Romanian Reports in Physics **70**, 514 (2018)

NEW DIRECTIONS IN DEVELOPING OF PLANAR POTENTIOMETRIC CERAMIC MULTILAYERED OXYGEN SENSOR TYPE λ

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Received August 24, 2017

Abstract. A new generation of lambda potentiometric compact lambda sensor operating at low intermediated temperature (400–800°C) for real-time control of the residual oxygen concentration of exhaust gases from internal combustion engines will deposited by Pulsed Laser Deposition technique (ArF excimer laser, λ = 193 nm). These electro-ceramic devices are based on a high-k solid electrolyte 8YSZ (Yttria Stabilized Zirconia) with oxygen ionic conductivity and two solid state electrodes with a differential catalytic activity between the sensing $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) and reference electrodes (40%Ni-8YSZ). To improve time of operation, an interface of approximately 10 nm thickness of $Gd_{0.1}Ce_{0.9}O_{1.95}$ thin film will be deposed between LSCF and 8YSZ to block the interdiffusion. Methods of structural, optical and electrical characterizations will influenced technological development of new performant lambda oxygen sensor with stabilized measurements into a defined field of lambda variation avoiding frequent errors specific in classical configuration. The new sensor will have a fast response time by placing then to the exhaust zone with a good withstand at high temperatures (400–800°C) for a long time; sensor output must be insensitive to the moisture content.

Key words: planar ceramic multilayer, potentiometric oxygen sensor, lambda sensor, solid state planar electrodes.

1. INTRODUCTION

Automotive emission controls correlated with continuous improvement of fuel efficiency by implementing lean burn engine technologies have a great influence in development a wide diversity of designed potentiometric lambda sensor (λ) based on enhanced oxygen ions conduction electrolyte [1, 2]. Potentiometric zirconia solid electrolyte cells are for the first place where all produced oxygen sensor economic effects of their applications. Most of lambda sensor used today are fabricated as macroscopic ceramic devices or miniature thick films; the next step of miniaturization is based on thin film and multilayered technologies [3, 4].

The global performance depends on ohmic resistance of the electrolyte and over potential losses at electrode. It is necessary to apply at a large scale the thin film technique to fabricate less resistive electrolyte films as well as a lower operation temperature [5].

Classical configuration of potentiometric ZrO_2 sensor developed initially like tubular shape and since 1997 like heated planar macroscopic ceramic devices operates on the Nerstian principle at high temperature with the output influenced mainly by the stability of air reference electrode. Using the air tight structures for reference electrode make them unsuitable for developing in thin film technologies [6].

To avoid limitations in sensing in the last 10 years it is proposed a multilayered planar ceramic configuration with solid state reference oxygen made on mixed oxide conductors necessary to reduce the variation of voltage between 1000 mV to 100 mV in classical from to 600 mV to 250 mV with better measurements of residual pO_2 in lean field by avoiding the processing of electrical signal on a large filed of variation; the precision of oxygen sensing is also limited also by reduction conduction of O^{2-} in YSZ electrolyte under extremely condition. In this respect the core of new technologies for sensing electrodes are ceramic multi component oxides like perovskites that have important properties resulted from complex phase relations and crystals structures [7]. New type of lambda (λ) sensor will be developed by applying the advantage of the film technologies like Pulsed Laser Depositions (PLD) for low fabrications costs and high reproductibility. The new design which is extreme in size (maximum 20 × 20 mm^2) will be in accordance with advance in novel thermodynamic combustion concepts of automobile engines [8, 9]. Structural, optical and electrical properties of compact ceramic planar multilayer O_2 with different functionality are dependent from the control parameters like fluence, pressure of oxygen, number of pulses, temperature of substrates, distance target – substrate; PLD technique is very useful for high-k dielectric ceramics film processing [10].

The purpose of this paper is to report some trends regarding the development of a miniature Nerstian – type oxygen sensor operating at moderate temperature (450–800°C) as an alternative vision to classical configurations by analyzing the advantage of ceramic multilayer; it will be presented results based on structural and optical characterizations.

