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OPTICAL AND STRUCTURAL CHARACTERIZATION OF YSZ THIN FILMS DEPOSITED BY EXCIMER LASER ABLATION FOR PLANAR POTENTIOMETRIC OXYGEN SENSORS APPLICATIONS

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Abstract. We have performed optical and structural characterization of Yttria Stabilized Zirconia (YSZ) thin films prepared by pulsed laser deposition (PLD) on Si (100) and Pt/Si (100) substrates from the ablation of a 8YSZ target by ArF excimer laser. X-ray Diffraction (XRD) analysis stated orthorhombic films with [111] preferential orientation for Pt/ Si substrate and cubic phase for Si (100) substrate. Secondary Ion Mass Spectrometry (SIMS) investigation shows a stoichiometric transfer of target composition to the substrates. By using Atomic Force Microscopy (AFM) and Variable Angle Spectroscopic Ellipsometry (VASE) we have determined the thickness, roughness, and refractive indices of thin films. Ellipsometric data were obtained with the Cauchy model in the spectral range 400-1000 nm, at three angle of incidence: 60°, 65°, and 70°. It was obtained high-k dense YSZ thin films deposited on Si (100) with applications for electrolyte of ionic devices, like oxygen sensors.

Key words: planar potentiometric oxygen sensors, YSZ thin films, PLD, XRD, SIMS, AFM, VASE.

1. INTRODUCTION

High-k dense YSZ thin films can be used as solid state electrolyte for oxygen sensors in optimisation of the engine exhaust compositions [1–3]. The performance and reliability of ionic devices are function of temperature for activation that involved the implementation of thin films techology for fabrication of electrolyte in order to reduce ohmic resistance.

The pulsed laser deposition (PLD) techniques are used to grow adherent crystalline planar YSZ thin films on Si (100) and Pt/Si substrates. Both optical and structural features were investigated on a number of samples deposited after a selection of control parameters.

It has been demonstrated that the pulsed laser deposition of YSZ thin films on Si(100) and Pt/Si (100) substrates is a very powerful technique for generation of a series of structures necessary for characterization and evaluation of new compact oxygen sensor techniques [4–6].

2. EXPERIMENTAL METHODS

We have used a PLD system without RF, which was fabricated by COMPexPro, based on an excimer laser ArF (λ = 193 nm), at 10 Hz rate of deposition, with 15 ns pulse duration and a fluence of 5 J/ cm^2. The sintered target is a (8%mol Y_2O_3) ZrO_2 produced by American Elements that is ablated by the laser beam at incidence angle of 45°. The substrate temperature was 600 °C, an optimal temperature to grow a well designed phase with a high ionic conductivity [7, 8]. The distance between target and substrate was 50 mm to avoid the frontal shock wave to the substrate; the free space between shock waves and substrate assures a diffusion of all elements to the surface of substrate with a high kinetic energy. The oxygen pressure for deposition was 8×10^{-2} mbar in PLD deposition without RF.

The crystalline structures of the thin films were investigated by X-ray diffraction (PANalytical X'Pert MRD) [9], the chemical compositions of the surfaces were investigated by SIMS (Hiden SIMS Workstation) [10], the surface morphologies were investigated by AFM (XE-100) [11] and the thickness, roughness and optical properties were measured by Variable Angle Spectroscopic Ellipsometry (VASE, Woollam Co.) at three angles of incidence [12, 13].

3. RESULTS AND DISCUSSION

3.1. X-RAY DIFFRACTION

The structural characteristics of the thin films were investigated by XRD. Figure 1 shows the XRD characterization of ceramic target of YSZ used for laser ablation.

The stabilization process of YSZ in the cubic symmetrical fluorite bulk structure is generated by the dissolution of Y^{3+} in the ZrO_2 matrix and made from the concentrations of Y_2O_3 over 8% molar rate. The substitution of Zr^{4+} with Y^{3+} besides the stabilization of crystalline lattice leads also to an excess of O_2 vacancies that will produce a expansion of elementary cell by the difference in Shannon ionic radius. From experiment it was obtained an ionic radius of Zr^{4+} of 0.59 so Zr^{4+} substitutions with a chemical element with higher Shannon ionic radius like Y^{3+} will stabilize the lattice.

