Optical Characterization of Nanoporous Alumina-based Structures Modified by ALD Technique

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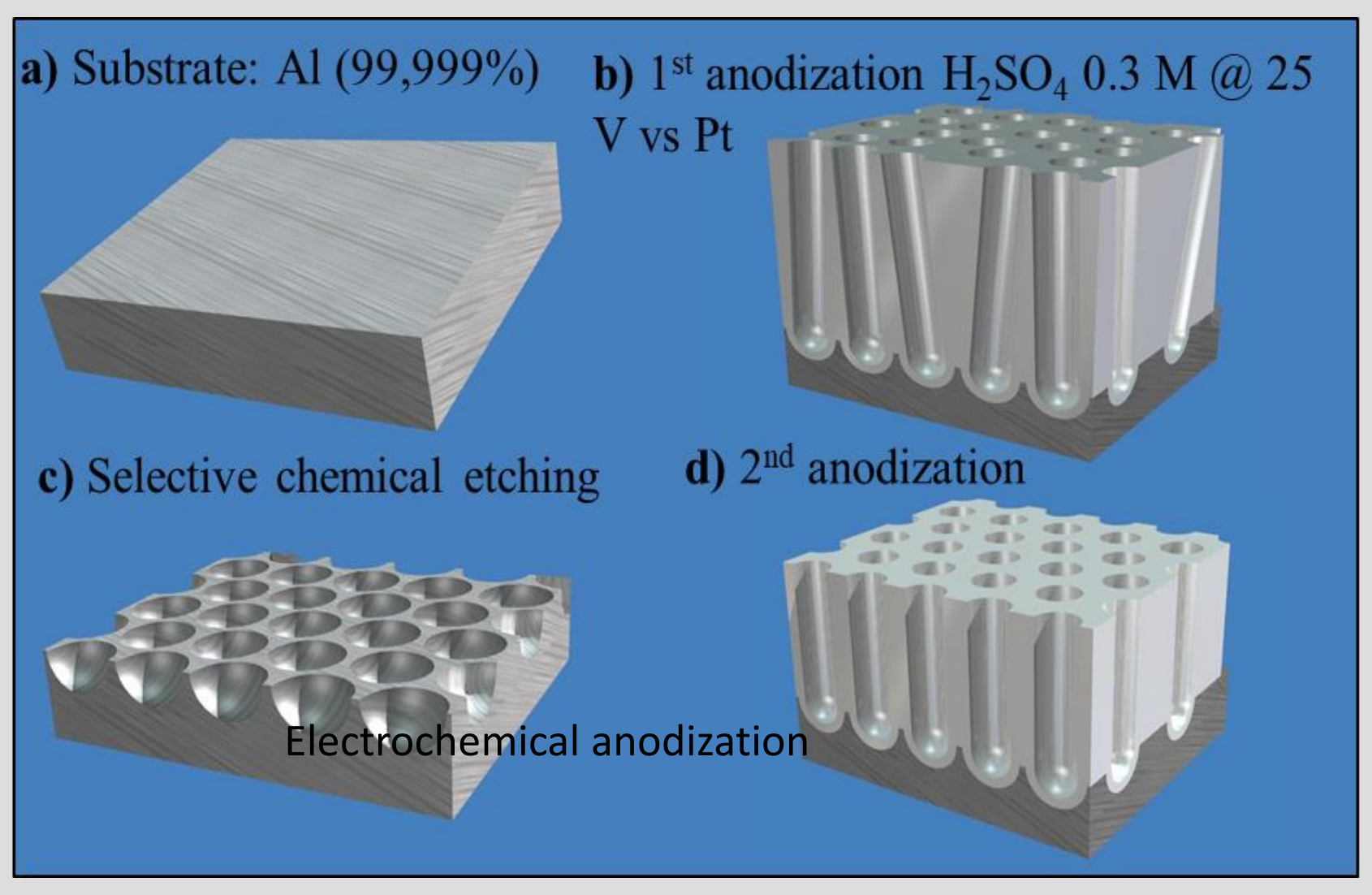
Nanoporous alumina structures (NPASs) obtained by the two-step anodization method exhibit well-defined morphology (parallel array of straight cylindrical nano-channels without practically pore radii dispersion), high surface area and aspect ratio, being of interest in nanotechnology (nano-templates, drug delivery, nanofilters, photonic crystals,…). Moreover, the possibility of easy surface material and pore radii walls modification by a well-established technique such as atomic layer deposition (ALD) makes of these new nanoporous alumina-based structures (NPA-bSs) excellent platforms for other applications (chemical, biological or optical sensors). In this work, we study optical changes in a NPAS as a result of its coverage by a layer of a metal oxide by ALD technique (NPAS+X samples). Different metal oxides (X = Al_2O_3, TiO_2, Fe_2O_3 or ZnO) were used as coating layer of these new nanoporous alumina-based structures (NPA-bSs) which maintain similar geometrical parameters; moreover, the effect of pore size/porosity for samples with the same surface material on light transmittance and refraction index is also considered.

