Sol-Gel SiO_2-based Hybrid Coatings doped with Oxide Nanoparticles

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Outline of the presentation

- General consideration on the sol-gel method
- General consideration concerning doping of the hybrid coatings with oxide nanoparticles
- Sol-Gel SiO_2-based Hybrid Coatings doped with Oxide Nanoparticles
- Applications
- Conclusions

General consideration on the sol-gel method

Among the non-conventional ***wet chemical processes*** of obtaining oxide materials, the sol-gel method is most frequently used and studied.

The ***sol-gel process*** *represents:*

- *the formation of an* ***inorganic polymeric network*** by reactions in the solution at low temperatures
- *the conversion of the* ***inorganic amorphous polymers into glasses*** at temperatures far lower then the melting temperature of the corresponding oxides or in ***crystalline materials*** at temperatures much lower than the usually needed temperatures

Precursors in the sol-gel processes are:

- Alkoxides [$M(OR)_n$, R_x-$M(OR)_{n-x}$]
- Inorganic salts [chlorides, nitrates, etc]
- Organic salts [acetates, acetylacetonates, etc]

General consideration on the sol-gel method

Transition form solutions to gels - sol-gel reactions

$Si(OR)_4 + H_2O$	⇔	$HO\text{-}Si(OR)_3 + ROH$	(1)
$HO\text{-}Si(OR)_3 + H_2O$	⇔	$(HO)_2Si(OR)_2 + ROH$	
$(HO)_3SiOR + H_2O$	⇔	$Si(OH)_4 + ROH$	(2)

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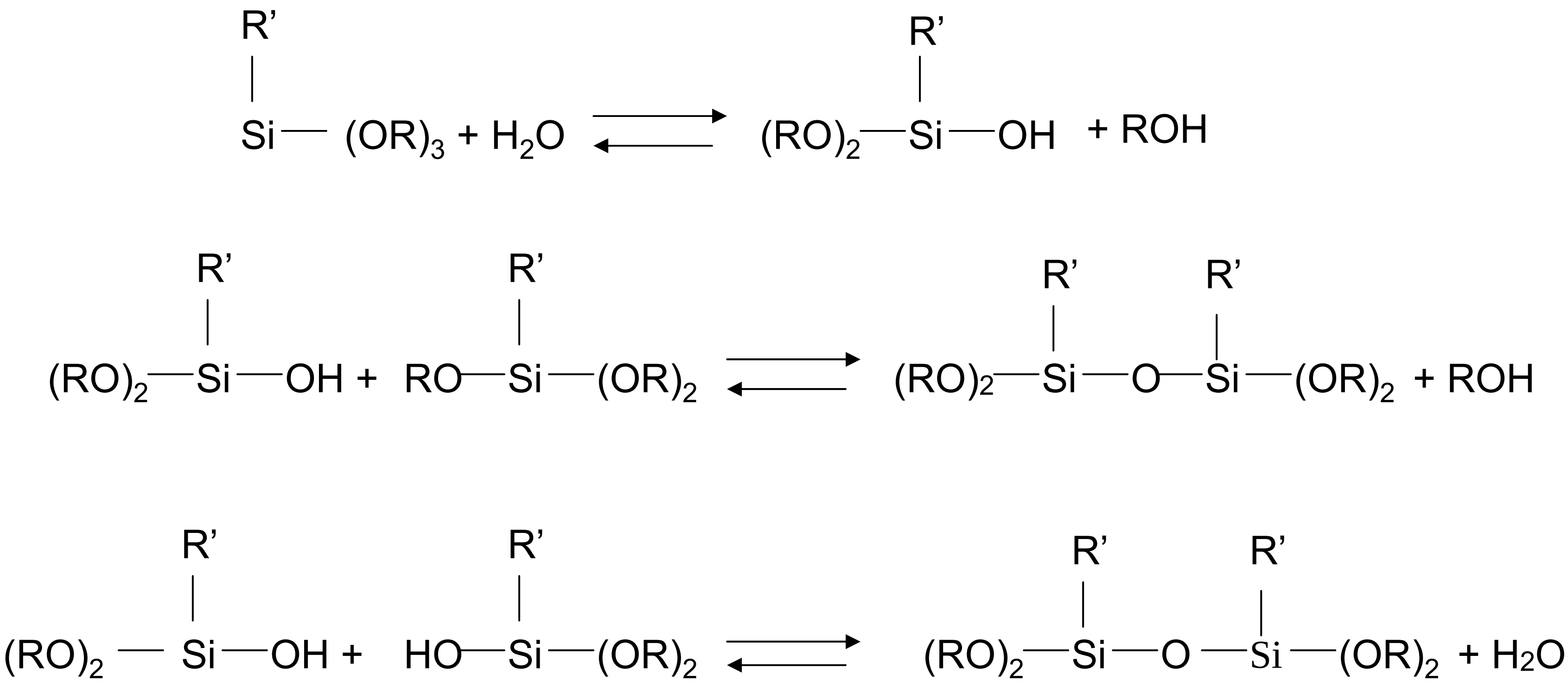
≡Si-OR+ HO-Si≡	⇔	≡Si-O-Si≡ + ROH	(3)
≡Si-OH+ HO-Si≡	⇔	≡Si-O-Si≡ + H_2O	(4)
$Si(OR)_4 + 4H_2O$	⇔	**$Si(OH)_4 + H_2O$**	(5)

