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OPTICAL AND STRUCTURAL CHARACTERIZATION OF Ni DOPED YSZ THIN FILMS DEPOSITED BY EXCIMER LASER ABLATION

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Abstract. Thin films of 5%Ni:YSZ and 10% Ni: YSZ where grown on Si (100) and Pt/Si (100) substrates by Pulsed Laser Deposition (PLD) and Radio Frequency Pulsed Laser Deposition (PLD-RF). It were reported optical and structural characterization methods like X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Secondary Ion Mass Spectroscopy (SIMS), Variable Angle Spectroscopic Ellipsometry (VASE). XRD spectra was influenced by the nature of substrate that was also confirmed in VASE analyses of roughness and refractive index. Also AFM and SIMS measurements demonstrate a stoichiometric transfer of target composition on thin films. Optical properties are characterized by the refractive index values of 5%Ni: YSZ and 10%Ni: YSZ measured by VASE in the spectral range 400–1000 nm, at three angles of incidence: (45°, 65° and 70°). The thin films being highly transparent it was selected Cauchy dispersion relation for fitting the measured data with optical model. The obtained of dependence of the refractive index as a function of the wavelengths of incident light, from comparasion of data there were some significant differences between values of refractive index, thickness and roughness; influenced by conditions of deposition, type of substrates and level of doping with Ni.

Key words: YSZ doped with Ni, PLD and PLD-RF, XRD, SIMS, AFM, VASE.

1. INTRODUCTION

Thin films like 5% and 10% Ni-YSZ have been studied intensively in the last period as a promising and technology in new ionic devices with high efficiency and stability [1, 2, 4, 8]. PLD and RF-PLD technologies are resticted only at planar thin films at small areas but very useful in development of new devices. A number of research groups reported Ni-YSZ thin films of good quality, grown mainly by optimization of PLD control parameters [3]. The global performance of an electrochemical device based on Ni-YSZ thin films like is influenced by dispersion of nano-sized Ni particles like in the porous matrix of YSZ [5]; agglomeration of NiO on the surface must be avoided in the range of 5% to 10% Ni contents [10]. To reach such a difficult task is necessary to produce planar thin films of anode by controlling structural and optical characteristics [6].

2. EXPERIMENTAL

The equipment used in this study for deposition of 5%Ni:YSZ and 10%Ni:YSZ thin films consists of a PLD system with and without RF device, based on an excimer laser ArF (λ = 193 nm), COMPex Pro, at rate of deposition 10 Hz, pulse duration 15 ns and fluence 5 J/ cm^2. RF-PLD is used for deposition of such complex oxides like a supplementary, controlled pressure of O_2 and the influence is compared with the clasical PLD [3, 5, 7, 9]. The power of RF is in the range 50–200 W, at a frequency of 13.56 MHz, for the O_2 plasma is flowing 50 – 200 standard cubic centimeters per minute (sccm). The substrate temperature was 600°C and the distance between target and substrate is 50 mm. The thickness of thin films is controlled by number of pulses (36,000 and 14,400). The values of p_{o2} for 5%Ni:YSZ are 2.5×10^{-4} mbar and 2.1×10^{-5} mbar and for 10% Ni:YSZ the value of p_{o2} is 3×10^{-5} mbar. The crystalline structures of the thin films were investigated by, X-ray diffraction (PANalytical X'Pert MRD) [11]; the chemical compositions of the surfaces were determined by SIMS (Hiden SIMS Workstation) [12], surface morphologies were determined by AFM (Quesant Q- Scope 250) [13] the thickness and optical properties were measured by Variable Angle Spectroscopic Ellipsometry (VASE, Woollam Co.) [15] at three angles of incidence.

3. RESULTS AND DISCUSSION

3.1. X-RAY

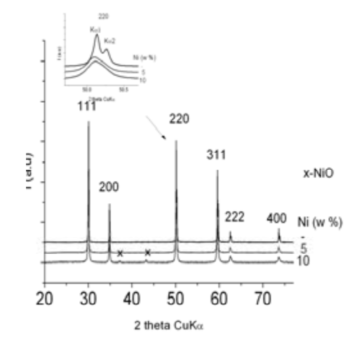


Fig. 1 – XRD spectra of 5%Ni: YSZ and 10%Ni: YSZ targets.