- ✓ **Highly ordered nanoporous alumina structure** (NPAS) obtained by two-step anodization. Pore radius r_p =12 nm; porosity Θ =12 %; Thickness 63 μm.
- ✓ Surface modification by **ALD** (Savannah 100, CNT) of a functional oxides (Al_2O_3, Fe_2O_3, ZnO, TiO_2)
- ✓ **Morphological characterization**: SEM micrographs of samples surfaces and image analysis ($\Theta = (2\pi/3^{1/2})(r_p/D_{int})^2$)
- ✓ **XPS analysis** (ESCA 5701) with a non-monochromatic MgK_α radiation (300 W, 15 kV, 1253.6 eV) (Table 3, surface atomic concentration percentages (A.C. %). **Depth-profile XPS analysis** (Ar sputtering, 4 kV and 1.5 mA, 8 min). This sample-destructive process allows estimation of layers characteristics evolution (Fig. 3)
- ✓ **Transmittance spectra** (Varian Cary 5000 spectrophotometer, Agilent Technologies) with an integrating sphere (wavelength interval of 200-2000 nm).
- ✓ **Spectroscopic Ellipsometry** (SE) measurements were carried out with a spectroscopic ellipsometer (Sopra-Semilab GES-5E) and wavelength ranging from 400 nm to 1600 nm at an incident angle of 70°. WinElli software (Sopra-Semilab) was used for data analysis and fittings.