2. TRENDS IN THE DEVELOPMENT OF HIGH PERFORMANCE OXYGEN MINI SENSOR IN PLANAR TECHNOLOGY

The main components of lambda sensor are a zirconia based Nernst cell. The electromotive force (EMF) in open circuit is calculated by Nernst equation:

$$E = -\frac{RT}{zF}\cdot\frac{\ln\ p(\mathrm{O}_2)^d}{\ln\ p(\mathrm{O}_2)^{ref}} \qquad (1)$$

where $p(O_2)^d$ is the oxygen partial pressure in the exhaust gas, $p(O_2)^{ref}$ is the reference air partial pressure, R is the universal gas constant, F is Faraday's constant,

T is the absolute sensor temperature, z is the number of electrons migrated from one electrode to another for each molecule of oxygen transferred in ion form through YSZ based electrolyte. The variation of E in function of lambda is a logarithmic one in the case of electrochemical equilibrium, influenced mainly by T in (Fig. 1) [2, 3, 7].

It is observed the influence of temperatures on variation of E, but the curves have the same "λ" shape and type of jump at λ = 1, zero percent exhaust oxygen. The transfer for λ = 1 the sensor lean to reach is insensible to temperature [1].

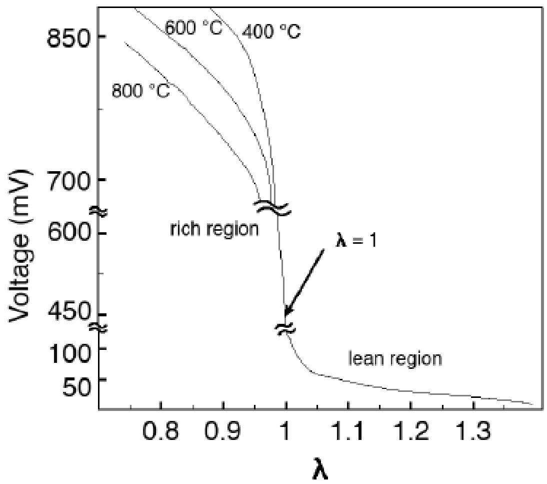


Fig. 1 – Voltage curve of a Lambda sensor [1].

In classical configuration the response does not entirely follow the Nernst low, with the voltage being 15% lower in rich air/ fuel mixture and 10% higher in lean mixture rapidity changing the temperature, high velocity of gases containing fine abrasive particle, lead the components etc. [7].

Sensors like these measures the equilibrium partial pressure of oxygen and not the true oxygen concentration, it exhibit very poor sensitivity when the difference between $p(O_2)^d$ and $p(O_2)^{ref}$.

The electrochemical potential E developed in open circuit is the result of reactions:

$$\begin{aligned} &4\,e^- + O_2\,(p(O_2)^d) \rightarrow 2O^{2-} \\ &2O^{2-} \rightarrow O_2\,(\,p(O_2)^{ref}\,) + 4\,e^-. \end{aligned} \tag{2}$$

Cell potential (E) from Eq. (2) is low (0.1V) for lean mixture – oxygen in excess (λ > 1) and high (0.9 V) at an excess of fuel – rich mixture (λ < 1). This signal is processed by electronic circuit unit and the value of λ to be optimized during the subsequent stroke. The transition from rich to lean mixture occur that $V = 450 - 600$ mV like an abrupt change in residual oxygen in the vicinity of $\lambda = 1$ ($9 \cdot 10$–15%vol for $\lambda = 0.99$ and 0.2% vol for $\lambda = 1.01$).

For excess of fuel (fuel rich region), CO would be the main residue product of combustion H_2/CO proportion; for excess of air (fuel lean region) free oxygen tougher with carbon dioxide and steam will be present in exhaust gas [2, 7].

For low temperature of operation $T \sim 350$°C the response time are in the range of seconds; at an optimum temperature ~ 600°C times is less than 500 ms. When the engine is started the electrical control is disabled not to introduce false data in control of engine; it is put in function at the minimum operating temperature necessary for activation a stable transfer of O^{2-} through zirconia YSZ electrolyte. From theoretical equation (1) it is noted that the potential E is not influenced by geometry parameters. Main advantage offered by these theoretical results generates the possibilities to develop mini oxygen sensor with performance compatible with classical bulk configurations [7].