Figure 1 shows the XRD characterization of ceramic targets 5%Ni:YSZ and 10%Ni:YSZ used for laser ablation and deposition on Si (100) and Pt/ Si(100) substrates. The mean dimension for crystallites was estimated with average value over the all calculated dimensions on crystallographic directions that appear in spectra. These effects are shown in the insert diagram from Fig. 1. For the target 10%Ni: YSZ it was possible to identify the diffraction lines of NiO (JCPDS file 47–1049). NiO particles have the dimensions of approximately 109 nm and appear as a result of target preparation by sintering. At the target 5%Ni: YSZ it was not possible to identify lines generated by Ni and its compounds that indicated a high dispersion of Ni. It results that at 10%Ni: YSZ, a fraction of Ni concentration generates a disperse phase and another part is organized in NiO particles. The effect of Ni like dopping can be shown also by a small difference in dimension of particles that means an effect of crystalline order of YSZ matrix that appears between the two targets (Table 1).

Tabel 1

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

Thin Films	*a* (Å)	*D* (nm)
ZrO_2-cubic Standard JCPDS (089-9069)	5,1350	-
5%Ni:YSZ	5,1474	40
10%Ni:YSZ	5,1458	31

From these analyze of elementary cell parameters it results that 5Ni:YSZ target and 10Ni:YSZ target can be defined more like mixtures of oxides without the detection by XRD a solubility of Ni in YSZ matrix. Otherwise it can be estimated the Ni solubility being less than 5 mol % for the sintering temperatures higher than 1600°C. NiO phase in Ni: YSZ target is possible to be amorphous at XRD because the small dimension of particles, advanced dispersion and reduced concentration. The selected deposition conditions, substrate temperature, oxygen pressure generated a polycrystalline phase for thin films on substrates Si (100) and Pt/Si(100). The typical spectra from the thin films deposed on Si (100) and Pt/Si (100) comparative with the targets are presented in Fig. 3 and Fig. 4.

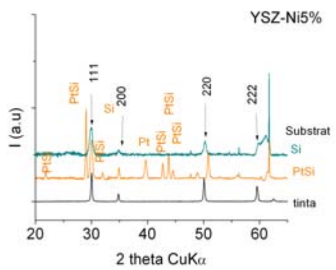


Fig. 2 – The spectra 5%Ni: YSZ thin films deposed on Si (100) and Pt/ Si (100) comparative with 5%Ni: YSZ target.

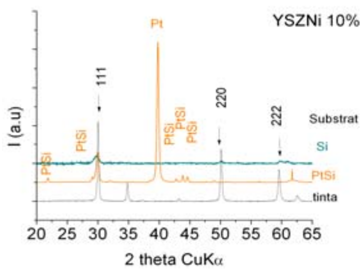


Fig. 3 – The spectra 10%Ni: YSZ thin films deposed on Si (100) and Pt/Si (100) comparative with 10% Ni: YSZ target.

The spectra reveal 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). The stuctural data reveal that the thin films maintaine a good stoichiometry of target with lattice constants similar into the dimension with smaller grains but keeping the dimension orders of crystallite of targets 5%Ni:YSZi > 10%Ni:YSZ (Table 2).

Table 2

Values of lattice constants and mean dimensions for crystallites for targets, YSZNi5 and YSZNi10

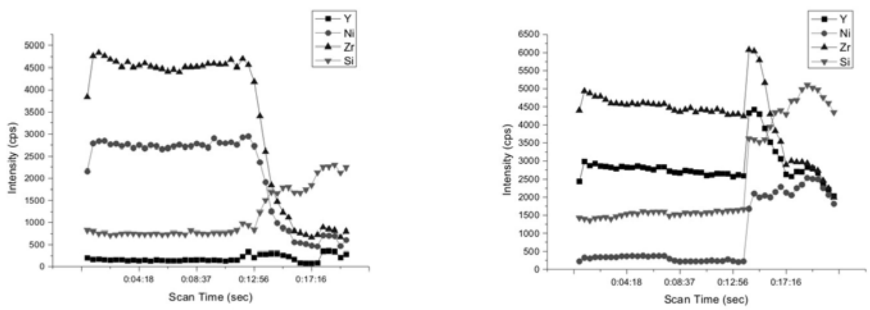
Target/ Substrate (thin films)	*a* (Å)	*D* (nm)
YSZNi5 target	5,1474	40
Si (785)	5,165	15
PtSi(764)	5,147	19
YSZNi10 target	5,1458	31
Si(781)	5,170	10
PtSi (782)	5,146	17