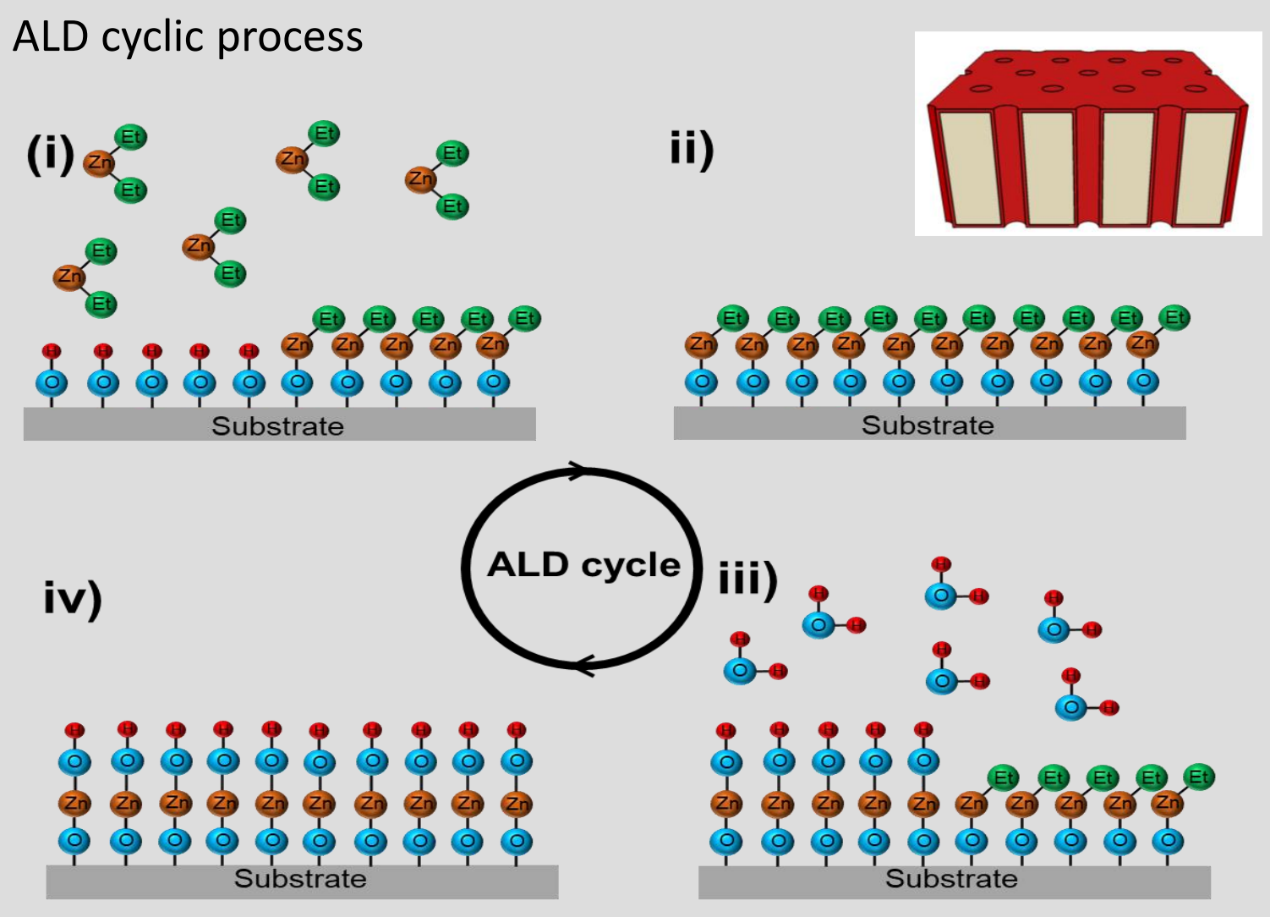
Nanoporous alumina structures synthesis and ALD coating



