Atomic force microscopy study of nanocrystalline ceria thin films

T Ristoiu, T Petrisor Jr, M S Gabor, M Nasui, B Mos, L Ciontea and T Petrisor
Materials Science Laboratory, Technical University of Cluj-Napoca, 15 C Daicoviciu, 400020 Cluj-Napoca, Romania
E-mail: tristoiu@phys.utcluj.ro

Abstract. This work reports on the structural and morphological characterization of ceria thin films grown by chemical solution deposition (CSD) techniques. The coating solution was prepared starting from cerium 2,4-pentadionate, Ce(CH$_3$COCHCOCH$_3$)$_3$, and propionic acid, C$_2$H$_5$COOH, further concentrated by distillation. The as-prepared solution was spin coated on single crystalline (100) SrTiO$_3$ (STO) substrates. The precursor films were heat treated in air at 900°C both by a rapid heating and quenching to room temperature (A) and annealing (B). The X-ray structural analysis and the SEM and AFM morphological analysis for the CeO$_2$/STO thin film have revealed the influence of the thermal treatment on the growth mechanism. The as-obtained polycrystalline nanostructured ceria thin films present an average grain size of 40-50 nm and a roughness of 1.5-5.4 nm, depending on the thermal treatment. The annealing renders the ceria thin film a smoother surface with respect to the rapid heat treatment followed by quenching, performed both at the same temperature.

1. Introduction
Cerium oxide thin films have a large range of applications in electronics, optics, catalysis, wear resistance, corrosion protection and superconductivity as buffer layer in the coated conductor architecture [1]. Lately, doped ceria is being extensively studied as a potential solid electrolyte for fuel cells [2].

Chemical solution deposition (CSD) has emerged as a highly attractive, non-vacuum method for producing oxide thin films. Metal 2,4-pentadionate ($\beta$-diketonates, acetylacetonates), due to their high volatility, low decomposition temperature, ease of use, commercial availability and relatively low cost have become adequate precursors for the chemical solution deposition of metal oxides thin films. The metal acetylacetonates easily dissolve in propionic acid up to high concentrations. The structure and the morphology of the thin films is strongly influenced by the thermal treatment performed in order to transform the precursor thin film into a crystalline one, the growth mechanism being still under investigation [3].

In this work we report on the fabrication and characterization of cerium oxide thin films deposited on single crystalline (100)STO substrates starting from cerium 2,4-pentadionate and propionic acid. The influence of the thermal treatment on the structural properties and surface morphology of the film were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively.
2. Experimental
The cerium acetylacetonate, Ce(C$_5$H$_7$O$_2$)$_3$·xH$_2$O and the propionic acid, CH$_3$CH$_2$COOH with a purity of 99% used in this work have been purchased from Alfa Aesar. The coating solution has been prepared by dissolving the Ce(C$_5$H$_7$O$_2$)$_3$·xH$_2$O in an excess of propionic acid under stirring to form a clear yellow solution. The as-obtained solution was concentrated by distillation (43 mbarr and 75°C bath temperature) resulting in a change of colour to red-brown.

The thin films were deposited by spinning on 10x10 mm$^2$ (100)STO substrates at 4000 rpm for 60s. Prior to the deposition, the substrates were ultrasonically cleaned with isopropanol.

The precursor films have been thermally treated in air at 900°C for 15 minutes by: (A) introducing the film directly in the heated furnace at 900°C, followed by quenching down to room temperature-named quenching hereafter, and (B) by annealing, with a heating rate of 10°C/min. These conditions have been proposed in agreement with the TG-DTA analyses of the precursor powdered solution [4]. The structural characterization of the thin films was performed using a X-ray Bruker D8 Discover diffractometer with CuK$_\alpha$ radiation, equipped with a graphite monochromator on the diffracted beam to suppress the K$_\beta$ component and the parasitic scattering. The morphology was investigated by Scanning Electron Microscopy (SEM) using a LEO 1525 field emission-high resolution scanning electron microscope and a Veeco D3100 AFM in contact mode with a SNL-10 Veeco contact tip, having a nominal tip radius of 2 nm. The AFM images were analyzed using the WSxM software [5].

3. Results and discussion
In order to study the influence of the heat treatment on the growth behavior of the ceria thin films, the thin films were subsequently characterized by X-ray $\theta$-2$\theta$ scans. The indexing of the reflections was based on the fluorite lattice cell of CeO$_2$ with a lattice parameter of $a_{\text{CeO}_2} = 5.4\text{Å}$. Figure 1, registered between 27-34°, significant for the main reflections, shows that both ceria films are polycrystalline, but no secondary phases have been identified. Thus, beside the (111) reflection at $2\theta = 28.58$°, the (200) reflection at $2\theta = 33.02$° is present in an almost equal intensity in the annealed film (B), while in the quenched film (A) it is undetectable. This suggests that the annealed film is partially [100](100) textured.

The SEM analysis of the thin films have revealed homogeneous, continuous, crack free CeO$_2$ surfaces for both thermal treatments, as shown in figure 2. It can be seen that they have very fine grains. Nevertheless, the quenched film (A) contains more dark zones, which can be attributed to bigger gaps between the grains.