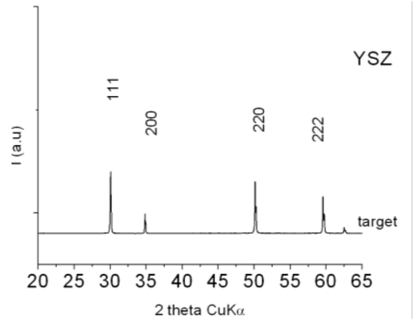


Fig. 1 – XRD spectra of YSZ target.

The lattice constants are presented in Table 1 that shows the expansion of elementary cell. The mean dimension for crystallites was estimated with average value over all calculated dimensions on crystallographic directions that appear in spectra (Table 1).

Table 1

The value of lattice constant and mean dimension for crystallites for YSZ target

Targets	*a* (Å)	*D* (nm)
ZrO_2-cubic Standard JCPDS (089-9069)	5.1350	–
$(8\%Y_2O_3)\cdot ZrO_2$	5.1429	85

The selected deposition conditions, target temperature, oxygen pressure generated a polycrystalline phase for thin films on substrates Si (100) and Pt/Si (100). The typical spectra of the thin films deposed on Si (100) and Pt/Si (100) in comparison with those of targets are presented in Fig. 2.

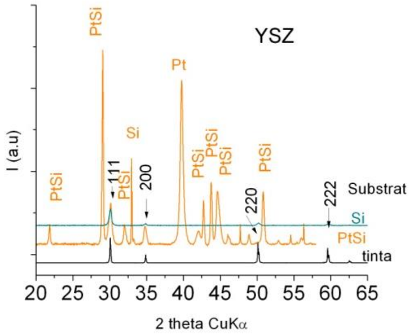


Fig. 2 – The spectra of YSZ thin films deposited on Si (100) and Pt/Si (100)
in comparison with those of targets.

The spectra presented in Fig. 2 reveals some characteristics generated mainly by the nature of substrates. The high temperature of deposition (600 °C) leads to the formation in the case of Pt/Si (100) of an orthorhombic Pt/Si (100) compound (JCPDS 083-0152). In YSZ spectra deposited by Si (100) it is identified all the reflections originating from cubic YSZ phase that demonstrates the polycrystalline character of the phase. The YSZ deposited on Pt/Si (100) has a preferential orientation on direction (111). Structural data are presented in Table 2. The stuctural data reveals that the thin films maintain a good stoichiometry of target with lattice constants similar in dimension with smollar grains but keeping the dimension orders of crystallite of YSZ targets.

Table 2

The value of lattice constants and mean dimensions for crystallites for YSZ target, YSZ / Si (100), and YSZ/Pt/Si

Target/ Substrate (thin films)	*a* (Å)	*D* (nm)
YSZ target	5.1429	85
Si (926)	5.144	25
PtSi(925)	5.146	14

3.2. SECONDARY ION MASS SPECTROMETRY

SIMS investigations on the thin films have been made using an incident Ar^+ ions beam with energy of 5 keV at a fixed angle of incidence of 30°. In function of time of exposure, the primary beam eroded in depth of films resulting the chemical composition. For YSZ thin film 926 on Si (100) and 925 on Pt/Si (100) it is observed that the variation of Zr^{4+} is almost identically in both cases. Differences appear in the distribution of Y influenced by Pt (Fig. 3).

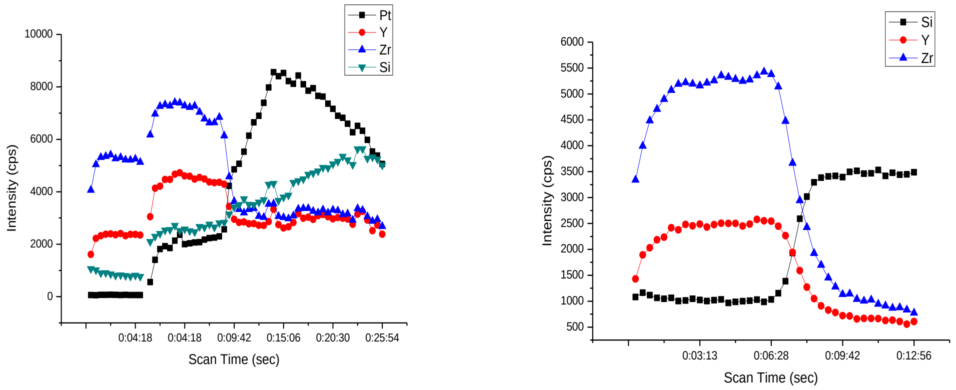


Fig. 3 – Distribution of chemical components from the secondary beam eroded from the surface of YSZ thin films: 925YSZ/Pt/Si (left panel), 926 YSZ/Si (right panel).

