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# EXCIMER LASER ABLATION OF YSZ CERAMIC TARGET; IMPROVED PULSED LASER DEPOSITION CONTROL PARAMETERS FOR YSZ THIN FILMS GROWN ON SI (100) SUBSTRATES

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*Abstract.* Yttria Stabilized Zirconia thin films are of great technological interest, mainly as high-k dielectric materials, having potential applications as electrolytes for ionic devices. In this work, we explore the influence of growth parameters, such as target-substrate distance and number of ablation pulses, on the properties of YSZ thin films with variable thicknesses, which are of interest for the fabrication of micro-sized solid oxide fuel cells (μSOFC) and lambda sensor operating at low temperatures. Yttria Stabilized Zirconia (8YSZ) thin films with crystalline cubic structures were grown by pulsed laser deposition (PLD) on Si (100) substrates at a temperature of 600°C, in oxygen atmosphere. The structural and optical properties of the target and thin films were investigated through different techniques.

*Key words*: 8YSZ thin films, Pulsed Laser Deposition, Structural and Optical Characterization, μSOFC, Oxygen Sensor.

## 1. INTRODUCTION

The new developments in the field of high quality 8YSZ thin film electrolytes by PLD fabrication for μSOFC and multilayer planar potentiometric oxygen sensors [1, 2] involve the generation of controlled microstructure, with influence on structural and optical properties [3, 4, 5]. Experimental techniques for structural and optical characterization of YSZ thin films grown by PLD can offer quantitative data for technological design of new ionic devices [6]. To improve the global performance of such device it is necessary to optimize the complex problem of PLD by correlation the experimental data with some qualitative results of plasma plume expansion [2, 4]. In the same time is necessary to minimize the number and size of particulates by controlling the oxygen pressure and assure a correct stoichiometry by chosen properly the level of fluency. Planar electrochemical devices like μSOFC and mini potentiometric oxygen sensor fabricated mainly with PLD have a critical operation component 8YSZ thin film acting like an oxygen ion conducting solid electrolyte [7]. Zirconia ($ZrO_2$) is non-conducting material with crystalline structure influenced by temperature but with a high solid solubility up to 20 mol % for many oxides including $Y_2O_3$. The dopant $Y^{+3}$substitute for $Zr^{+4}$ site in a crystalline cubic fluorite phase of $ZrO_2$ generating the stabilization of such crystalline structure on a large field of operating temperatures. Oxygen vacancies resulting from doping process maintain the neutrality of crystal and facilitate diffusion of oxygen, resulting high oxygen conductibility. By creating oxygen vacancies in $ZrO_2$,$O^{2-}$ ions can move in the solid mixture like a solid electrolyte and activation is function of temperature; becomes effective above 300°C. 8YSZ thin films have advantage over bulk 8YSZ having a low ohmic resistance; the electrolyte resistance decreases linearly as thickness decreases [8]. The nonlinear conditions in PLD deposition generate crystalline films at temperature of 500–600°C [9]. Because the trend is to reduce the temperature of operation of YSZ based ionic devices, it is necessary to improve PLD deposition parameters. Spectroscopic ellipsometry possesses the unique advantage of allowing cross-checking of thickness and roughness values with morphology analysis techniques [6]. The accurate determination of these parameters is crucial for the fitting procedures and modeling used to extract optical coefficients with physically meaningful values. Structural and morphological characterization of PLD grown layers will be done by XRD, SEM and AFM measurements [10].

## 2. EXPERIMENTAL METHODS

In experiments it was used an ArF excimer laser (CompexPro), with a wavelength $\lambda$ = 193 nm, pulse duration $\sigma p$ = 15 ns, laser repetition frequency $\nu$ = 30 Hz and 10 Hz; fluency was $F$ = 5 J/cm$^2$. Wafer substrate composed of Si (100) was positioned at 50 mm and 70 mm from the target and was maintained at a temperature of 600ºC; the number of pulses was 36,000 and 72,000. The depositions were made with $p_{o2} = 8 \times 10^{-2}$ mbar. Ceramics targets (8% mol $Y_2O_3$)· $ZrO_2$ made by American Elements have been prepared by sintering technologies and structural characterization were investigated by XRD (Fig. 1).

