LIPSS nanostructuring by picosecond laser beam of GDC/YSZ oxide thin films

W. Karim[1]*, A. Petit[1], H. Rabbat[1], M. Tabbal[2], A.L. Thomann[1] and N. Semmar[1]

[1] GREMI-UMR 7344-CNRS-University of Orleans, 14 rue d'Issoudun, BP6744, 45071 Orleans Cedex2, France

[2] Department of Physics, American University of Beirut, Bliss St., P.O. Box: 11-0236, Beirut, Lebanon 1107 2020.

Corresponding author's E-mail: *wael.karim@univ-orleans.fr

Abstract

In ceramic solid oxide electrochemical cells (SOEC), a thin film of gadolinium-doped cerium oxide (GDC) is deposited (by plasma sputtering) between the electrolyte (yttrium-stabilized zirconia, YSZ) and the oxygen electrode (lanthanum-strontium-cobalt ferrite, LSCF) to reduce the formation of insulating phases at the electrode/electrolyte interface. In order to improve the adhesion between these layers as well as the ion exchange surfaces, we have considered a micro/nanoscale morphological structuring process using laser beams. The challenge is to successfully fabricate well-organized nanostructures, commonly referred to as LIPSS (Laser Induced Periodic Surface Structures), on complex oxide thin films such as GDC.

In this work, a Nd: YAG laser beam operating at the third harmonic (355 nm) with a relatively large laser beam spot (~500 µm) and emitting 40 ps laser pulses, is employed to irradiate a 2x2 cm^2 surface of 700 nm GDC thin layer under both static and scanning irradiation conditions. Using high resolution scanning electron microscopy (HR-SEM), it is found that LIPSS are produced at a low fluence laser multi-pulse regime close to the ablation threshold. In the static mode and under appropriate values of laser fluence F and number of pulses N, we have also identified two types of LSFLs that are distinct in their direction and spatial period. $LSFL_{//}$ are parallel to beam polarization, with a typical period of 238 nm and found in the center of the irradiated zone, whereas $LSFL_{\perp}$ are oriented perpendicular to beam polarization with a spatial period of 296 nm and found on the rim of the irradiated zone (Fig.1).

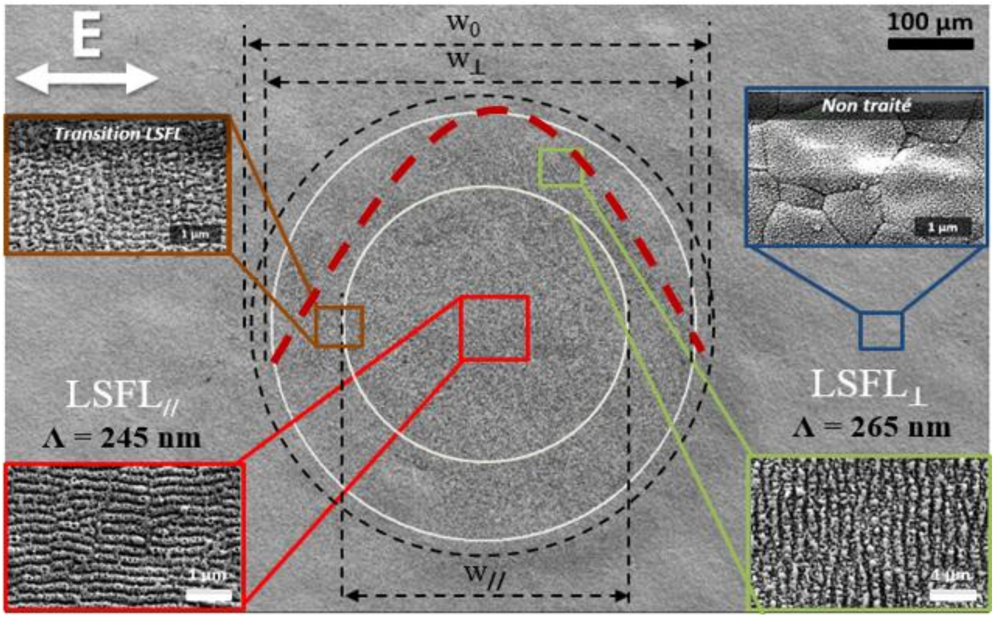

Fig.1: SEM image of the irradiated GDC film, for F=125 mJ/cm2 and N=10 pulses. The insets show the non-irradiated (untreated) surface as well as two different LIPSS patterns ($LSFL_{//}$ and $LSFL_\perp$) and the transition zone. W_0 is the beam spot size; $W_\perp$ and $W_{//}$ are the estimated diameters of $LSFL_\perp$ and $LSFL_{//}$ regions, respectively [1].

Our results suggest that the generation of parallel $LSFL_{//}$ is mainly attributed to a thermochemical process, while perpendicular $LSFL_\perp$ are due to a soft ablation process. A transition zone between these two types of LSFL manifested by the appearance of 'nano-squares' is due to the superposition of $LSFL_{//}$ and $LSFL_\perp$. We have also optimized the process parameters to generate well resolved LIPSS under beam scanning conditions.