The most important component in lambda sensor is a solid electrolyte from a high-k group of ceramic with a high ionic O^{2-} conductivity. Most frequently it is used 8YSZ with a conductivity of 0.1 $\Omega^{-1} \cdot cm^{-1}$. Purity of 8YSZ influences the conduction of O^{2-} and therefore the U values. Zirconia (ZrO_2) is a non conducting material with crystallinity influenced by temperature but has a high solid solubility, up to 20 mol%; in the case of doping with the Y_2O_3 the optimal percentage is 8 mol%. The best properties are the conservation of cubic structure on large domain of operation. The conductivity of O^{2-} is activated at $T > 300$°C; smooth, cracks and droplets free 8YSZ layers has been fabricated for a wide range of deposition conditions [10].

Maintaining 8YSZ thin film electrolyte the trend is to fabricate lambda sensor without air reference; the structure consists in measured gas/ sensing electrode/ 8YSZ/ reference electrode / measured gas. According to equation (1), where $p_{ref} = p_{sens}$, ln 1 = 0 and $U = 0$V. Measures are taken to generate $U \neq 0$ by fabrications of reference electrode from different materials than sensing electrode (Ni-YSZ; $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)) with improved selectivity to oxygen by different catalytic activities and not respecting the principle of symmetry [11,12]. In classical configuration it is respected the symmetry of configuration; electrodes are made on Pt or other noble materials. For mini planar configuration it is necessary a correct dimensioning of the detection area because the ceramic electrodes do not respect diffusion theory on a limited Triple Phase of Boundary (TPB); diffusion is made over entire length of contact of electrodes, that allows transport of a large quantity of O_2 by generating an larger interface area for chemical reaction.

The small areas of electrodes assure a better control of chemical reaction on the surface. In the same time small volume of sensor reduces time for activation, requiring lower power consumption for heating at activation temperature. It has been identified the positive effect of the LSCF/ 10GDC/ 8YSZ interface on the control of the diffusion elements in the electrolyte; 10GDC provides improved contact between electrolyte and LSCF because the thin film of $Gd_{0.1}Ce_{0.9}O_{1.95}$ (10 GDC) (~10 nm) does not react with 8YSZ [13]. It is necessary to reduce the deposition process at $T < 650°C$. Also the Ni-YSZ electrode, acting like a solid state electrode without air reference has different functionality activated by variation of temperature of operation. 40Ni-YSZ is the most used material for such purpose, having a low cost, thermal and chemical stability, very good electronic, ionic conductivity and high catalytic activity for fuel oxidation (CO, CH_4 and H_2); 5Ni-YSZ and 10Ni-SZ thin films are acting like a high-k dielectric, and can be used for interface between 8YSZ and 40Ni-YSZ [14, 15, 16].

3. EXPERIMENTAL METHODS

In experiments it was used an ArF excimer laser (CompexPro), with a wavelength λ = 193 nm, pulse duration σ_p = 15 ns, laser repetition frequency ν = 30 Hz and 10 Hz; fluence was F = 5 and 3 J/cm^2 respectively. Si (100) substrate was positioned at 50 mm and 70 mm respectively from the target and its temperature varied in the range of 500–600ºC; the number of pulses was 100.000. The depositions were made with $p_{O_2} = 8 \times 10^{-2}$ mbar. Ceramics targets (8% mol Y_2O_3) · ZrO_2 and 40% Ni-YSZ prepared by sintering technologies (American Elements). Perovskite target $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) made by MaTeck and 10 GDC have been prepared by sintering technologies (Fig. 2).

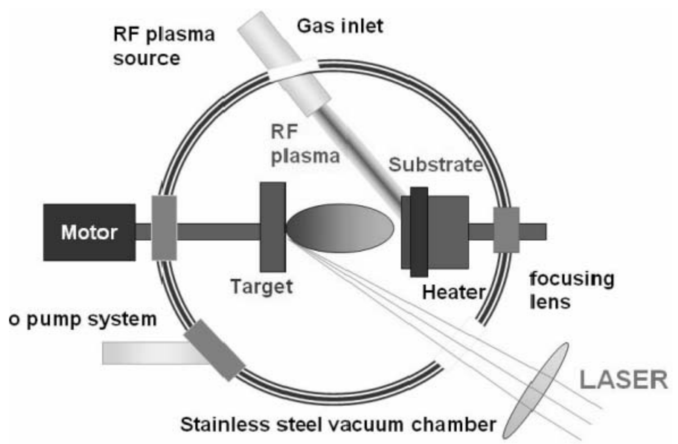
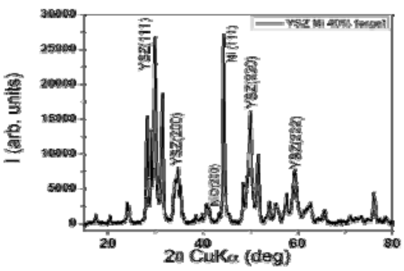


Fig. 2 – A schematic diagram of the pulsed laser deposition setup.

