

Laser Ablation Ceramic Target for 8YSZ High-k Dielectric Electrolyte thin Films Precessed by PLD on Si(100) and Pt/Si(111)

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Abstract. The cubic structure 8YSZ (8%Yttria-Stabilized Zirconia) thin films deposited by PLD(Pulsed Laser Deposition) on substrates Si (100) and Pt/Si (111) by identical control parameters have potential applications as electrolytes for planar micro electrochemical devices like Lambda oxygen sensors and IT- μ SOFC. It appearance differences in polycrystalline structural and optical characterization by XRD (X-ray Diffraction), SEM (Scanning Electron Microscope), AFM (Atomic Force Microscopy) and V- VASE (Variable Angle Spectroscopic Ellipsometry. The differences are relating on crystalline dimensions, lattice parameters; surface roughness measured by V- VASE and AFM are presented synthetic to evidence the differences generated by substrates.

Keywords: thin films, electrolytes, potentiometric planar oxygen sensor, Cauchy- Urbach models, electrochemical devices

1.Introduction

The 8 YSZ (8% Y_2O_3 doped ZrO_2) thin films are high-k dielectrics advanced materials used as electrolytes in many fields like electrochemical devices - gas sensors for automotive application and intermediated temperatures (IT) solid oxide fuel cell (SOFC). 8YSZ electrolytes have high oxygen ionic conductivity and high ionic resistivity [1, 2]. This material assures a good compatibility with electrodes, is gas tight and chemically stable at high temperatures ($t < 1200^\circ\text{C}$) [3]. The cubic phase of 8 YSZ is stabilized on a large field of temperatures including low temperature ($t < 450^\circ\text{C}$) that involves applications in electrochemical devices with long life time of operation by avoiding thermal and mechanical degradation at high temperature [4]. Being operating according Nerst equation, the temperature is the main parameter for working with direct influence on the global efficiency of the cell. Other parameters like methods of deposition, new design configurations and new materials with optimal properties using thin films technologies it can be generate the reduction of thickness of electrolytes with low ohmic resistivity. In the range of 1-1000 nm, CVD (Chemical Vapor Deposition), plasma enhances CVD [5, 6] and PLD [7] can be used to produce good quality thin films. PLD can grow cubic crystalline 8YSZ thin films with good adherence to the substrate and respecting the stoichiometric the target [8]. Planar 8YSZ thin films have lower degradation on different types of gas composition. The thickness and the structures of the film can be controlled by deposition parameters (laser fluency, laser wavelength, deposition time, substrate material, substrate temperature, distance target- substrate etc.).The task of this paper is to investigate the effects of Si (100) and Pt/Si (111) substrates on the optical and structural properties [10, 11]. Such properties are studied by XRD, SEM, AFM and V-VASE.

2.Materials and methods

8YSZ target with 14 mm diameter x 5mm thick was manufactured by American Elements (SUA) by sintering powder of 99, 99%Zirconia and 8mol% Yttria –Stabilized. The deposition of 8 YSZ thin films with different substrates were fabricated on CompexPro 50 PLD equipment using ArF excimer

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laser ($\lambda = 193\text{ nm}$) with energy of 230 mJ pulse^{-1} and repetition rate $= 10\text{ Hz}$, fluence $= 5\text{ J/cm}^2$, in oxygen partial pressure of $8 \times 10^{-2}\text{ mbar}$, the laser beam was focused at an angle of incidence of 45° on YSZ target. Two sets of experiments were made by using Si (100) and Pt/Si (111) substrates ($15 \times 15\text{ mm}$) at 500° C and 50 mm distance target- substrates with the same number of pulses and time of depositions sample (72.000/ Si (100)) and (72.000/ Pt/Si (111)) configurations. The vacuum chamber has a base pressure $2 \times 10^{-4}\text{ mbar}$ for both samples by operating a turbo pump (Figure 1).