Transition form gels to oxides - gels densification

$Si(OH)_4$	⇔	**$SiO_2 + 2H_2O$**	(6)

General consideration on the sol-gel method

Sol-gel reactions in the case of substituted alkoxides



General consideration on the sol-gel method

Advantages of the sol-gel method

The most promising advantages of the sol-gel method is the fact that offers the possibility to prepare ***solids with pre-determined structure*** by varying the experimental conditions.

- solutions containing a ***large amount of water and/or catalyzed by ammonia*** lead to ***non-linear*** or ***network colloidal polymers***, that could be converted to ***bulk gels or powders***;

- solution with ***small water content when catalyzed by HCl,*** lead to ***linear polymers. Fiber*** *could be easily drawn* from such solution immediately before gelation or ***films could be deposited***.

In the same time materials in different shapes as: ***films, fibers, powders, bulk, could be obtained.***

General consideration on the sol-gel method

Advantages of the inorganic-organic hybrid sol-gel materials

- Inorganic-organic hybrid materials can **offer multifunctionality** and **allow properties tailoring** from atomic to mesoscopic length scales

- **The organic groups** can modify the inorganic backbone **reducing the connectivity** of the gel network **allowing thick film deposition** and lessening the processing temperature

- These films could play a significant role in the **field of micro- and nano-photonic devices** (waveguides, emitting devices, quantum dot devices, photonic band gaps and holographic materials)

- **Doping/embedding** in the hybrid materials of **monocomponent and/or binary oxide nanoparticles** could enhance the properties required for micro and nano-photonics applications but could also **add supplementary properties** to the coatings, as sensing or anticorrosive ones

General consideration concerning doping of the hybrid coatings with oxide nanoparticles

- The **doping of the hybrid materials** with monocomponent oxides nano-particles is a well known procedure
- The introduction of the oxide nanoparticles in a hybrid matrix is made usually by **in situ generation** or **by dispersion of pre-synthesised** nanoparticles
- **For in situ** formation of the nanoparticles, an interaction between the particles' precursors with the silica based matrix is not excluded, leading to the formation of **Si-O-M-O-Si oxide network**
- These aspects **are more complex when binary particles** are under investigation
- At low post deposition thermal treatment (below 150^0C) it is very probably that intermediates of the sol-gel process are retained in the film
- The embedment of **the pre-synthesized oxides nanoparticles** is a more appropriate way of controlling the composition of the particles introduced in the hybrid material
- Usually in order to obtain the required dispersion of the nanoparticles in the matrix their prior functionalization is required

Sol-Gel SiO_2-based Hybrid Coatings doped with Oxide Nanoparticles

Aim of the work

- The main objective of our work was to establish the correlation between the method of embedment of binary (TiO_2-CeO_2) nanoparticles in a hybrid silica matrix and influence on the composition, structure and morphology of the deposited films
- Why did we choose this type of nano-particles?
- They have catalytic, sensing, anticorrosive, electrochromic so on properties.