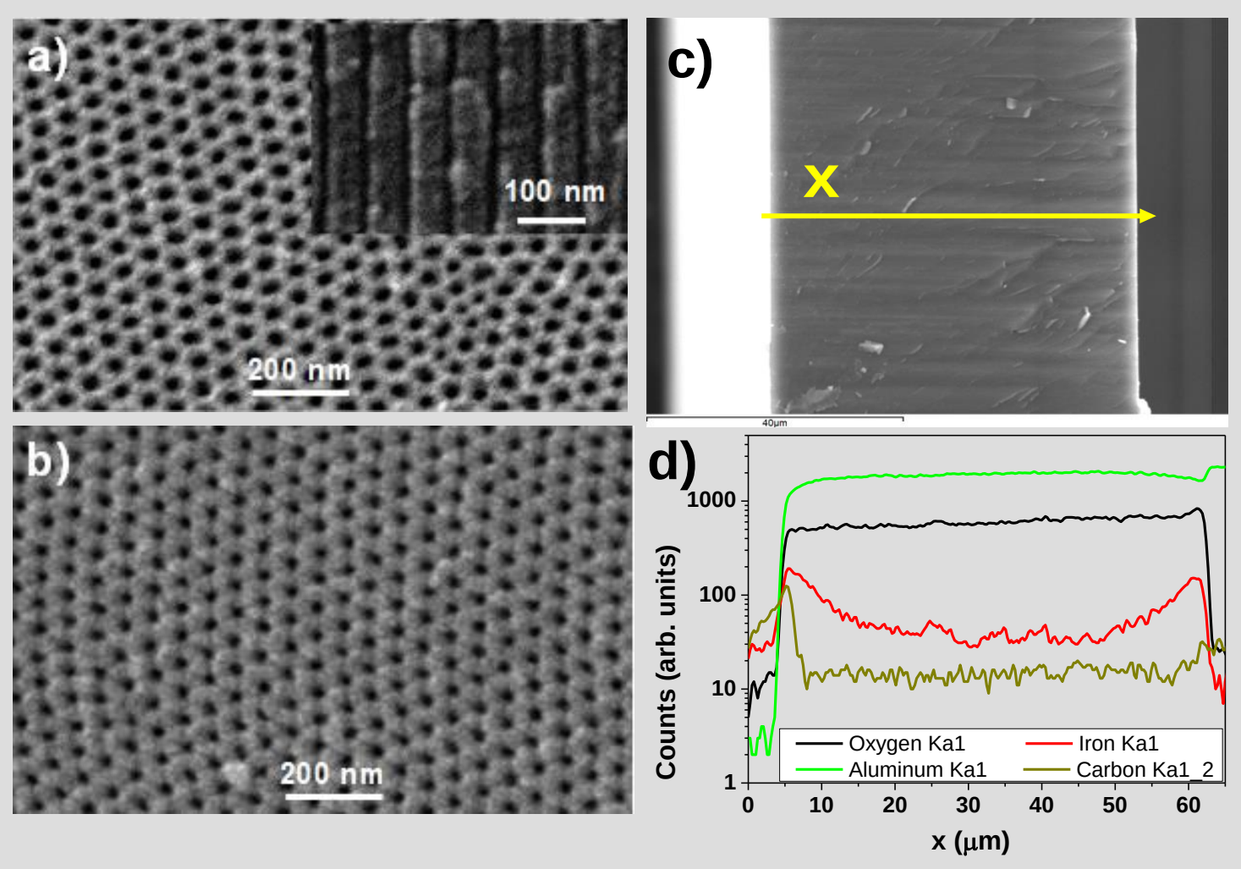
ALD precursors & conditions

Oxide layer	ALD precursors	Precursor temperature (ºC)	Substrate temperature (ºC)
Al_2O_3	H_2O	60	200
	Trimethylaluminum ($C_6H_{18}Al_2$)	20	
Fe_2O_3	O_3	20	230
	Ferrocene ($C_{10}H_{10}Fe$)	100	
ZnO	H_2O	60	200
	Diethylzinc ($C_4H_{10}Zn$)	20	
TiO_2	H_2O	60	200
	Titanium tetraisopropoxide ($C_{12}H_{28}O_4Ti$)	75	

ALD cyclic process



Morphological and Chemical Characterizations



SEM images: (a) NPAS and (b) NPAS+ZnO (c) cross section and (d) EDX analysis

Average pore radius $<r_p>$ and porosity Θ.

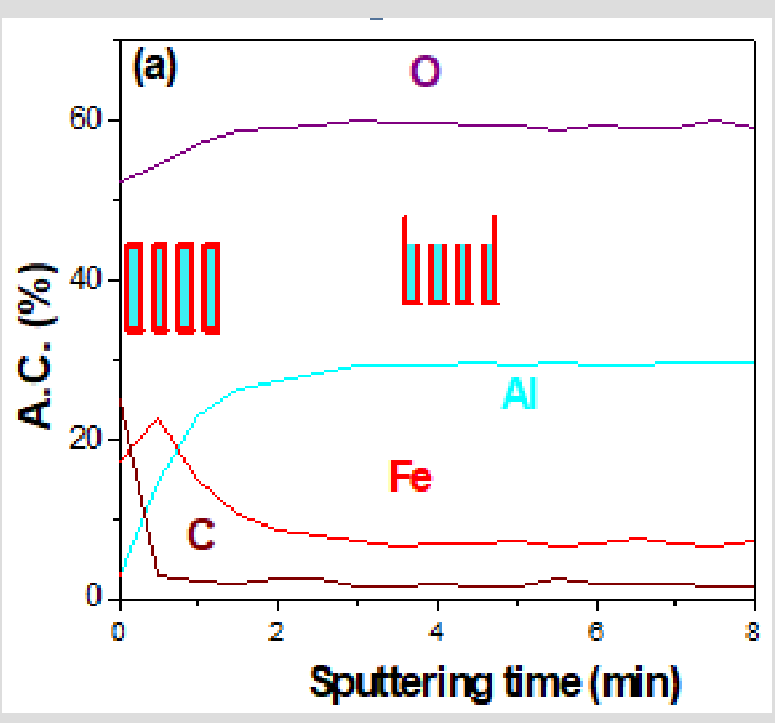
Sample	$<r_p>$(nm)	Θ (%)
NPAM+Al_2O_3	10 ± 2	9
NPAM+TiO_2	10 ± 2	9
NPAM+Fe_2O_3	9 ± 3	8
NPAM+ZnO	9 ± 3	8