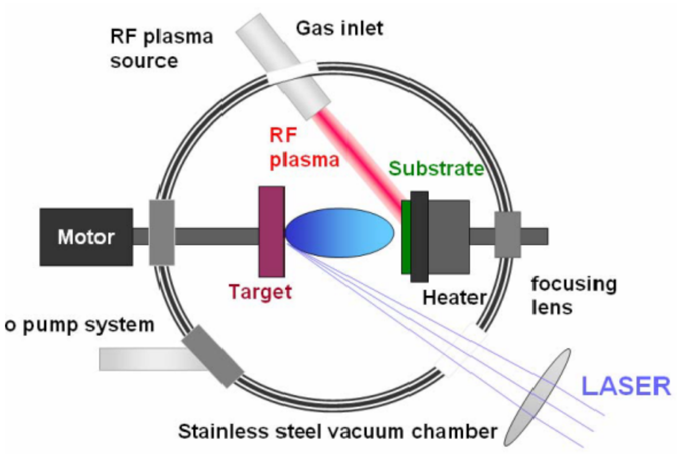



Fig. 1 – A schematic diagram of the pulsed laser deposition setup.

## 3. RESULTS AND DISCUSSION

### 3.1. X-RAY DIFFRACTION MEASUREMENTS

The X-Ray diffraction patterns (Fig. 2), reveal cubic symmetry (space group Fm-3m), the unit cell was used X'Pert HighScore Plus software from Panalytical resulting the lattice parameters: $a = b = c = 5.138$ Å. From the Fig. 2 it can be seen that the resulting films have the same crystalline structure as the used target.

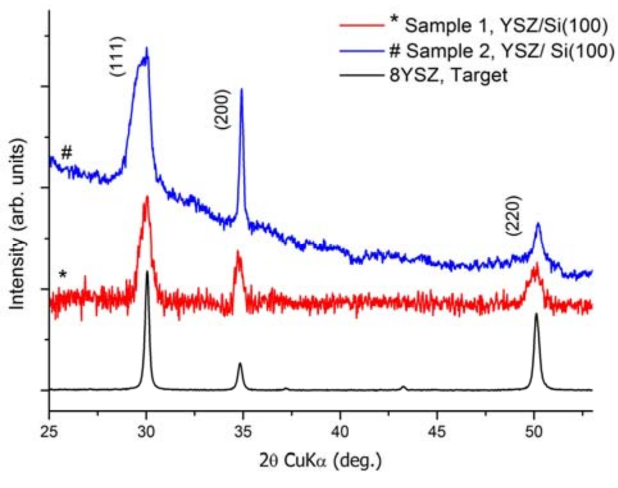



Fig. 2 – XRD spectra of 8YSZ targets, two thin films 8YSZ thin films
with different number of pulses.

### 3.2. SCANNING ELECTRON MICROSCOPY MEASUREMENTS

Figure 3 reveals that the (no. 36,000 pulses and no. 72,000 pulses) variation of the total number of pulses is very important for obtaining thin films, with 72,000 pulses where the process of deposition is more stable.

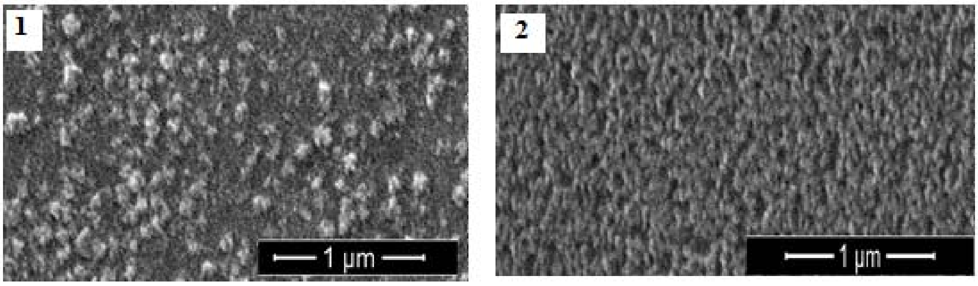



Fig. 3 – SEM for two thin films 8YSZ thin films with 1 with 36,000 pulses and 2 with 72,000 pulses.