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Experimental

- The hybrid **matrix** was generated using **methylthryethoxsilane (MTEOS)**
- The (TiO_2-CeO_2) nanoparticles were obtained using as precursors:
  $Ti(O\text{-}iC_3H_7)_4$ - titaniumisopropoxide
  $Ce(NO_3)_3.6H_2O$ – cerium nitrate
- The (TiO_2-CeO_2) particles were generated *in situ* and were also pre-synthesized

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Experimental

- Starting solution and experimental conditions for **hybrid silica matrix preparation**

Samples	Metallic precursors	Molar ratios		pH (HCl)	Experimental conditions		
		$\frac{ROH}{\sum Precursors}$	$\frac{H_2O}{\sum Precursors}$		T(°C)	t(h)	η cP
SiO_2 matrix	**CH_3-$Si(OC_2H_5)_3$**	11	2	3	RT	2	2.14

- Starting solution and experimental conditions for **binary oxide particles preparation** used for further embedding

Sample	Metallic precursors	Molar ratios			pH	Experimental conditions	
		$\frac{ROH}{\sum Precursors}$	$\frac{H_2O}{\sum Precursors}$	$\frac{NH_4OH}{\sum Precursors}$		T(°C)	t(h)
TiO_2:CeO_2 4:1	**$Ti(O\text{-}iC_3H_7)_4$ $Ce(NO_3)_3.6H_2O$**	35.6 R=-C_2H_5	3	3	8	80	1

→ The binary oxide nanoparticles were thermally treated at 400^0C for 1 hour

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Experimental

- Starting solution and experimental conditions for in **situ generation of the binary oxide nanoparticles**

Sample	Metallic precursors	Molar ratios		pH	Experim. conditions	
		$\frac{ROH}{\sum Precursors}$	$\frac{H_2O}{\sum Precursors}$		T(°C)	t(h)
$TiO_2:CeO_2$ 4:1	$Ti(O\text{-}iC_3H_7)_4$ $Ce(NO_3)_3.6H_2O$	35.6 R=$-C_2H_5$	3	5	RT	24

- The composition of the studied coatings in molar percentage is the following: 90mol% SiO_2-10mol% (TiO_2-CeO_2):

- Two type of sols for coating depositions were prepared by:
  - mixing the two appropriate amount of solution for matrix preparation with the solution for in situ particles generation
  - adding the corresponding quantity of the pre-synthesized particles dispersed in ROH to the solution of hybrid matrix

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Experimental

Coatings deposition

- **Substrate**: silicon wafer
- **Method of deposition**: “dip-coating” with a withdrawal rate of 5 cm/min
- **Thermal treatment:** 120 ^{0}C
- **Heating rate**: 1^0 C/min
- **Heating ramp**: 30 minute

Materials characterization

- Transmission Electron Microscopy (TEM)
- Dynamic light scattering
- Spectroellipsometry (SE)
- Atomic Force Microscopy (AFM)
- FT-IR Spectroscopy
- Thermogravimetry and Differential Thermal Analysis (DTA/TGA)

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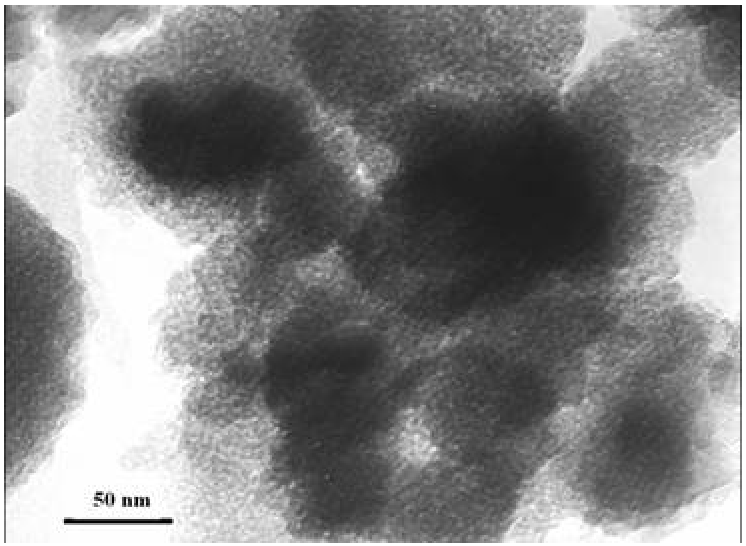
Results and discussions: Particles characterization