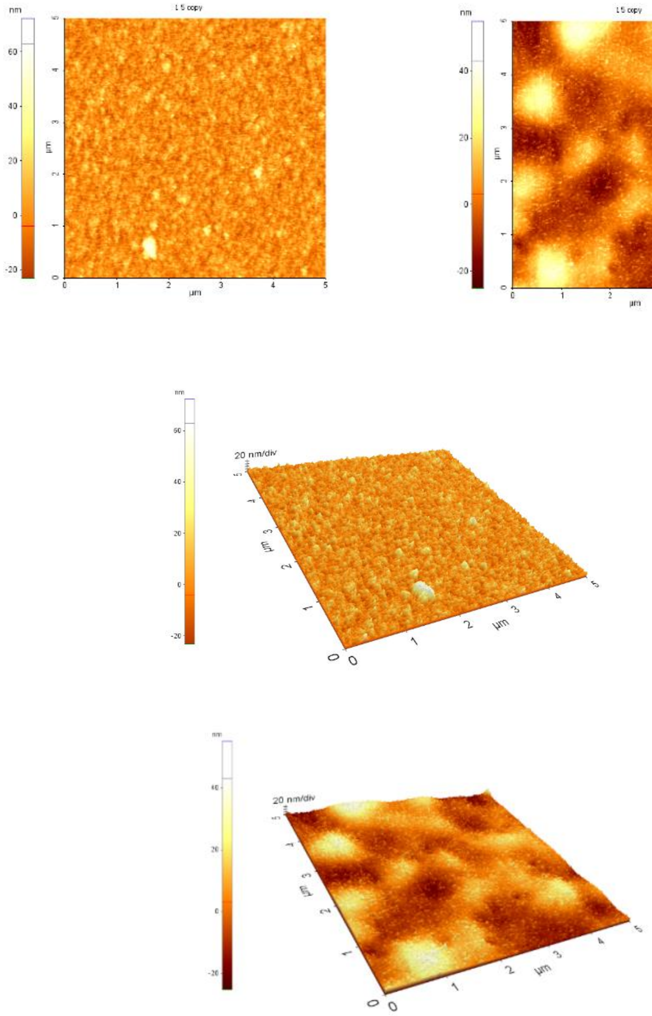


Fig. 4 – AFM images (planar and 3D views, non-contact) YSZ /Si (left panel), and YSZ /Pt/Si (right panel) on thin films with 5 × 5 μm^2 area.

3.3. ATOMIC FORCE MICROSCOPY

AFM images in three different windows are used to characterize the morphology of YSZ thin films. Figure 4 shows the surface morphologies of YSZ thin films; it were obtained uniform structures with a small number of droplets.

The Pt/Si substrate has an influence on deposition of YSZ and the RMS is higher than that corresponding to the film on Si (100). These features are observed on the images presented in Fig. 4.

The values of RMS presented in Table 3 indicate higher values for Pt/Si substrate.

Table 3

The value of Root Mean Square of roughness for three windows

Sample No.	RMS Deviation (nm)		
	5 × 5 μm^2	10 × 10 μm^2	20 × 20 μm^2
(8%molY_2O_3)·ZrO_2/Pt/Si(100)	10.6	11	12.6
(8%molY_2O_3)·ZrO_2/Si(100)	9	9.6	12

3.4. SPECTROSCOPIC ELLIPSOMETRY MEASUREMENTS

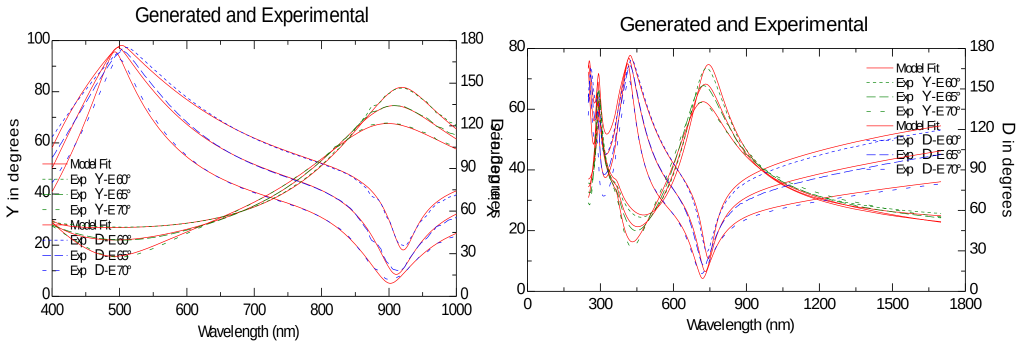
The refractive index values of the thickness and the roughness of YSZ thin films were measured by VASE in the spectral range 400–1000 nm, at three angles of incidence: 60°, 65°, and 70°. Because the thin films are highly transparent it was selected the Cauchy dispersion relations for fitting the measured data.