Reduction ~ 20 % respect to NPAS

NPA-bSs surface atomic concentration % of NPA-Ss elements (other elements with A.C. % ≤ 0.5 are not indicated)

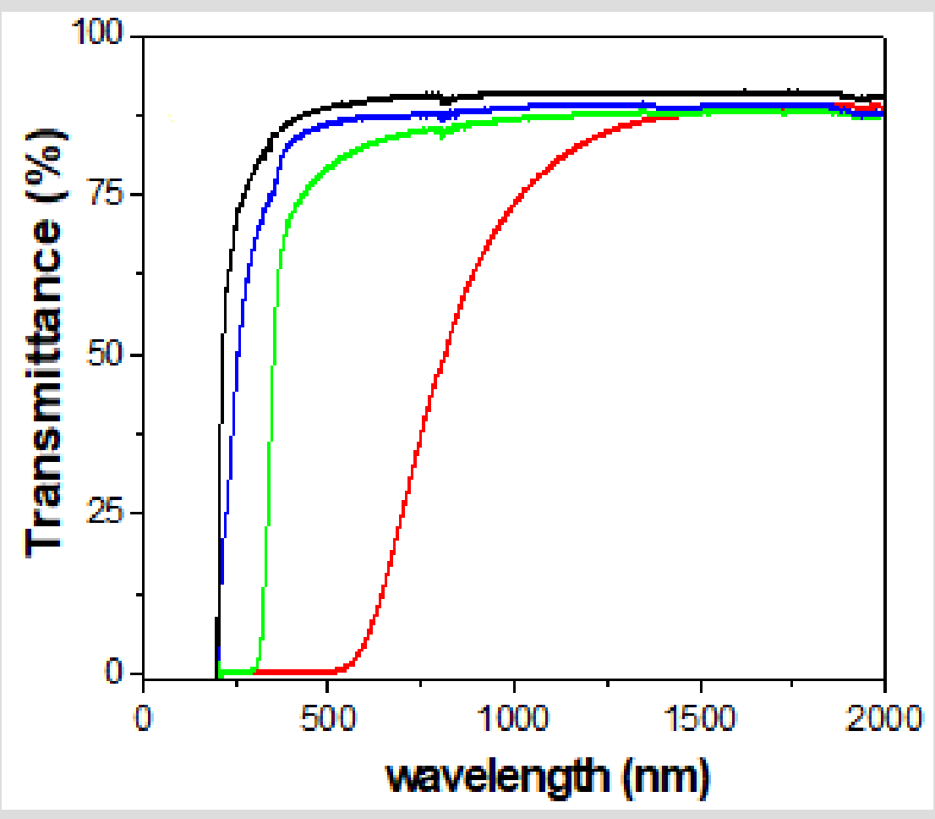
Sample	C (%)	Al (%)	O (%)	Ti (%)	Fe (%)	Zn (%)	N (%)
NPAM+Al_2O_3	43.6	15.7	37.7	---	---	---	2.0
NPAM+TiO_2	19.2	0.6	55.5	23.5	---	---	0.7
NPAM+Fe_2O_3	25.9	2.1	54.6	---	16.3	---	0.5
NPAM+ZnO	43.3	8.7	37.6	---	---	10.2	0.4