![Figure 1. X-ray diffraction pattern of the quenched film (A) and of the annealed film (B).](image1)

![Figure 2. SEM images (200.00 kx) of the quenched film (A) and of the annealed film (B).](image2)

From the AFM images, figure 3 and figure 4, of the as-grown CeO$_2$ films it is found that the surface has a granular structure, similar to the one presented in the SEM analyses. However, the crystallites are larger in size in the AFM images due to tip convolution. For the same reason, the
narrow gaps between the grains, visible in the SEM images, appear to have less sharper borders. The root mean square roughness (RMS) of the ceria thin films, maximum value and average height, calculated on an area of 1 µm x 1 µm and 10 µm x 10 µm, respectively, are synthetically presented in table 1. The values indicate that the annealed thin films are smoother than the quenched ones. The grain size estimated from the accompanying line profiles are 35 nm for the annealed film (B) and 45 nm for the quenched film (A) and have a more uniform distribution, as shown in the topographic representation, figure 3. The observed surface grain structure did not allow any conclusions to be drawn concerning the structure within the volume of the film.

| Area          | RMS   | Maximum value | Average height |
|---------------|-------|---------------|----------------|
| A 1 µm x 1 µm | 2.3 nm| 1.5 nm        | 20.9 nm        |
| B 1 µm x 1 µm | 5.4 nm| 3.7 nm        | 73.5 nm        |
| A 10 µm x 10 µm | 5.4 nm| 3.7 nm        | 73.5 nm        |
| B 10 µm x 10 µm | 5.4 nm| 3.7 nm        | 73.5 nm        |

The 3D representation, figure 4, reveals the slight wavy nature of the film surface due to thermal stress induced by the rapid heat treatment (A).

|Area| RMS| Maximum value| Average height|
|---|----|--------------|---------------|
| A 1 µm x 1 µm | 2.3 nm| 1.5 nm| 20.9 nm|
| B 1 µm x 1 µm | 5.4 nm| 3.7 nm| 73.5 nm|
| A 10 µm x 10 µm | 5.4 nm| 3.7 nm| 73.5 nm|
| B 10 µm x 10 µm | 5.4 nm| 3.7 nm| 73.5 nm|

Figure 3. 2D AFM images, the accompanying line profiles (a, b) and the topographic profile (c) of the quenched film (A) and of the annealed film (B) for 1 µm x 1 µm area.

Table 1. Principal data obtained from the AFM analysis.
The interpretation of the experimental results can be done taking into account the two types of thermal treatments: a one step and two step crystallization processes. In the case of a one step process the pyrolysis and crystallization are concurrently and take place simultaneously at an upper temperature; this corresponds to the quenching thermal treatment (A). Due to the fast heating, the decomposition of the precursor is not complete, although the temperatures are sufficiently high to initiate crystallization. This contributes to grain growth and results in a larger average grain size film. In the two step process, pyrolysis and crystallization take place successively: pyrolysis corresponds to the burn-off of the organic moieties, resulting in an amorphous film, and crystallization which takes place at a higher temperature. In our case, since the heating rate is relatively low (10°C/min) and the temperature range for the precursor powder decomposition being 300-500°C [4], the annealing of the film (B) can be treated as a two step process, in spite of the lack of an intermediate thermal treatment.

From a thermodynamic point of view it has been demonstrated that the driving force that governs the transformation from the amorphous film to into a crystalline oxide film can play a significant role in defining the active nucleation events, and thereby the film microstructure [1]. It is known that the crystal growth from solution derived films is more complicated and difficult than in vacuum deposition techniques, because the nuclei form not only at the interface between the film and the substrate, but also at the film surface and/or on impurity particles in the film [6]. In our case, in spite of the fact that the films are not epitaxially grown, we assume that during the quenching process (A) the nucleation takes place in the film volume, while during the annealing process (B) the nucleation takes place rather at the interface between the film and the substrate. This assumption is sustained by the oriented character of the annealed films and the smaller roughness with respect to the quenched ones.

4. Conclusions
Ceria thin films have been prepared by CSD using cerium 2,4-pentadionate and propionic acid as reactants. The structural and morphological analyses have demonstrated that the annealing thermal treatment at 900°C is more adequate for the growth of nanocrystalline, smooth, quasi-oriented ceria thin films. The film growth has been interpreted in terms of volume and interface nucleation for the applied thermal treatments. In case of volume nucleation the film presents larger grain size and higher surface roughness, while the interface nucleated film exhibits smaller grain sizes, lower roughness and a [100](100) partial texture. The results of this study are promising for the use of ceria as buffer layers in the coated conductor architecture. Higher temperatures are necessary for the epitaxial growth of ceria thin films.

Acknowledgments
The authors thank ENEA-Frascati, Italy, Superconductivity Division for the X-ray and SEM analysis. The financial support from PN II under contract number 71-045 was highly appreciated.

References
[1] Bhuiyan M S, Paranthaman M and Salama K 2006 Supercond. Sci. Technol. 19 R1
[2] Chockalingam R, Amarakoon V R W and Giesche H 2008 J. Eur. Ceram. Soc. 28 959
[3] Coll M, Gazquez J, Huhne R, Holzapfel B, Morilla Y, Garcia-Lopez J, Pomar A, Sandiumenge F, Puig T and Obradors X 2009 J. Mater. Res. 24 1446
[4] Ristoiu T, Ciontea L, Petrisor Jr T, Gabor M S, Thalmaier Gy and Petrisor T 2009 submitted to J. Optoelectron. Adv. Mat.
[5] Horcas I, Fernández R, Gómez-Rodríguez J M and Colchero J 2007 Rev. Sci. Instrum. 78 013705
[6] Schwartz R W, Schneller T and Waser R 2004 C. R. Chimie 7 433.