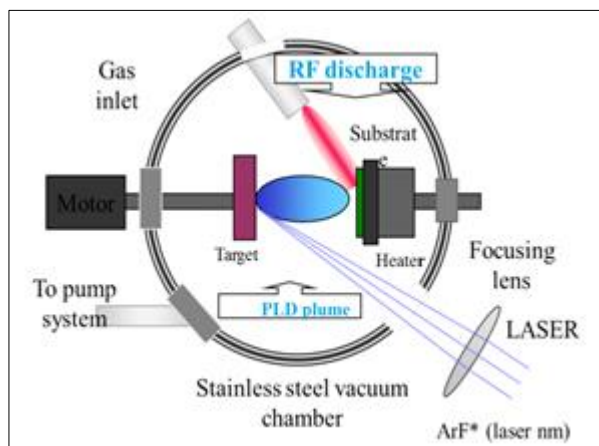


Figure 1. A schematic diagram of PLD system

The XRD measurements have been performed by using a Panalytical X'Pert PRO MRD diffractometer equipped with monochromatic X-ray radiation of $\text{CuK}\alpha\ 1$ (0.154056 nm) in Bragg-Bretano geometry with 2θ in the angular range $15\text{--}75$, scanned in steps of 0.02 with an acquisition time of 0.2 s/step . The Joint Committee on Powder Diffraction Standards (JCPDS) database from the International Center for Diffraction Data (ICDD) was utilized for structural characterization like phase identification, crystalline dimensions and lattice constant. The Scanning Electron Microscope (SEM) manufactured by FEI – SEM FEI Inspect S is designed to investigate the surface quality of 8YSZ on Si (100) and Pt/Si (111) thin films. Atomic Force Microscopy (AFM) XE-100 Park Systems is used to characterize the morphology and Root Means Square (RMS) roughness, in non-contact mode; allows a maximum horizontal scan area of about $50 \times 50\ \mu\text{m}^2$ and a vertical movement up to $12\ \mu\text{m}$. The investigated areas were $2 \times 2\ \mu\text{m}^2$, $5 \times 5\ \mu\text{m}^2$, $20 \times 20\ \mu\text{m}^2$, for revealing both the general aspect of the samples as well as their topographic details. V-VASE with variable angles of incidence ($60^\circ\text{--}70^\circ$) is used for optical characterization, having high accuracy and precision with a wide spectral range $250\text{--}1700\text{ nm}$. Optical models are generated by WVASE32 software; n , k parameters and roughness are measured [12].

2. Results and discussions

XRD characterization of 8YSZ ceramic target and thin films deposited on Si (100) and Pt/Si (111) are lay out in Figure 2. This is necessary to identify the crystalline structure that will be transferred on the substrates. Also, the structural characterization of the thin films of 8YSZ/Si (100) and Pt/Si (111) are presented in relation to the same diagrams for identification of crystalline phases. The (111) crystalline phases are cubic phase, and are identified using the standard base XRD JSCPDS file 089-9069.

The average crystallite sizes were calculated at the peak position of the (111) reflection ($\theta = 40^\circ$), a strongly preferential orientation. The spectra indicate that the deposited films have polycrystalline structure, with lattice constants $a = 0.4256\text{ nm}$ (YSZ/ Si (100)) film and respectively $a = 0.4987\text{ nm}$ (YSZ/ Pt/Si (111)). From Table 1 it is observed also the influence of Pt/Si (111) substrate on lattice parameter.

Surface morphology of thin films are characterized by AFM, measuring variable RMS (Root Mean Square Roughness) of 12.423 nm, 12.108 nm and 9.762 nm for Pt/Si (111) respectively 10nm, 9.22 nm and 7.822 nm for Si(100) (Figure 3).

AFM images shows nanoscale grains with homogeny distribution; variation in RMS is a function of dimensions of widows of exploration $2 \times 2 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$, and $20 \times 20 \mu\text{m}^2$ [13].