In Table 4 are presented the fitted data of optical Cauchy model (An and Bn), the thickness values of multilayer system and the planar uniformity. The fitting procedure is evaluated by MSE (Mean Square Error); the values obtained (32.58 for YSZ/ Pt/ Si and 76.81 for YSZ/ Si (100)) indicated good fittings and are presented in Fig. 5.

Table 4

The fitted data for thickness and roughness of YSZ thin films, Cauchy coefficients dispersion functions and the value of MSE

925 YSZ/ Pt/ Si		**926 YSZ/ Si**	
MSE = 32.58		**MSE = 76.81**	
ThkUni	5.0379±0.13	ThkUni	6.8404±0.691
Thick.1	6.782±0.102	Thick.3	34.168±0.799
Thick.2	10.219±0.141	Thick.2	107.616±0.507
An.2	2.6844±0.0068	An.2	1.6921±0.00221
Bn.2	0.074499±0.000944	Bn.2	0.016922±0.000374
Thick.3	123.248±0.475		



3	srough	123.248 nm
2	cauchy	10.219 nm
1	pttatat	6.782 nm
0	si_jaw	1 mm

3	srough	34.168 nm
2	cauchy	107.616 nm
1	sio2_jaw	3.000 nm
0	si_jaw	1 mm

Fig. 5 – Fitted Ψ and Δ spectroellipsometer parameters at three angles of incidence and the corresponding values of mltilayer system.

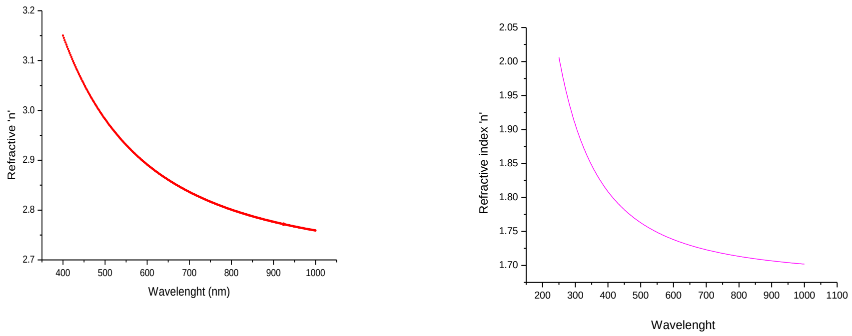


Fig. 6 – Variation of refractive index *n* (λ) for 925 YSZ/ Pt/Si (left panel) and for 926 YSZ/Si (100) (right panel).

The variation of refractive index *n*(λ) for YSZ/ Pt/Si and YSZ/Si (100) presented in Fig. 6, are in accordance with the values presented in Ref. [4]. However, it resulted higher refractive index values for YSZ/Pt/Si.

4. CONCLUSIONS

The deposition by PLD of YSZ thin films at 600 °C substrates led to an orthorhombic compound for Pt/Si with a preferential orientation on direction (111). In YSZ deposited on Si (100) it was identified all the reflections originating from the cubic YSZ phase. Structural data of thin films reveal the maintaining of a good stoichiometry of target with the same dimension in lattice constant and keeping the dimension orders of crystallites target YSZ. By SIMS it is observed that the variation of Zr^{4+} is almost identical in both cases with a difference in distribution of Y, influenced by Pt. Only RMS values determined by AFM for YSZ/Si (100) are correlated with VASE measurements. For YSZ/ Pt/Si deposited at the same numbers of pulses (36,000) it appeared different values for thickness and roughness mainly by influence of Pt. Also, the refractive index n (λ) of YSZ/ Pt/Si is higher than that of YSZ/ Si (100), in conditions of good fittings for the Cauchy optical model. YSZ/ Si (100) is a planar, dense thin film than can be used mainly like electrolytes in ionic devices, for large scale production [7].

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