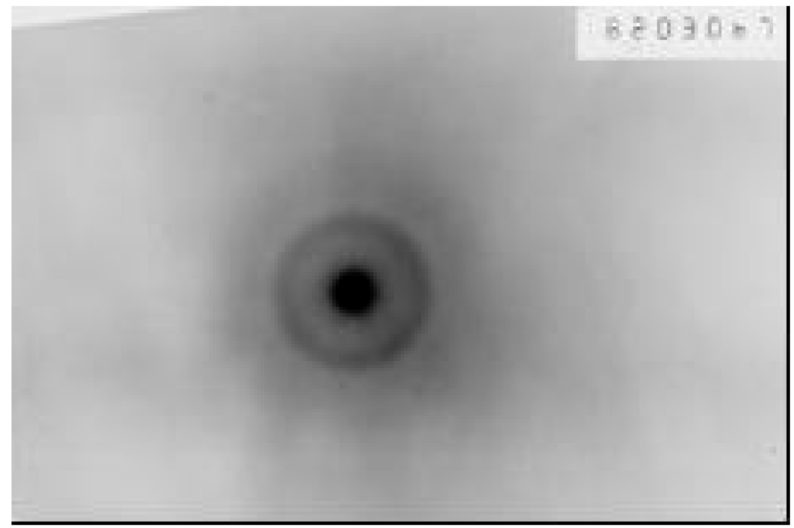


Figure 1. TEM micrograph and SAED image for the (TiO_2-CeO_2) particles thermally treated at 400°C

→ Granular aggregates of around 50 nm with 2-3 nm particles size could be observed.

→ The SAED image confirms the structural ordering tendency and the quasi-crystalline character of the particles.

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Results and discussions: Particles characterization