Almost total coverage by TiO_2 or Fe_2O_3 layers but partial for ZnO

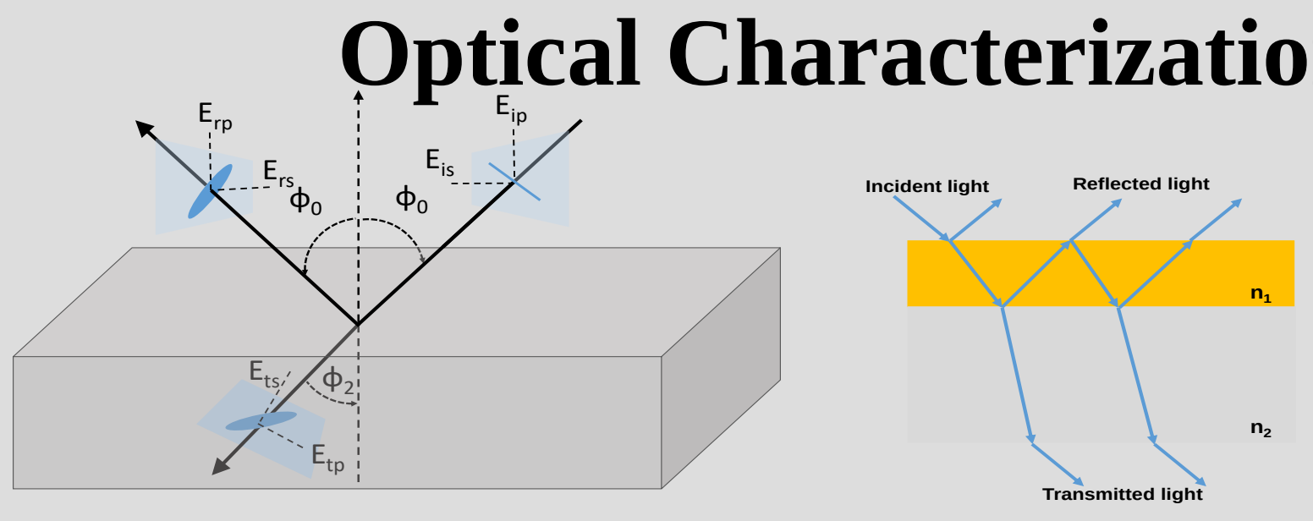


Profile curves as a function of Ar sputtering time for iron, aluminum, oxygen and carbon for NPAS+Fe_2O_3 sample.

Optical Characterization



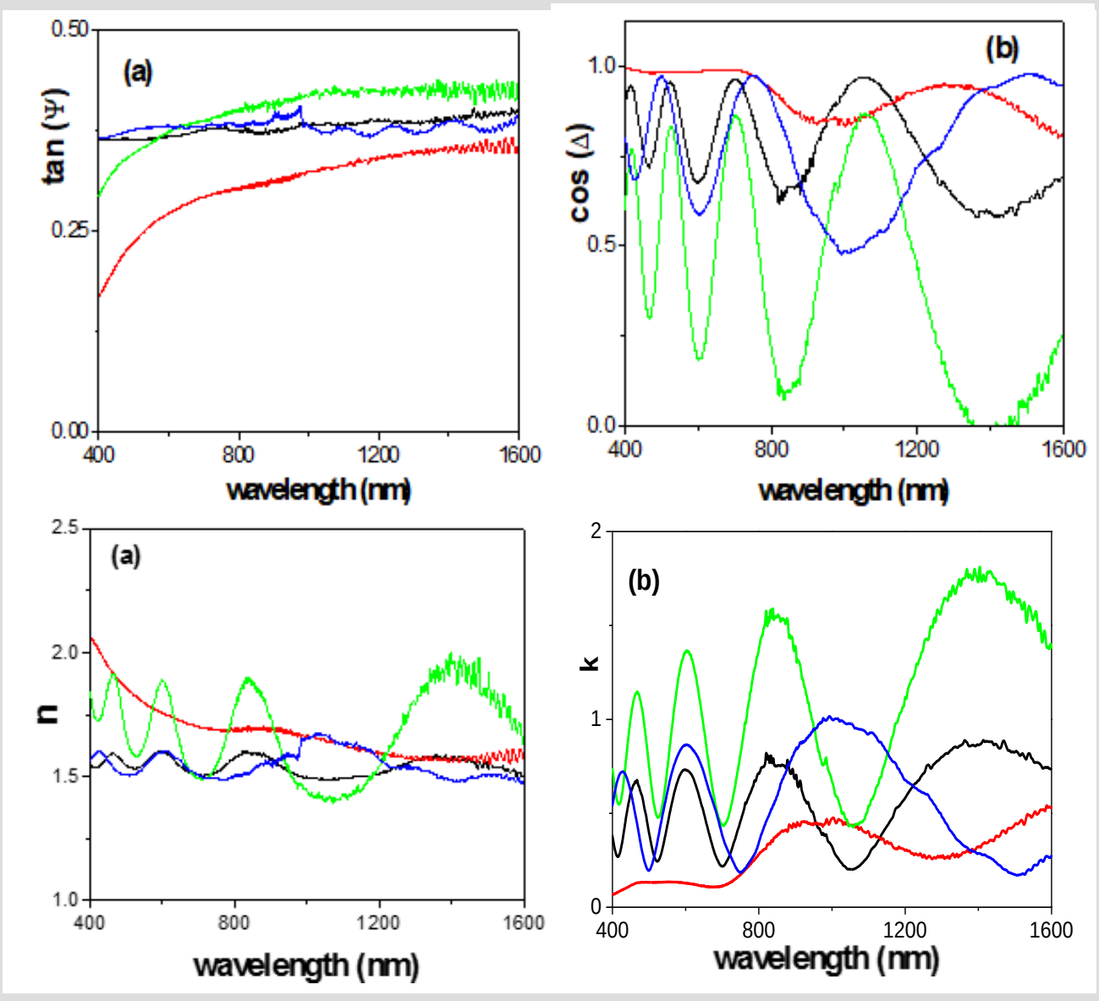
Sample	band gap
NPAM+Al_2O_3	196.5 nm
NPAM+TiO_2	317.5 nm
NPAM+Fe_2O_3	585.1 nm
NPAM+ZnO	193.4 nm