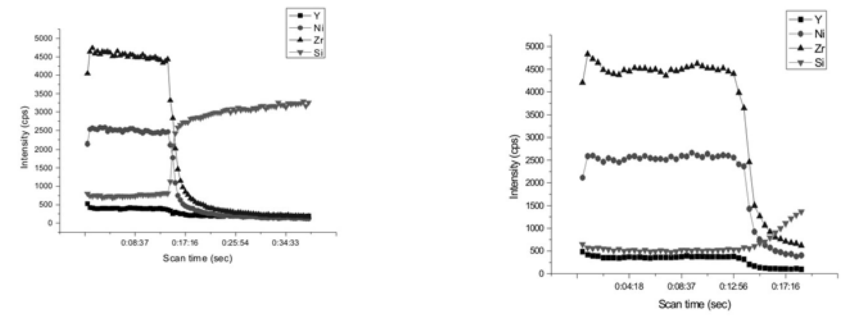
3.2. SECONDARY ION MASS SPECTROMETRY

SIMS investigations on the thin films has been made using an incident Ar^+ ions beam with energy of 5 keV at a fixed angle of incidence of 30^0. In function of time of exposure, the primary beam eroded in depth of films result the chemical composition. In the case of Ni:YSZ dopped with 5% Ni:YSZ and 10% Ni:YSZ it is observed the following: distribution of Ni in 764 5%Ni:YSZ/ Pt/Si compared with 785 5% Ni:YSZ/Si is limited in the first part of interaction due to the layer of Pt; for 781 10%Ni:YSZ/Si compared with 782 10%Ni:YSZ/Pt/Si, the configuration for variation of Ni quantity is very simillar in both cases (Fig.4).

764 5% Ni: YSZ/Pt/Si

785 5% Ni:YSZ/Si





782 10%Ni:YSZ/Pt/Si 781 10%Ni:YSZ/Si

Fig. 4 – Distribution of compositional chemical components from the secondary beam erroded from the surface of Ni:YSZ thin films.

3.3. ATOMIC FORCE MICROSCOPY

AFM reveals in the imagies for different windows (5×5 μm^2, 10 × 10 μm^2 and 20 × 20 μm^2) the morphologies of the film surface; it also oserved a variation from 5%Ni:YSZ and 10% Ni:YSZ just grown in the same PLD conditions. The differences are evident with variation of oxygen pressure. Every image has a distinct peak and valley structure distributed in distinct shape, that increases locally the roughness of the film and can reduce the surface quality.

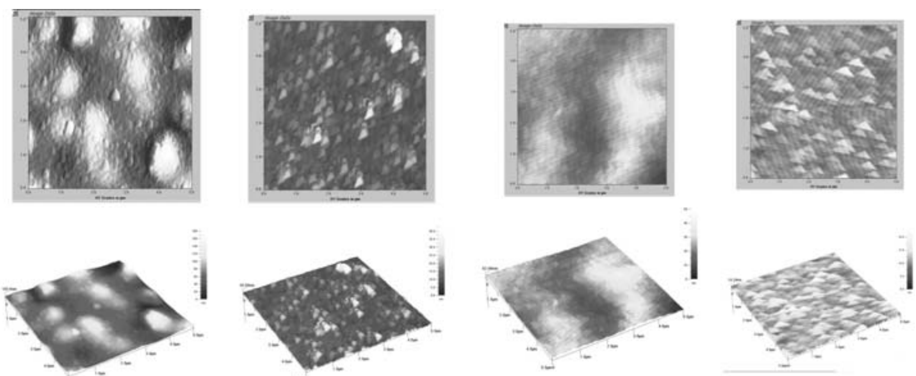


Fig. 5. – AFM images (plane and 3D views, non - contact) the 5%Ni:YSZ and 10%Ni:YSZ thin films on Si(100) and Pt/Si(100) on thin films with 5 × 5 μm^2 area.

