

NANOSCALE CeO₂-ZrO₂ THIN FILMS:
A COMBINED APPROACH BY CVD AND
SOL-GEL ROUTES

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In the last years, a great scientific effort has been devoted to the preparation of CeO₂-based materials, thanks to their catalytic performances in the conversion of automotive and industrial plants emissions (1). To this regard, the preparation of CeO₂-ZrO₂ mixed systems is a valuable tool in order to stabilize ceria against thermal ageing and improve its catalytic redox properties (2). The functional behaviour of such materials can be suitably tailored by the dispersion of defective ceria nanoparticles on a porous zirconia matrix, allowing to fully exploit the synergy between ceria-zirconia interactions and high surface area nanosystems. In this context, CVD and sol-gel techniques are gaining increasing importance for the synthesis of nanoscale materials. A peculiar feature of the CVD method is the possibility of achieving a *vapor infiltration* into porous or fibrous structures, while sol-gel routes allows the preparation of oxide-based *xerogels* by a low temperature solution approach.

The present work was aimed at exploring the synergy between PA-CVD and sol-gel techniques in the synthesis of mixed CeO₂-ZrO₂ nanosystems. Such a combined synthetic pathway joins the advantages offered by the high porosity of the zirconia matrix and by the competition of ablation and growth processes characterizing glow discharges (3). In particular, PA-CVD deposition of CeO₂ was performed on sol-gel zirconia *xerogels* as substrates and the obtained systems were subsequently annealed in air at 600 and 900°C in order to investigate the temperature influence on microstructure, morphology, surface and in-depth composition.

ZrO₂ *xerogels* were prepared on silica substrates by dip-coating from ethanolic solution of Zr(OBu)₄ (OBu^t = *ter*-butoxy; C(ZrO₂)=30 g/l) at withdrawal speed of ≈8 cm/min (4). Ceria layers were deposited on zirconia *xerogels* by a Radio Frequency PA-CVD reactor (RF=13.56 MHz) described elsewhere (7). Ce(dpm)₄ (Hdpm = 2,2,6,6-tetramethyl-3,5-heptanedione) was used as Ce precursor and vaporised at 170°C, while the substrate temperature was fixed at 200°C. Based on previous results (3), depositions were carried out in Ar-O₂ plasmas in optimized conditions ($\phi(\text{Ar})=20$ sccm, $\phi(\text{O}_2)=5$ sccm; RF power = 40 W; total pressure = 1.5 mbar; deposition time = 1h). Film composition and microstructure were studied by X-ray Photoelectron Spectroscopy (XPS) and Glancing-Incidence X-ray Diffraction (GIXRD) respectively, while their surface morphology was analyzed by Atomic Force Microscopy (AFM).

Preliminary XRD investigations showed that no crystallization occurred for the ZrO₂ *xerogels* and for the *as-prepared* PA-CVD CeO₂/sol-gel ZrO₂ film. Thermal treatment at 600 and 900°C in air resulted in the appearance of three peaks at $2\theta \approx 30.6^\circ$, $\approx 35.5^\circ$, and 50.9° , attributed to the reflections of crystalline ZrO₂. Estimation of the average crystallite size by the Scherrer formula yielded ≈ 12 nm for coatings annealed both at 600°C and 900°C. The presence of signals attributable to CeO₂ (*ceria*) could not be clearly observed. Moreover, a significant peak shift towards higher 2θ values was observed ($\approx 0.3^\circ$ with respect to the tetragonal zirconia positions (4)). Such an effect could not be clearly related

to the formation of a solid Zr-Ce-O solution, because in this case lower 2θ values would be expected (4). On the other hand, the presence of a ternary phase cannot be completely ruled out because the low Ce content may not have induced an appreciable peak shift. These aspects are actually under further investigation in order to attain a deeper insight on sample microstructure as a function of processing conditions.

XPS analyses confirmed the presence of ZrO₂. On the other hand, Ce3d peak shape and position always showed the co-presence of Ce(III) and Ce(IV) states. Such effect, that was not observed for PA-CVD CeO₂ nanoparticles deposited on silica substrates in the same conditions (3), could be attributed to a *promotional* zirconia effect on ceria reducibility. Interestingly, Ce(IV) percentage increased almost linearly with the processing temperature due to a progressive oxidation on annealing in air, thus allowing to obtain mixed CeO₂-ZrO₂ systems with tailored Ce(IV)/Ce(III) ratio. Depth-profiles of the *as-prepared* sample revealed that Ce percentage rapidly decreased from $\approx 7\%$ up to disappearance after $\approx 25\text{Å}$, indicating that an *outside clusters*-like composite was probably obtained. On annealing at 900°C, a matrix densification and a more uniform distribution of ceria in the ZrO₂ was observed, as a consequence of an increased intermixing between the two oxides.

Significant morphological differences were detected by AFM as a function of the treatment conditions. All *as-prepared* samples (fig.1(a)) showed a porous-like surface texture with no well-defined grains as expected for *xerogel* coatings.

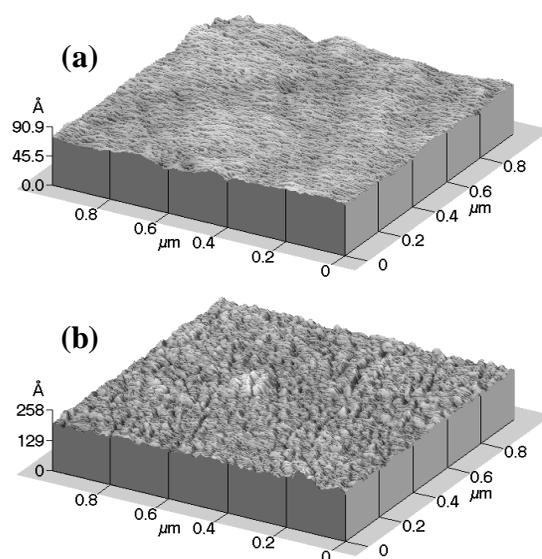


Figure 1. Representative AFM surface micrograph ($1 \times 1 \mu\text{m}^2$) of PA-CVD CeO₂/sol-gel ZrO₂ films: (a) *as-prepared*; (b) annealed in air at 900°C for 1h.

Conversely, sample annealed at 900°C (fig.1(b)) was characterised by the presence of aggregates with a mean average size of ≈ 35 nm. Such a result, supported by GIXRD investigation, might be related to the matrix crystallization process induced by the annealing treatment.

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