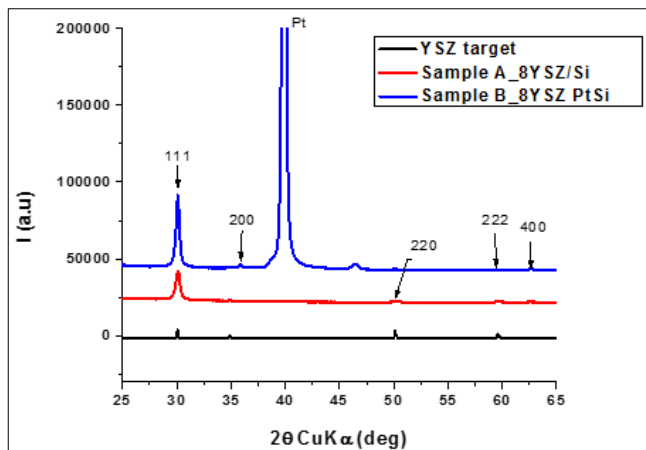


Figure 2. XRD spectra of the 8YSZ / Si (100) and 8YSZ /Pt/Si (111) thin films and 8YSZ target. Diffractograms show the films are crystalline with fluorite cubic structures

Table 1. The value of lattice parameter and mean dimension for crystallites for 8YSZ targets and 8YSZ thin films on different substrates

Sample and target	Substrate type	YSZ phase	
		Lattice parameter a (nm)	Crystallite dimension D (nm)
8YSZ	Target	0.5155	18
8YSZ	Si	0.4256	10
8 YSZ	Pt/Si	0.4987	16
ZrO ₂ -cubic Standard JCPDS (089-9069)		5,1350	

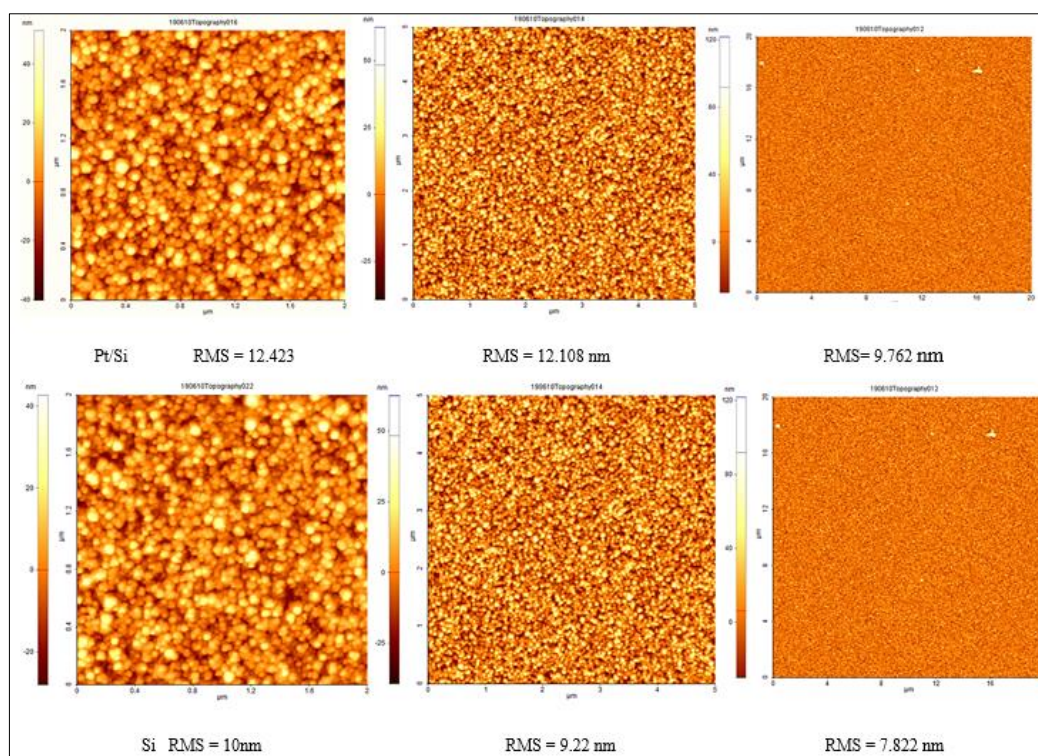


Figure 3. AFM images (2D) $2 \times 2 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$, $20 \times 20 \mu\text{m}^2$ areas of 8YSZ deposited on Si (100) and Pt/ Si (111) deposited at 500°C