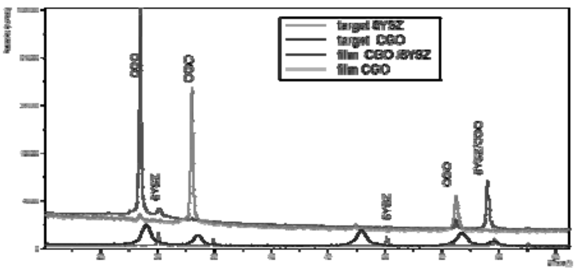
4. RESULTS AND DISCUSSION

4.1. X-RAY DIFFRACTION MEASUREMENTS

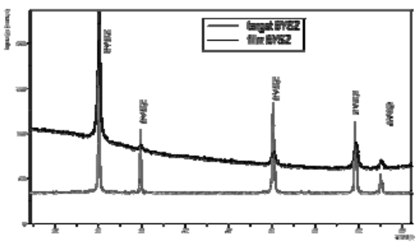
The target and films X-ray's spectra indicates dense cubic crystalline structures influenced by the oxygen pressure values. Structural characterization indicates homogeneous structures over a wide range of wavelengths, demonstrating ordered crystalline structures (Fig. 3).



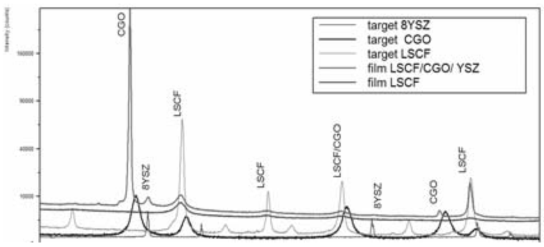
The 40%Ni-YSZ target diffractogram.



Diffractograms for 8YSZ and 10 GDC target; the 8YSZ/10CGO thin film.



The 8YSZ target and the 8YSZ thin film diffractograms.



Diffractograms for YSZ, GDC and LSCF targets; 8YSZ, 10CGO and LSCF thin films.

Fig. 3 – XRD spectra of 8YSZ, 40Ni-YSZ, LSCF and 10CGO targets, thin films 8YSZ, LSCF, 40% Ni-YSZ and 10GDC thin films with different number of pulses.

4.2. SCANNING ELECTRON MICROSCOPY MEASUREMENTS

Figure 4 reveals the variable number of pulses is very important to obtained an stablel free cracks and droplets thin films. With 100,000 pulses (a and b) generates a more stable structures. Cross-section revels columnar grains with pores neccesary for air circulation.

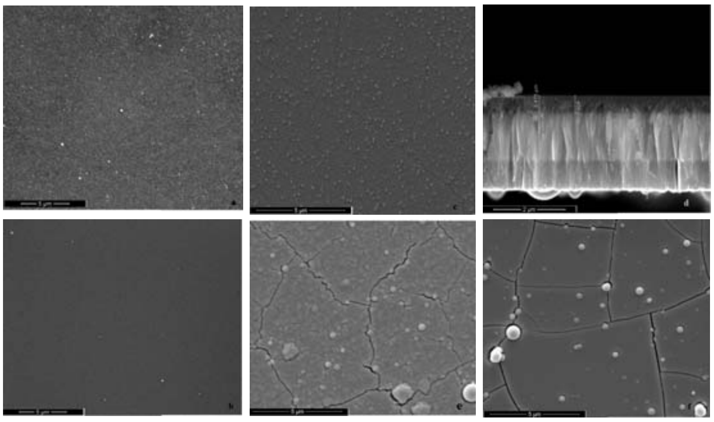


Fig. 4 – Microstructures of thin films: a) 8YSZ thin films at 600°C; b) 40% Ni-YSZ/Si (001) at 500°C; c) $Gd_{0.1}Ce_{0.9}O_{1.95}$/ 8YSZ/Si (001); d) cross-section $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$/ $Gd_{0.1}Ce_{0.9}O_{1.95}$/8YSZ/Si (001) thin films at 600°C; e) $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)/Si (001) at 600°C; f) LSCF/CGO/YSZ/Si(001) at 600°C.

