**Thin film samples: a new methodology for investigating the mechanisms of fission gas releases from nuclear fuel during a LOCA**

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# SUPPLEMENTARY MATERIAL

The mesoporous thin films are synthesized using the dip coating technique. The other thin films are synthesized by magnetron sputtering technique. The choice of the deposition parameters is important to achieve the desired microstructure and it is optimized. A SEM picture of the mesoporous microstructure is given below as supplementary material

**Synthesis of poly-crystal films (CeO2 and UO2).** Poly-crystal thin films are prepared as described in [R. Springell, S. Rennie, L. Costelle, J. Darnbrough, C. Stitt, E. Cocklin, C. Lucas, R. Burrows, H. Sims, D. Wermeille, J. Rawle, C. N., W. Nuttall, T. Scott and G. Landerh; Water corrosion of spent nuclear fuel: radiolysis driven dissolution at the UO2/water interface. *Faraday Discussions* **2015**, 180, 301-311]. Poly-crystal thin films of UO2 were grown in a dedicated DC magnetron sputtering facility at the University of Bristol under UHV conditions. Samples were deposited on Al2O3 substrate of dimensions 1 cmx1 cmx0.5 mm. Reactive sputtering was used to deposit uranium in an argon pressure of 7.2 10^(-3)bar and an oxygen partial pressure of 2 10^(-5) mbar, to give a sputtering rate of 1.2 A˚UO2/s. Substrate heating was used to elevate the growth temperature to 550°C, providing thermal energy to improve the crystalline quality, monitored using in situ reflection high-energy electron-diffraction (RHEED). Several samples were grown in order to verify the reproducibility of the experiment, and these were characterized using X-ray reflectivity (XRR) and high angle X-ray diffraction (XRD) on a Philips X'Pert Pro MRD.

**Synthesis of Mesostructured CGO films.** Mesostructured CGO films are prepared as described in [Hierso, J.; Sel, O.; Ringuede, A.; Laberty-Robert, C.; Bianchi, L.; Grosso, D.; Sanchez, C., Design, Synthesis, Structural and Textural Characterization, and Electrical Properties of Mesoporous Thin Films Made of Rare Earth Oxide Binaries. *Chemistry of Materials* **2009,** 21, (11), 2184-2192.]. A Ce0.8Gd0.2O2-x solution was prepared with CeCl3.7H2O (0.670 g) and GdCl3.6H2O (0.074 g) put in solution (A) with 5 ml of ethyl alcohol and 0.75 ml of water (Millipore) then is stirred for 1h. Another solution (B) of 100 mg of PS-*b*-PEO dissolved in ~2.3 ml of THF is stirred for 1h too, to homogenize the formation of the micelles in solution. The mixture of both solutions (A+B) is stirred for a minimal time of 24h for obtained optical deposit. Because of the contrast between hydrophilic and hydrophobic groups, spherical micelles (∼30 nm) are formed in the solution; these micelles are surrounded by both hydrated Ce(III) and Gd(III) cations. The films were deposited by dip-coating approach on Si substrates with a speed of 3 mm.s-1 for withdrawn. The films were immediately heated in static air at different temperatures, ranging from 400 to 600°C. The heat treatments crystallized films with a heating rate of 1°C.min-1, during 0.2h and cooling rate of 5°C.min-1 to ambient temperature. The compositions of the films was assessed by grazing incidence Xray diffraction using a Bruker D8 diffractometer in a grazing geometry [D. Simeone, G. Baldinozzi, D. Gosset, G. Zalczer and J-F Berar, Rietveld refinements performed on mesoporous ceria layers at grazing incidence. J. Appl. Cryst. (2011). 44, 1205–1210]. A typical crystallite size of 12(1) nm is obtained after a calcination at 500°C. The samples consist of a single phase fluorite structure (a=5.413(1)Å).

**Physical Characterization.**

*Spectroscopic ellipsometry porosimetry* (Woollam, U.S.A.) was used to characterize the pore size distribution and dimension. In this type of experiment, a dynamic flux of controlled the relative pressure of toluene in air is applied onto the mesostructured films. The relative pressure was adjusted using a mass flow controller. In this case, ellipsometry was conducted at room temperature (25 °C) using the adsorption-desorption isotherm of toluene after calcinations at 500°C, analyzed with an isotropic inorganic pore contraction model and a modified Kelvin equation for ellipsoidal pores [Boissiere, C.; Grosso, D.; Lepoutre, S.; Nicole, L.; Bruneau, A. B.; Sanchez, C., Porosity and mechanical properties of mesoporous thin films assessed by environmental ellipsometric porosimetry. *Langmuir* **2005,** 21, (26), 12362-12371.]. Using toluene instead of water allow the characterization of the pore with larger diameter compare to water. This is mainly related to their difference in surface tension [Baklanov, M. R.; Mogilnikov, K. P.; Polovinkin, V. G.; Dultsev, F. N., Determination of pore size distribution in thin films by ellipsometric porosimetry. *Journal of Vacuum Science & Technology B* **2000,** 18, (3), 1385-1391.].

**Electron Microscopy**

*Scanning electron microscopy* (SEM, S 440 de LEICA) was used to characterize the surface (7kV, InLens, 250Kx) and the thickness (5kV, InLens, 500Kx) of the mesostructured CGO thin films. For analysis, the specimen was prepared by attaching a small portion of the mesostructured films to an aluminum stub using conductive carbon tape. The specimen was not gold sputter coated prior to analysis, in order to not change the surface of the mesostructured films.