### 3.3. ATOMIC FORCE MICROSCOPY MEASUREMENTS

AFM determinations were made with an atomic force microscope; model XE-100 from Park Systems. The measurements were carried out in non-contact mode (Nanosensors Inc.). Both tested sample 1 and 2 shows smooth aspect, with RMS (roughness) values of relatively small (7.8 nm or 4.1 nm) on areas of 20 × 20 µm$^2$. AFM images obtained on areas of 5 × 5 µm$^2$ with the presence of particles with different sizes; from a few tens of nanometers to several hundred nanometers (see topographic profiles in Fig. 4).

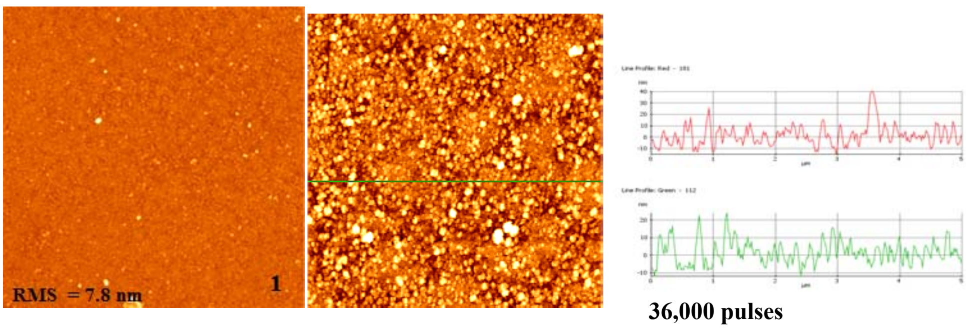



Fig. 4


**72,000 pulses**

Fig. 4 (continued) – AFM images (20 × 20 μm$^2$ and 5 × 5 μm$^2$) areas for two samples of YSZ.

### 3.4. SPECTROSCOPIC ELLIPSOMETRY MEASUREMENTS

Optical modeling and data analysis were done using WVASE 32 soft – ware package. Ellipsometric parameters Ψ and Δ were acquired at three angle of incidence (60°, 65° and 70°) over the spectral range of 250–1700 nm. Because 8YSZ for 36,000 pulses and 8YSZ for 72,000 pulses are transparent over 400 nm, it is possible to take $k = 0$ and to use the Cauchy dispersion relation, by relation:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2}, \quad (1)$$