The top view surface characterized by SEM are observed in Figure 4 a and 4b; the surfaces are free of cracks with small droplets and small particles.

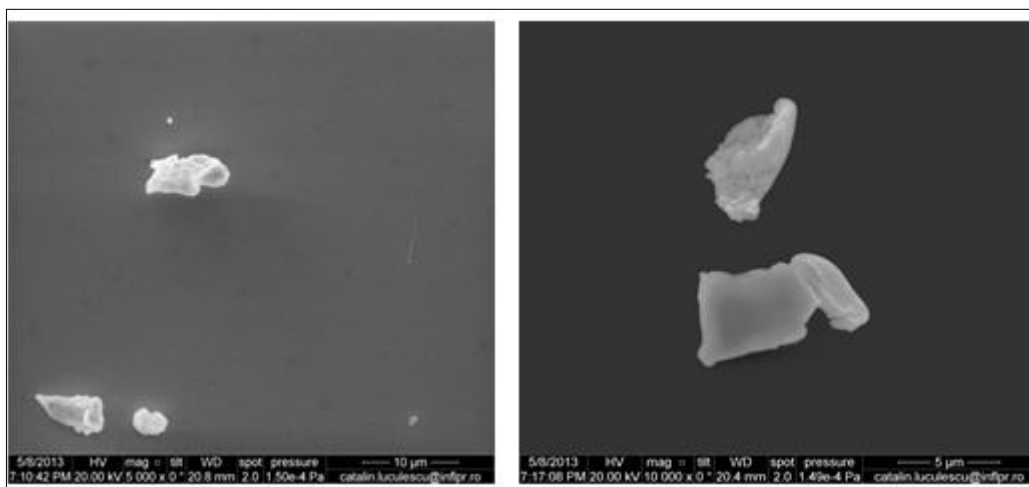


Figure 4. Top view SEM surface morphology of microstructures samples (a) and (b)

High - k ceramic electrolyte 8YSZ thin films are transparent over a large range of the spectrum and it was selected a Cauchy optical model for characterization. In the operating range (250-1700nm), optical characterizations were made using a VVASE (Variable Angle Spectroscopic Ellipsometry) (Woollam, SUA) assisted by the WVASE 32 software package for processing ellipsometric parameters, acquired at three angles of incidence (60°, 65° and 70°). The best fit of experimental data for deposition on Si (100) has been obtained by dispersion formula, called generalized Cauchy functions:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \quad (1)$$

and $k=0$ all measured wavelength, where: A_n , B_n , C_n parameters [14]; Cauchy – Urbach was applied for deposition on Pt/Si (111) substrate.

The first term A_n is a constant that has the largest contribution in shaping the curve and an initial estimate is required. The coefficient B_n has an influence on the curvature and C_n has a reduced contribution, also on the curvature, and in the last upgrade of VVASE 32 it is take $C_n = 0$. In Table 2 value of thickness of each layer and Cauchy - Urbach parameters are presented.

Table 2. Values of estimated parameters for assumed models for both thin films

	8YSZ/ Si (100) Thin films	8YSZ/ Pt/Si (111) Thin films
Thickness 8YSZ	9.872	22.992 nm
Roughness	61.878	215.834 nm
A_n	0.0923	2.7196
B_n	0.40121	1.8095
C_n	0	0.03676
Platinum substrate	-	67.426 nm
SiO ₂	3.000 nm	3.000 nm
λ	400 nm	400 nm

These parameters give the best fitting between experimental and theoretical curves. On Figure 5 a and b are measured ellipsometric parameters (Δ and Ψ), shown in green lines that correspond to experimental and theoretical data. Almost perfectly arrange between these two curves is seen for that models are three different angles of incident. That mean our model describe real structure very well. (Figure 5 a and b).

