Pulsed Injection MOCVD of YSZ thin film for membrane applications

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The preparation of high quality YSZ thin membranes on porous substrates to be used as solid electrolyte in solid state devices such as SOFC and oxygen sensors and generators, is still an unsolved problem with conventional methods [1].
In the present investigation, YSZ films were produced by the Pulsed Injected-MOCVD technique [2]. Particular emphasis was given to demonstrating the potential of this method as a viable processing route for dense coatings deposited at high growth rate on porous substrates.
The injected solution consist in the desired amount of $Zr(tmhd)_4$ and $Y(thd)_3$ metalorganic precursor solved in monoglyme. The reaction chamber was maintained at 10 torr with a gas flow rate of 600sccm Ar and 400 sccm O_2. Other experimental parameters used are described in the following table.

$T_{deposition}$	Inj. opening (msec)	Inj. frequency (Hz)	concentration $Zr(tmhd)_4$
550-800ºC	1 - 3	1 a 2 Hz.	100 mg/ml

The effect of substrate temperature on growth rate was determined from 550ºC to 950ºC using silicon substrates. The Arrhenius plot shows two different regime, kinetic control regime from 550ºC to 750ºC with an activation energy of 23 Kcal/mol, and a mass-transfer limited regime for temperatures comprised between 750 and 900ºC. The activation energy was much higher than that obtained with conventional MOCVD [3,4], probably due to the high precursor vapour pressure joined to the pulsed system and the presence of a solvent near the reaction zone. The chemical composition of the layers was determined by WDS. The Y/Zr ratio in condensed films decreases as the deposition temperature increases showing that the apparent yield of yttria is higher than that of zirconia for temperatures above 800ºC. For films deposited at 800ºC, the layer composition follows exactly the vapour composition contrarily to conventional MOCVD where the yield of yttria is always lower that the yield of zirconia (4-6). The structure of the layers was determined using XRD. The fully stabilized YSZ layers were obtained for composition larger than 11.4 % wt of Y_2O_3, for composition between 4.2 and 8.4 partially-stabilised zirconia was obtained. The tetragonal phase appears for yttria concentration lower than 4%wt. The effect of deposition temperature on phase stability and preferred orientation was determined for yttria concentration as high to stabilize pure cubic phase at 800ºC. Films doped with 11.4%wt of yttria showed a tetragonal phase for films deposited below 600ºC, preferred 002 oriented films between 650 and 750ºC and non-oriented polycrystalline films for deposition temperature over 750ºC.
Fully-stabilised YSZ films, 4-5 microns thick, have been deposited on several porous substrates such as porous alumina, Ni-YSZ cermet and perovskite-coated asymmetric alumina. The morphology of the layers was characterized by SEM using surface and cross-section observations. YSZ films prepared at 800ºC showed a flat surface an perfect conformable coverage. The layers were adherent and no evidence of cracks was detected. Figure 1 present the images of the cross-section of the prepared layers. As it can be seen the layers deposited onto porous substrates showed quite dense and compact and oriented columnar microstructure. No evidence of segmentation and voids along grain boundaries have been detected.
In summary, high crystalline and dense YSZ films have been prepared on porous substrates by PIMOCVD. Gas leak tests of samples deposited on porous substrates are underway. Different membranes thickness are tested in order to obtain perfect gastight membrane even after thermal cycling.

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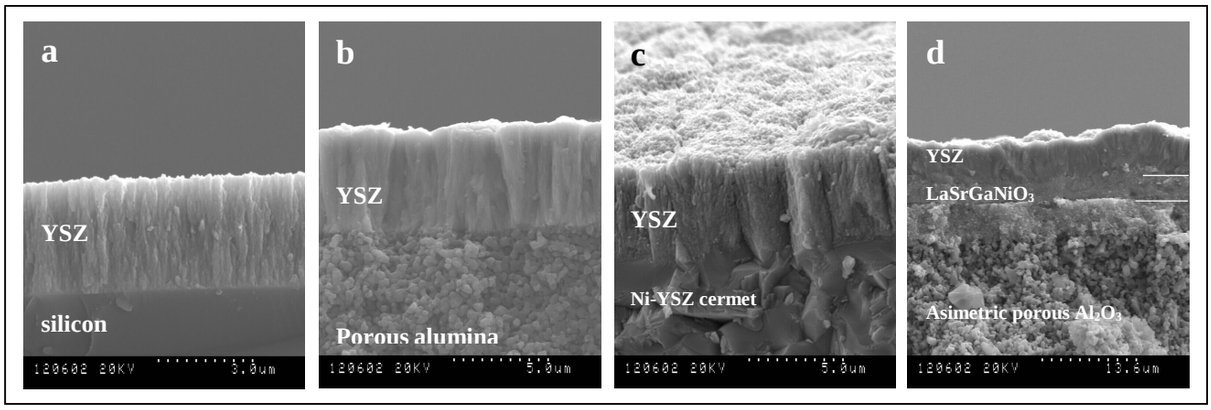

Figure 1: fracture cross-section images of YSZ layers prepared by PIMOCVD on a) silicon substrates, b) porous alumina substrates, c) Ni-YSZ cermets and d) $LaSrGaNiO_3$ coated asymmetric porous alumina