

# MOCVD OF NANOCRYSTALLINE Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> AND Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> THIN FILMS

Giovanni A. Battiston<sup>a</sup>, Rosalba Gerbasi<sup>a</sup>, Davide Berto<sup>a</sup>,  
Davide Barreca<sup>b</sup>, Eugenio Tondello<sup>c</sup>

<sup>a</sup> Istituto di Chimica Inorganica e delle Superfici del  
C.N.R., Corso Stati Uniti, 4 - 35127 Padova, Italy.

<sup>b</sup> Istituto di Scienze e Tecnologie Molecolari del C.N.R.  
and INSTM, Via Marzolo, 1 - 35131 Padova, Italy.

<sup>c</sup> Dipartimento di Chimica Inorganica, Metallorganica ed  
Analitica and INSTM - Università di Padova, Via  
Loredan, 4 - 35131 Padova, Italy.

## INTRODUCTION

In this work, the CVD technique is used for the synthesis of nanoscale Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coatings. In particular, the introduction of Y<sub>2</sub>O<sub>3</sub> was added to stabilize the cubic ZrO<sub>2</sub> phase.

## EXPERIMENTAL

Iron(III) tris-(2,4 pentanedionate) (Aldrich), zirconium(IV) tris-isopropoxy 2,2-6,6-tetramethyl-3,5-heptanedionate (Inorgtech), and yttrium(III) tris-(2,4 pentanedionate) (Aldrich) were used without further purification as CVD precursors for Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> respectively. Film depositions were performed in a low pressure hot-wall CVD system provided with a Pyrex pipe, 4.8 cm inner diameter, 31 cm long, in an O<sub>2</sub>-N<sub>2</sub> atmosphere at 420 °C. Nitrogen (50 sccm) was employed as carrier gas and oxygen (50 sccm) as reacting gas, keeping the whole system under a total pressure of 120 Pa. Suitable precursor mixtures were evaporated at a temperature of about 120°C. Estimated film thickness yielded typical values of ≈ 200 nm. The obtained films were subjected to a thermal treatment *ex situ* in air at 1000°C for 10 h, in order to examine the annealing effect on their composition, microstructure and morphology.

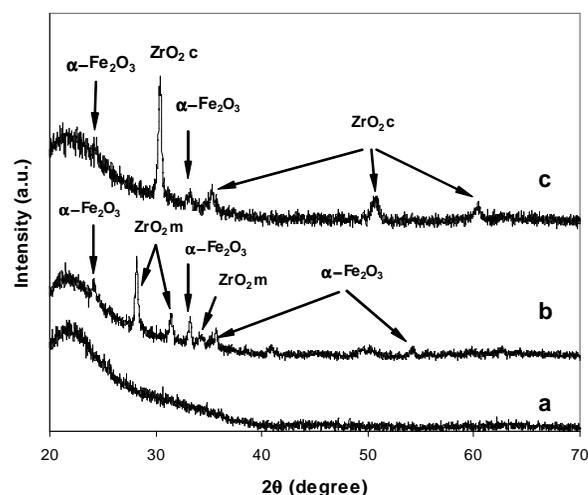
## RESULTS AND DISCUSSION

Irrespective of the starting precursor mixture, all the as-grown Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> films showed no clearly detectable X-ray diffraction (XRD) peaks (fig. 1, pattern **a**). Thermal treatment resulted in the formation of the hexagonal α-Fe<sub>2</sub>O<sub>3</sub> and the monoclinic ZrO<sub>2</sub> (*baddeleyite*) phases, with no appreciable preferred orientation (fig. 1, pattern **b**). Crystallite dimensions estimated by the Scherrer equation were found to be ≈30 nm for monoclinic zirconia and ≈45 nm for α-Fe<sub>2</sub>O<sub>3</sub>, confirming the nanoscale structure of the films obtained through the MOCVD methodology. However the high temperature cubic zirconia polymorph was not stabilized by the presence of iron(III) oxide alone.