As can be seen from sample 764 5%Ni:YSZ/Pt/Si and the corresponding values of RMS, the surface has a high roughness influenced by conditions of deposition, number of pulses 36.000 and p_{O2} = 2.5 × 10^{-4}mbar, compared with sample 785 5%Ni:YS/Si at ν = 30 Hz, number of pulses 14.400 and p_{O2} = 2.1 × 10^{-5} mbar. Other RMS values are in acceptable limits, that confirms the good quality of such samples. The value of RMS (Root Mean Square) roughness obtained by AFM is one of the most important parameter (Table 3).

Table 3

The value of Root Mean Square of roughness for three windows

Sample No.	**RMS Deviation (nm)**		
	5 ×5 μm²	10 × 10 μm²	20 × 20 μm²
764 5%Ni:YSZ/Pt/Si	26,05	53,64	55,38
785 5%Ni:YS/Si	3,417	3,831	7,488
782 10% Ni:YSZ/Pt/Si	6,681	7,466	9,160
781 10%Ni:YSZ/Si	5,039	4,299	4,906

3.4. SECTROSCOPIC ELLIPSOMETRY

Optical properties are characterized by the refractive index values of 5Ni: YSZ and 10Ni:YSZ measured by VASE in the spectral range 400–1000 nm, at three angles of incidence: (45°, 65° and 70°). The thin films being highly transparent it was selected Cauchy dispersion [14] relation for fitting the measured data with optical model. Figure 6 shows the dependence of the refractive index as a function of the wavelengths of incident light, Table 4 presents the fitted data for thickness and roughness. In Fig. 5 we are presented the fitting of Ψ and Δ, optical models are presented in Fig. 6. Also, the fitting the Cauchy parameters A_n, B_n, thickness, roughness and the value of MSE (Mean Square Error) are presented (Table 4, Fig. 7).

Table 4

The fitted data for thickness and roughness of 5% and 10% Ni-YSZ thin films, Cauchy coefficients dispersion functions and the value of MSE

Sample	**Thickness (nm)**	**An**	**Bn**	**ThickUni**	**MSE**
764 5%Ni-YSZ/Pt/Si	24.822±0.224	5.743±0.0306	0±0.00772	8.8867±0.766	22.55
785 5% Ni-YSZ/Si	26.165±0.484	3.234±0.0589	0.67494±0.0191	7.0819±0.916	59.56
781 10% Ni-YSZ/Si	26.165±0.484	3.234±0.0589	0.67494±0.0191	7.0819±0.900	60.56
782 10%Ni-YSZ/Pt/Si	31.182±1.54	1.051±0.0485	0.44131±0.0116	15.934±1.48	88.72