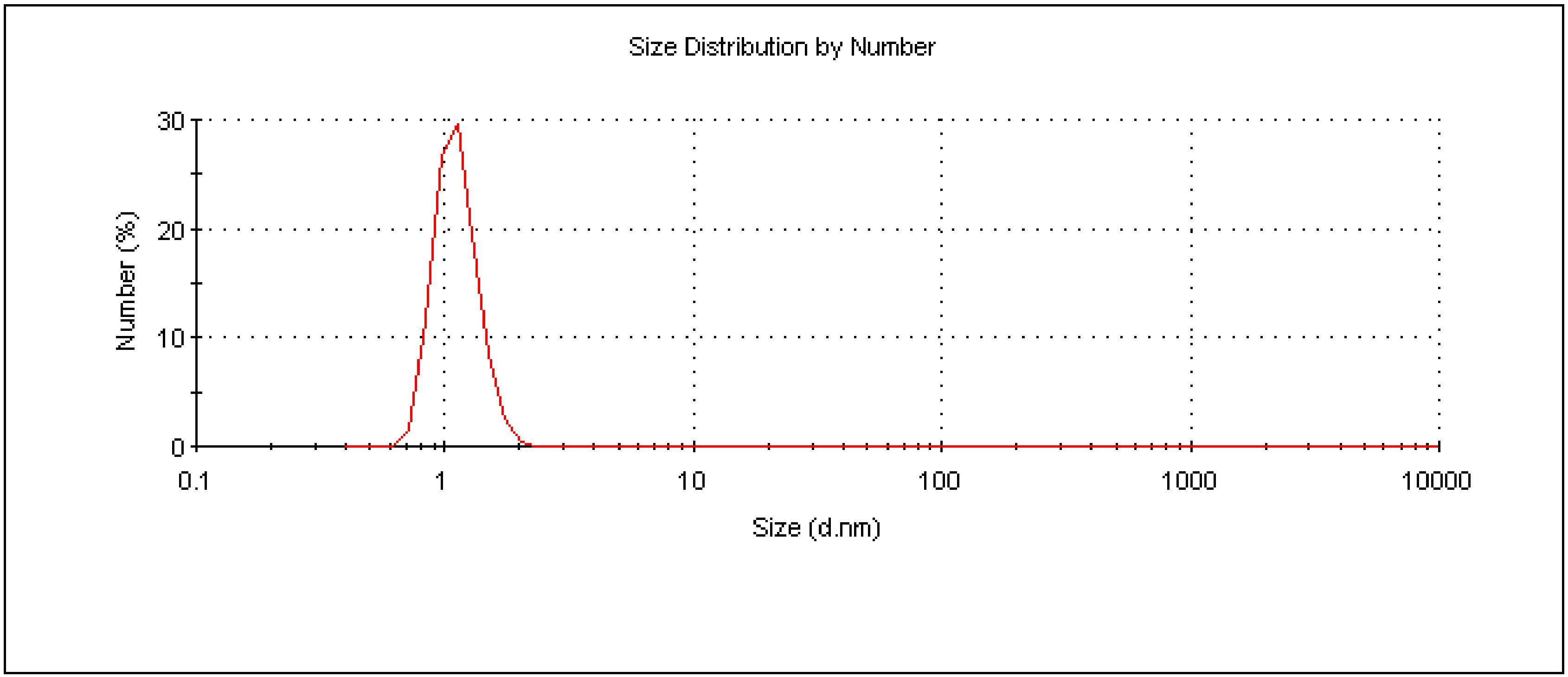

Figure 2. Particle size distribution for the "in situ" generated nanoparticles

- Nanoparticles of 1.3 nm were identified

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Results and discussions: Coatings characterization

Table 1 – Spectroellipsometric results

Sample	Substrate	Method	TT [°C]	d[Å]
S1	Silicon wafer	Particles *in situ* generation	-	2464
S2			120	2149
S3		Particles dispersion	-	2246
S4			120	2230

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Results and discussions: Coatings characterization