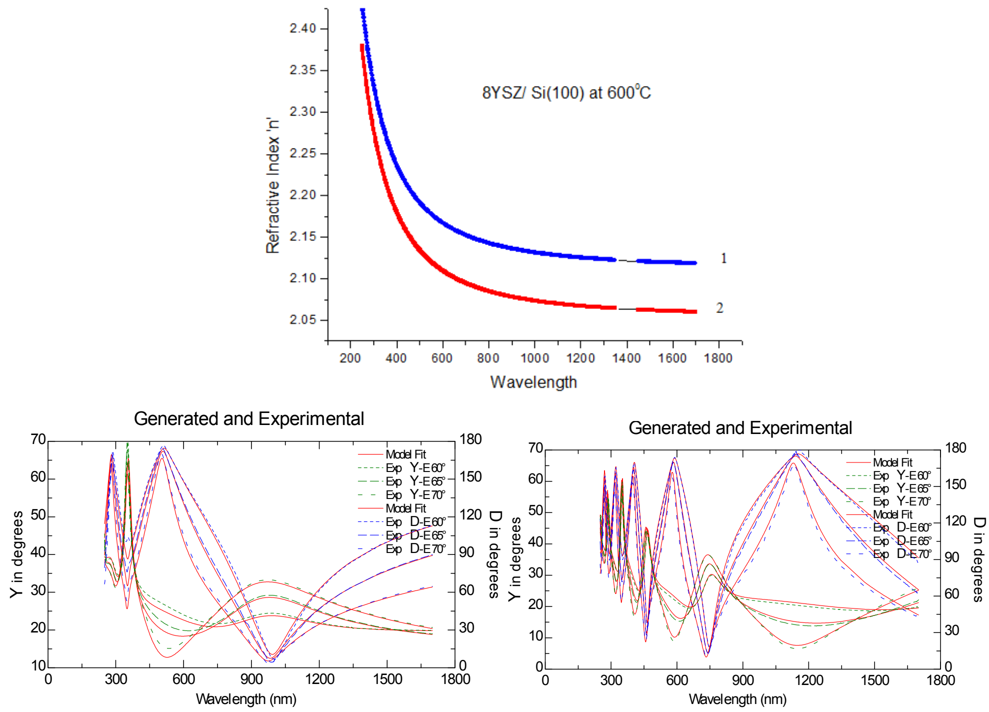
where $A_n$, $B_n$, are fit coefficients. The fitting of Ψ and Δ, optical models are presented in Fig. 5. Also, the fitting the Cauchy parameters $A_n$, $B_n$, thickness, roughness and the value of MSE (Mean Square Error) are presented in Table 1.

*Table 1*

Cauchy parameters for 8 YSZ/ Si (001)

| Sample | Thickness (nm) | Roughness (nm) | $A_n$ | $B_n$ | MSE |
|---|---|---|---|---|---|
| Sample 1 | 60,400 ± 4.8 | 18.069 ± 7.8 | 0.60446 ± 0.0089 | 0.10021±0.0027 | 62.02 |
| Sample 2 | 288,112 ± 0.341 | 20.290 ±0.135 | 2.0529 ± 0.0015 | 0.020433±0.0001 | 51.82 |

The refractive index presented in Fig. 5 evidenced a similar behavior of configuration $n$ (λ) and a small variation in function of thickness, being smaller for 72,000 pulses; the value is in accordance with the same measurements in the literature [11].




(1) (2)

Fig. 5 – Variation of refractive index for 8YSZ/Si (100) for two thin films.

The influence of native $SiO_2$ layer is observed in both thin films, prepared with 36,000 pulses and 72,000 pulses. The refractive index presented in figure evidenced a small variation in function of thickness, being smaller for 72,000 pulses; the value is in accordance with the same measurements in the literature [1, 10, 7]. The substrate optical constant is taken from literature and is not allowed to vary during the fit. The influence of native $SiO_2$ layer is observed both thin films for 36,000 pulses and 72,000 pulses. In Table 2 it is presented a comparation of roughness values determined by SE and AFM.

*Table 2*

Comparison of roughness values determined by SE and AFM

| No. thin film | No. of pulses | Srough (nm) | RMS (nm) | |
|---|---|---|---|---|
| | | | 5 × 5 μm$^2$ | 20 × 20 μm$^2$ |
| Sample 1 | 36,000 | 60.365 | 8 | 7.8 |
| Sample 2 | 72,000 | 20.290 | 5.8 | 4.1 |

## 4. CONCLUSIONS

Characterization of 8YSZ polycrystalline thin films deposited in different experimental conditions by Pulsed Laser Deposition has been carried out. Smooth, cracks and droplets free layers were found to be deposited for a wide range of deposition conditions. Correlated with other advantages of the PLD, this technique can prove more appropriate for YSZ thin films deposition than other techniques. Spectroellipsometric measurements evidenced a similar behavior of the refractive index with respect the wavelength, irrespective of the layer thickness, with smaller values for thicker layers. These results can improve the technological design of ionic devices; the variable number of pulses generates the same crystalline structures.

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