4.3. ATOMIC FORCE MICROSCOPY

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.). The four thin films shows smooth aspect, with RMS (roughness) values of 29 nm for 10GDC/8YSZ, 30 nm for 40Ni-YSZ, 1.70 nm for 8 YSZ and 33.3 nm for LSCF/10GDC/ 8YSZ on areas of 20 × 20 μm^2 (Fig. 5).

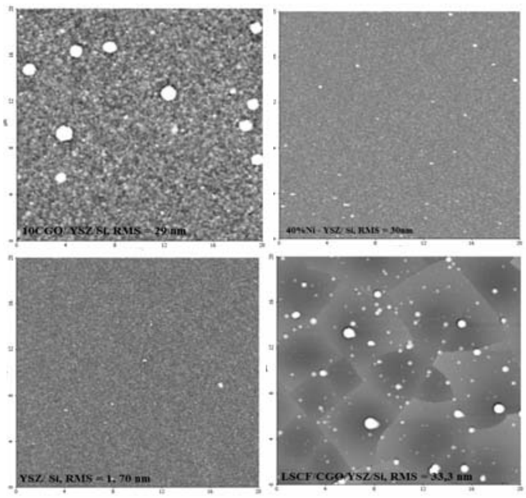
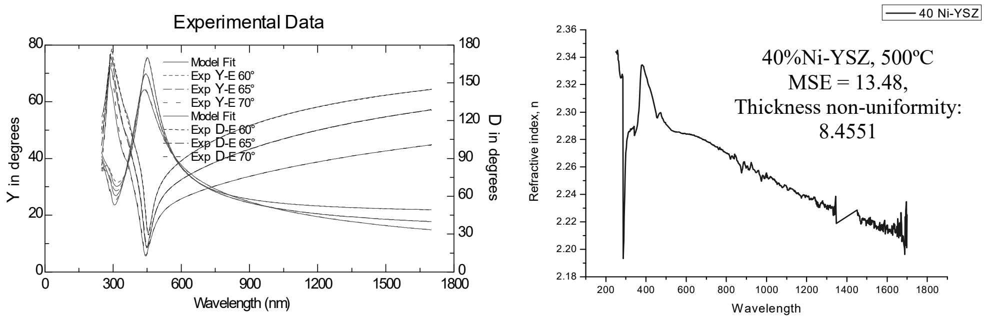


Fig. 5 – Atomic Force Microscopy images (20 × 20 μm^2) areas for samples of 8YSZ, 40%Ni-YSZ, LSCF and 10GDC deposited on Si (001) thin films with different temperatures and number of pulses.

4.4. 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 250 – 1700 nm.

The curves Ψ,Δ and variance n(λ), the optical model and the values obtained from the fitting of the An and Bn coefficients from the Cauchy dispersion function, for a thin film of 40% Ni-YSZ deposited on Si (001), are presented [17] (Fig. 6).



3	srough	54.300 nm
2	cauchy	25.630 nm
1	sio2	3.027 nm
0	si	1 mm

Fig. 6 – Variation of refractive index for 40%Ni-YSZ/Si(100) for thin film.

5. CONCLUSIONS

The interface LSCF/10CGO/8YSZ must be dense to block interfacial reactions (diffusion of Sr and La). The contact between electrolyte and LSCF as long as the thin layer of 10GDC (~ 10nm) does not react with LSCF but reacts with 8YSZ at $T > 1\,000$°C. As a result, deposits should be at a lower temperature $T < 500$°C. Purity of (8% Y_2O_3) · ZrO_2 (8YSZ) ceramic target influences the conduction of O^{2-} and therefore the U values. Epitaxial structures were identified with XRD measurements for robust sensor with long time operation.

Acknowledgments. The author thanks S. Brajnicov for AFM measurements and D. Marius for SEM measurements.

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