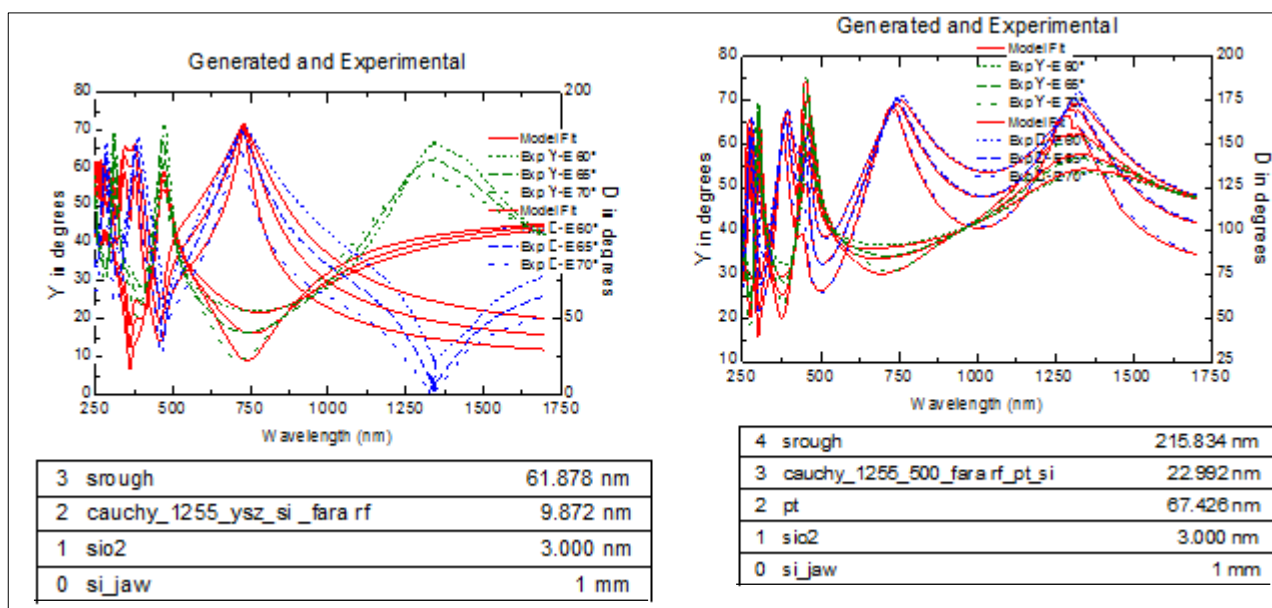


Figure 5. Theoretical and experimental ellipsometric data (Δ and Ψ) of 8YSZ thin films at three incident of angles

Using parameters form Table 2 of Cauchy- Urbach for model B, optical constants can be found (Figure 6).