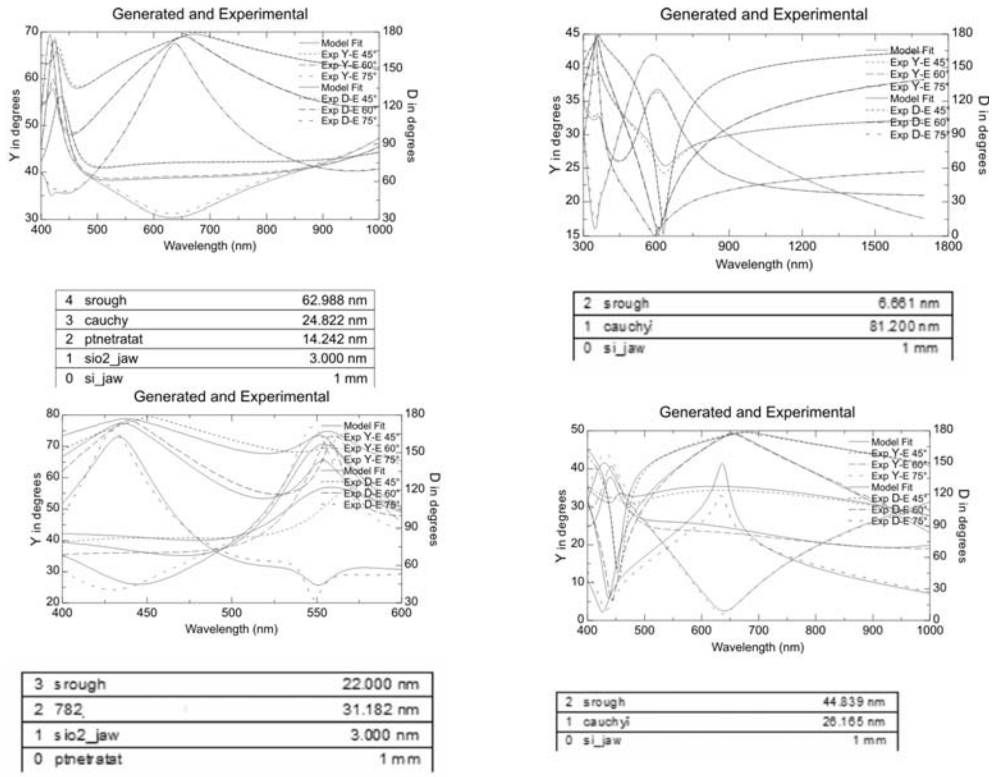


Fig. 6 – Fitted Ψ and Δ spectroellipsometer parameters at three angles of incidence and the corresponding values of multilayer system.

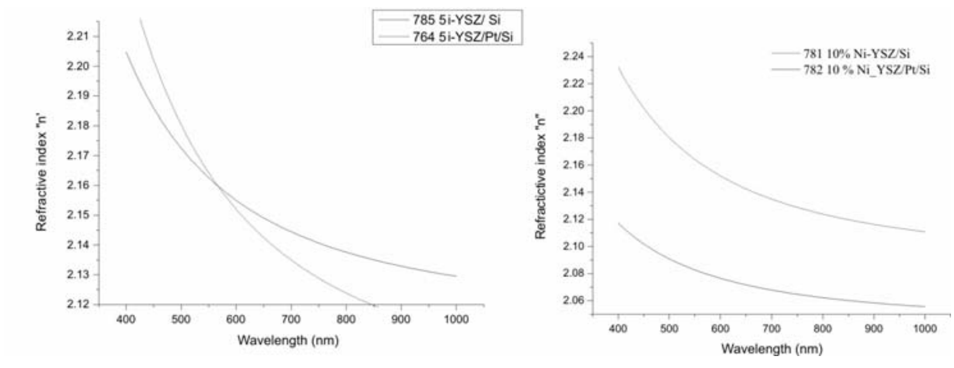


Fig. 7 – Variation of refractive index *n* (λ) for 5%Ni YSZ and 10% Ni:YSZ for Si (100) and Pt/Si (100).

From comparasion of data there were some significant differences between values of refractive index, thickness and roughness; influenced by conditions of deposition, type of substrates and level of doping with Ni.

4. CONCLUSION

This work demonstrates at laboratory scale the possibility of preparing by PLD and RF- PLD the 5%Ni YSZ and 10% Ni dopped YSZ thin films by PLD and RF-PLD, by deposition on Si (100) and Pt/Si (100) substrates at 600°C. The XRD spectra identified crystalline structure generated mainly by the nature of substrates and high temperature of deposition (600°C); in the case of Pt/Si (100) it was obtained on orthorombic structure. The structural data reveal the maintaing a good stoichiometry of targets with lattice constants similar into dimension with smaller grains with the following orders of cristallite of targets 5%Ni:YSZ > 10%Ni:YSZ.SIMS confirm the stoichiometric transfer; it was observed the influence of Pt layer in the first experiment on Ni distribution. AFM imagines reveal the morphology characteristiscs influenced by condition of deposition and the level of dopping with Ni. It appears a diffence for 5%Ni – 782 Pt/ Si with grater RMS, influenced by number of pulses and the value of p_{O2}. For other samples it was obtained porous structures with some agglomeration of Ni on the surface. Optical characteriztion by VASE indicates some significant difference between the values of refractive index.

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