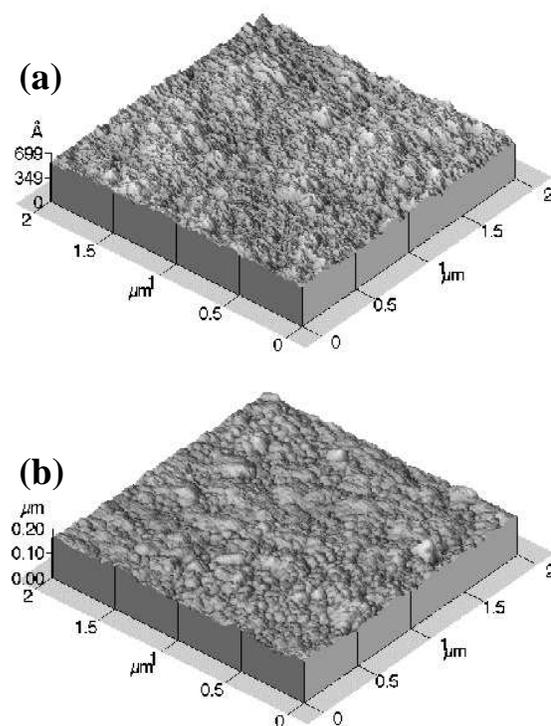
We considered therefore the utilization of yttrium(III) oxide for the stabilization of cubic zirconia. The formation of Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coatings was achieved by using mixtures of iron, yttrium and zirconium precursors, with Fe/Y/Zr molar ratios of 45/10/45, 40/20/40 and 35/30/35. Once again, XRD analysis revealed the amorphous nature of the as-grown films. After the annealing treatment, the hexagonal α-Fe<sub>2</sub>O<sub>3</sub> and cubic ZrO<sub>2</sub> reflections were clearly discerned (fig. 1, pattern **c**); no marked preferred orientation was detected. Crystallite dimensions were ≈30 nm for both cubic zirconia and α-Fe<sub>2</sub>O<sub>3</sub> phases, confirming the nanoscale dimension of the obtained films. Similarly to the previous case, iron oxide constituted a separate crystalline phase and the formation of a solid solution with zirconia did not occur, while the presence of Y<sub>2</sub>O<sub>3</sub> induced the stabilization of cubic zirconia. Finally, the precursor mixture containing the lowest amount of Y precursor proved to be effective for the cubic zirconia stabilization.

X-ray photoelectron spectroscopy (XPS) depth profiles indicated that the obtained films were pure and had a uniform composition. Surface morphology was analyzed by atomic force microscopy (AFM). Representative micrographs of an Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> film, before and after the thermal treatment, are displayed in fig. 2. As a general trend, films displayed a homogeneous surface texture with globular particles well interconnected between themselves, reminiscent of an island growth mode. The as-grown sample had an average roughness of ≈3 nm and a mean grain size of ≈38 nm, smaller with respect to Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coatings showing a mean grain size of ≈72 nm; on firing the film at 1000°C, both the average roughness and the grain dimensions underwent an appreciable increase, up to ≈5 nm and ≈78 nm respectively, while Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> grain dimension increased to ≈172 nm. On the basis of XRD results, such behavior may be related to the film crystallization.

We can conclude that the Y<sub>2</sub>O<sub>3</sub> addition proved useful for two purposes: the thermal stabilization of the cubic zirconia polymorph, and the obtaining of smaller grain and crystallite dimensions remained below 50 and 80 nm respectively.



**Figure 1.** XRD patterns of: **a**) an as-grown Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> film; **b**) an Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> film obtained from an equimolar mixture of Fe and Zr precursors and annealed at 1000°C; **c**) an Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> film obtained from a precursor mixture with Fe/Y/Zr molar ratios of 45/10/45, annealed at 1000°C. The labels **m** and **c** indicate reflections of the monoclinic and cubic ZrO<sub>2</sub> phases respectively.



**Figure 2.** AFM surface micrographs of an Fe<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> film, obtained from a precursor mixture with Fe/Y/Zr/ molar ratios of 45/10/45, as grown **(a)** and after annealing **(b)**.