Scheme of SE measurement for homogeneous (a) sand bilayer (b) samples..

Measured Ψ and Δ angles are related to the ratio of reflection coefficients for parallel (p) and perpendicular (s) polarized light by:

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan\Psi\, e^{i\Delta}$$



Visible (vr) and near infrared (nir) average values of refractive index <n> and extinction coefficient <k>

Sample	$<n_{vr}>$	$<k_{vr}>$	$<n_{nir}>$	$<k_{nir}>$
NPAS+ Al_2O_3	1.55 ± 0.03	0.48 ± 0.16	1.54 ± 0.03	0.64 ± 0.22
NPAS+ TiO_2	1.69 ± 0.14	0.87 ± 0.29	1.69 ± 0.19	1.27 ± 0.44
NPAS+ Fe_2O_3	1.81 ± 0.12	0.13 ± 0.04	1.62 ± 0.05	0.38 ± 0.08
NPAS+ ZnO	1.54 ± 0.04	0.51 ± 0.22	1.55 ±0.06	0.59 ± 0.29

Conclusions:

Geometrical parameters and surface material features of a nanoporous alumina structure (NPAS) with 12 ± 2 nm pore radii and 12-15 % average porosity have been successfully modified by covering their surfaces with layers of different metal oxides (TiO_2, Fe_2O_3, ZnO and Al_2O_3) by atomic layer deposition (ALD) technique, in order to get new nanoporous alumina-based structures (NPA-bSs) with modified transport and optical characteristics but similar morphology. These latter point has been confirmed by analyzing SEM images and XPS depth-profile spectra has permitted us to determine similar reduction in pore size and porosity with respect to the original support, and a cover-layer thickness of ~ 5-7 nm for the NPA-bS samples.

Coverage material affects the values of optical characteristic parameters of the NPA-bSs (band-gap, refractive index and extinction coefficient), mainly when wavelength for the visible and near-infrared regions are compared, being more significant in the case of Fe_2O_3 coverage. For similar surface material, higher porosity/pore-size reduce refraction index and slightly affecting light transmission.

Consequently, ALD technique seems to be an adequate method for geometrical and functional changes of alumina-based nanoporous structures, opening their most common field of application (nanotemplates, drug delivery or nanomebranes) to more specific performance or platforms for biosensors or optical sensing devices.

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