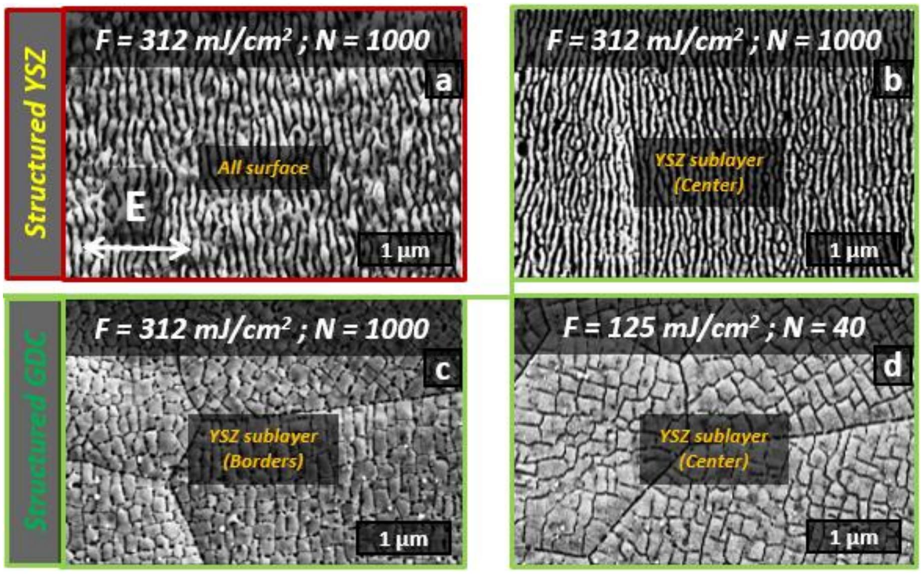

Fig.2: Comparison between the direct structuring of YSZ framed in red (a) and the structuring of YSZ functioning as the substrate of GDC thin film framed in green (b, c and d).

When ablation process of the GDC thin film takes place, the formation of organized patterns in form of square shaped cracks were observed on YSZ sublayer (Fig.2c-d). $LSFL_{\perp}$ were also identified on the YSZ surface, as well as HSFL (high spatial frequency LIPSS) formed on YSZ assisted by GDC thin film at a very large number of laser pulses (~1000) (Fig.2a).

The double scanning of laser beam in the same area of GDC with two different conditions (// and ⊥) leads to the formation of 2D structuring that were also obtained in scanning mode. Different surface characterization techniques (SEM-EDX, AFM, etc.), as well as COMSOL Mutliphysics simulations, have been used to interpret the obtained results. Considering the LIPSS sizes obtained in Fig.3 (better resolution of GDC cross section), with a geometric model, we were able to estimate a theoretical increase in developed area of 57% and 78% for 1D (regular LIPSS) and 2D periodic structures respectively. In this work, the largest experimental value reached is 42% for combined 2D structures of the 'nano-squares' type [1].

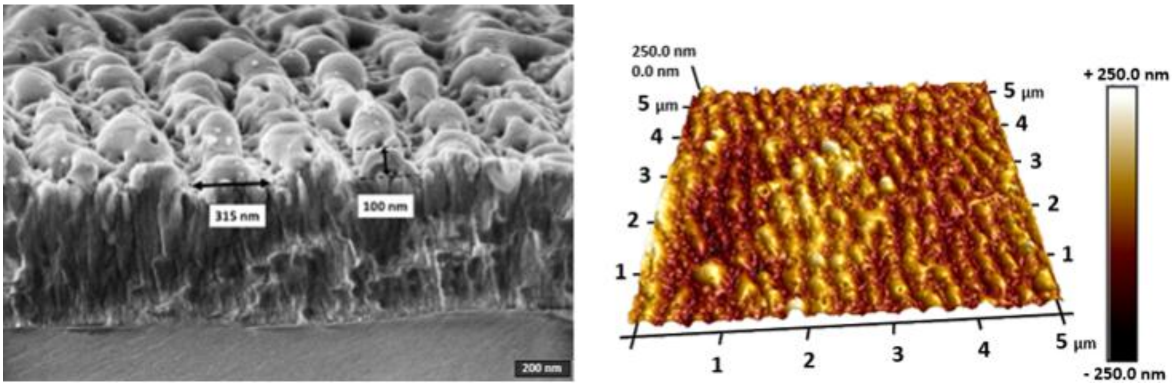

Fig.3: SEM cross section and 3D AFM images of 'nanosquared' surface of GDC/YSZ film for F=85 mJ/cm^2 [1].

REFERENCES

[1] Karim, W., Petit, A., Rabat, H. et al. Picosecond laser beam nanostructuring of GDC thin films : exchange surface enhancement by LIPSS.Appl. Phys. A 128, 731 (2022). https://doi.org/10.1007/s00339-022-05866-6