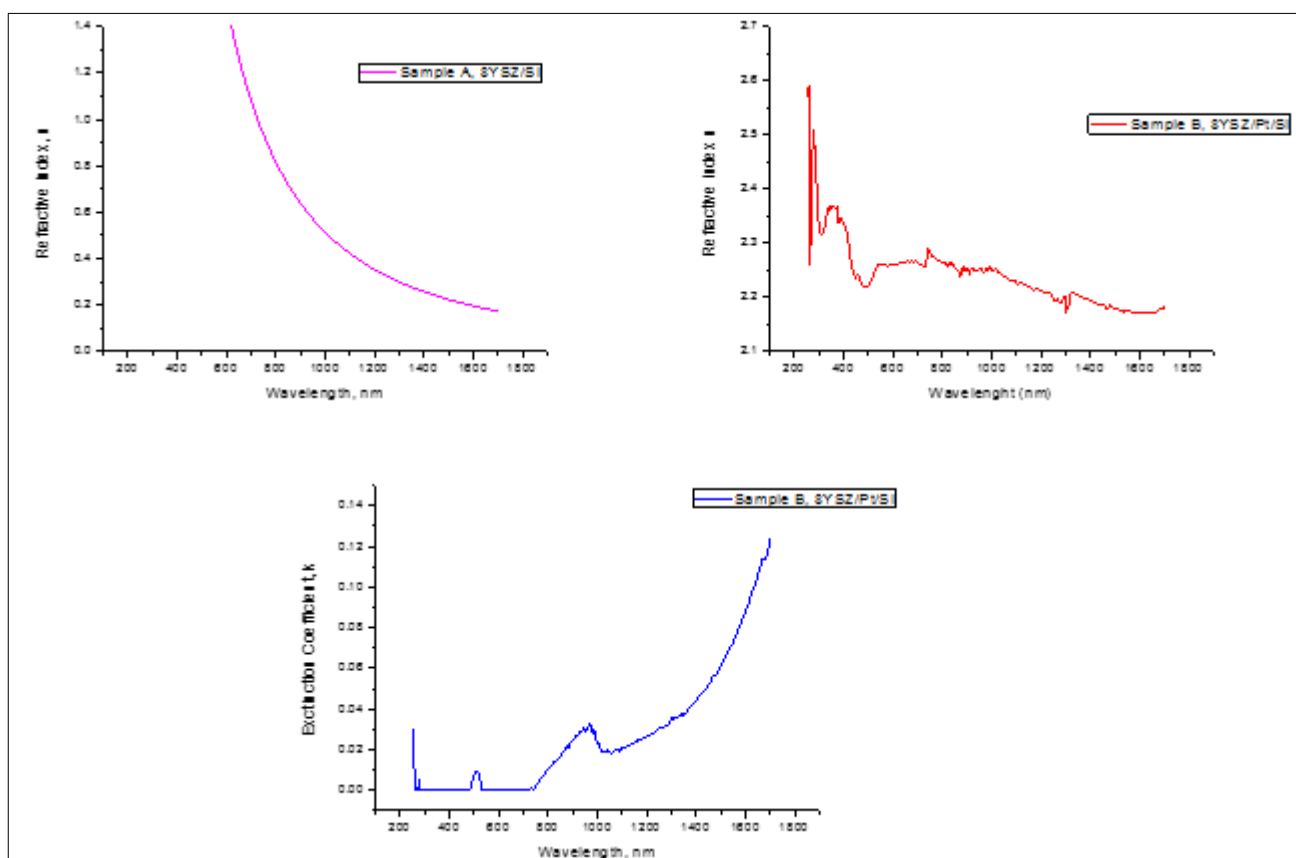


Figure 6. Variation the optical constants n and k for 8YSZ thin films estimated by ellipsometry

In Table 3 it is presented a comparison between roughness measured by SE and AFM; the differences are generated by the fundamental principal of measurement in SE and AFM.

Table 3. Surface roughness measured by SE and AFM

Sample	Type substrates	Deposition temperature (°C)	Roughness measured by SE (nm)	RMS roughness AFM (nm)			Thickens nonuniformity (%)	MSE
				2x2µm ²	5x5µm ²	20x20µm ²		
Sample A	Si(100)	500	61.878	10	9.220	7,822	34.56	281.5
Sample B	Pt/Si (111)	500	215.834	12.423	12.108	9.762	9.23	56.83

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4. Conclusions

Oxide ion electrolytes 8YSZ for clean energy and lambda oxygen sensor planar electrochemical devices have been deposited on Si (100) and Pt/Si (111) to study the influence of substrate on structural and optical properties. The cubic structure, the roughness and optical data are influenced in different scales. The task is to assure the reproducibility of PLD technology applied mainly for customized production.

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