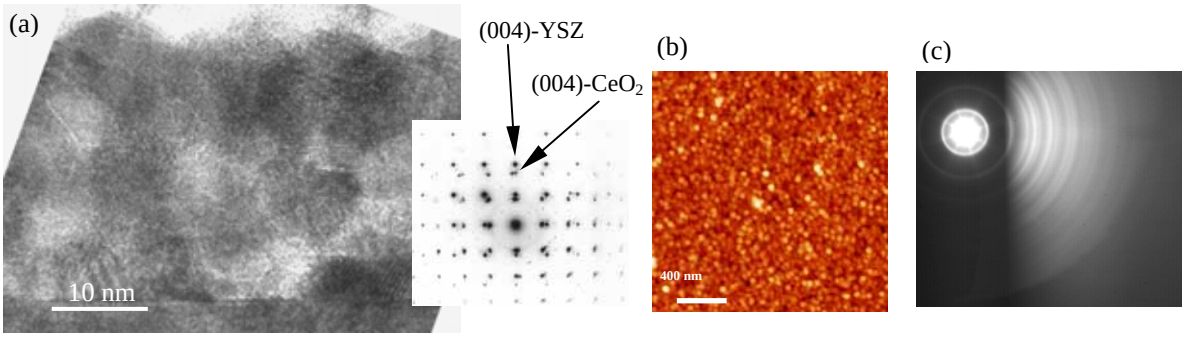

Fig. 1: Cross section TEM (a), AFM image (b) and RHEED pattern (c) of a film processed at 750ºC in Ar/5%H_2. The SAD pattern illustrates the epitaxial orientation of grains nucleated at the interface, in contrast with the disordered surface structure revealed by RHEED.

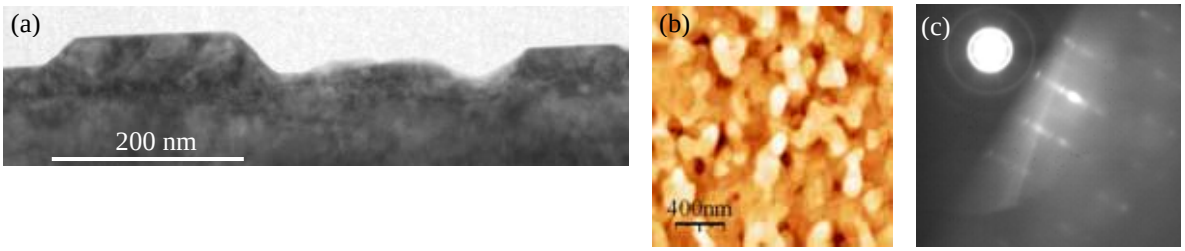

Fig. 2 Cross section TEM (a), AFM image (b) and RHEED pattern (c) of a film submitted to post-processing at 1000ºC in air. The film is fully epitaxial displaying an ordered terraced surface dominated by (001) planes.