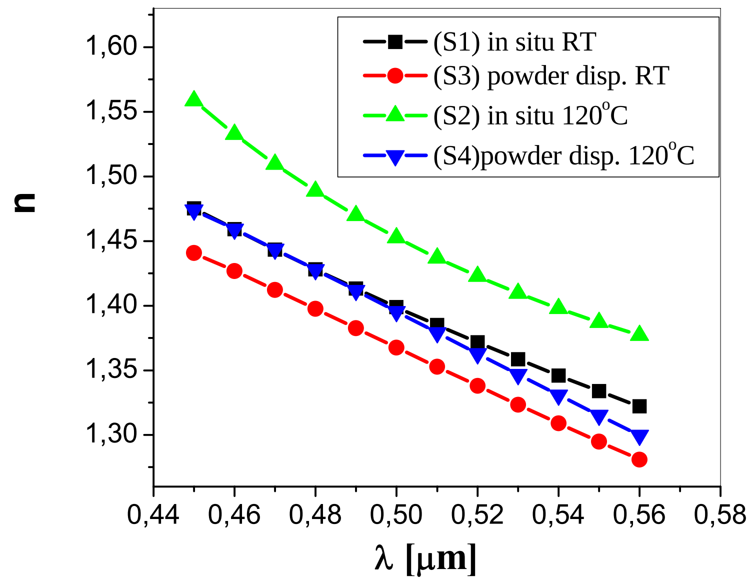

Figure 3. Refractive indices for the coatings deposited on silicon wafer

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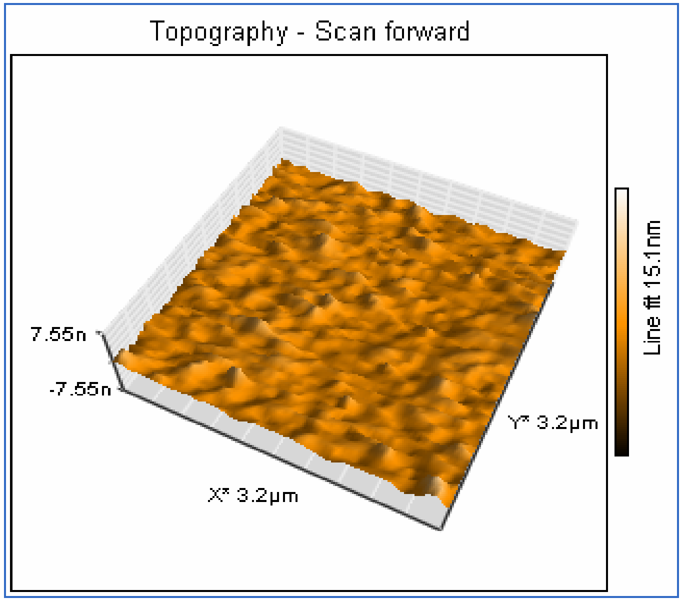
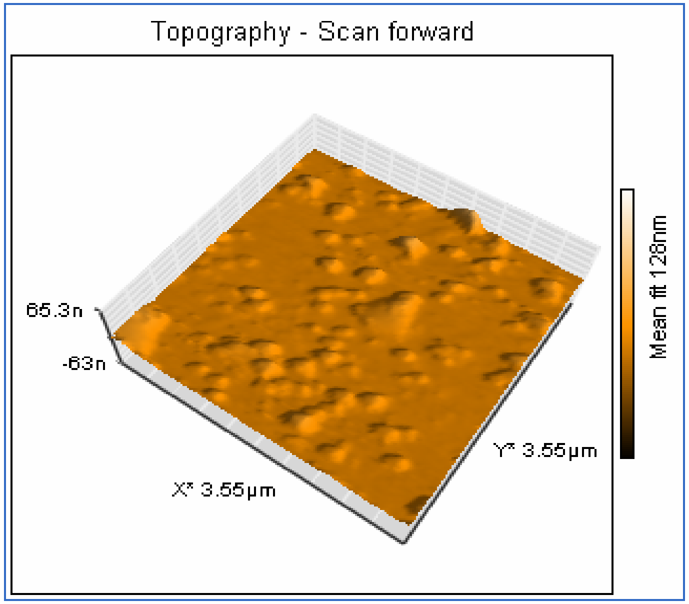
Results and discussions: Coatings characterization



a)



b)

Figure 4. AFM images for the films in the SiO_2-TiO_2-CeO_2 system: "in situ" generation of the oxides nanoparticles (a) dispersion of the previously prepared nanoparticles (b)

⟶ roughness of the coatings: 0.9 nm by in situ generation of particles
1.2 nm by dispersion of previously prepared particles

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Results and discussions: Coatings characterization

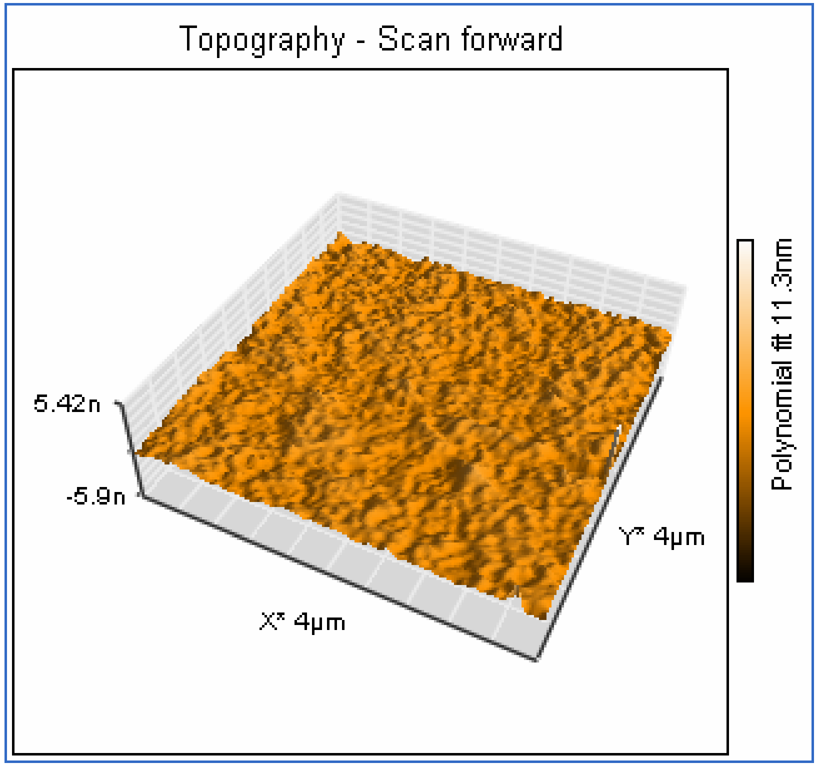

Figure 5. AFM image of a **tetraethylorthosilicate (TEOS): trimethoxysilyl propyl methacrylate (TSPM)(65:35)** based coating deposited on Si wafer using (TiO_2-CeO_2) particles previously prepared

→ roughness of the coating: 0.256 nm

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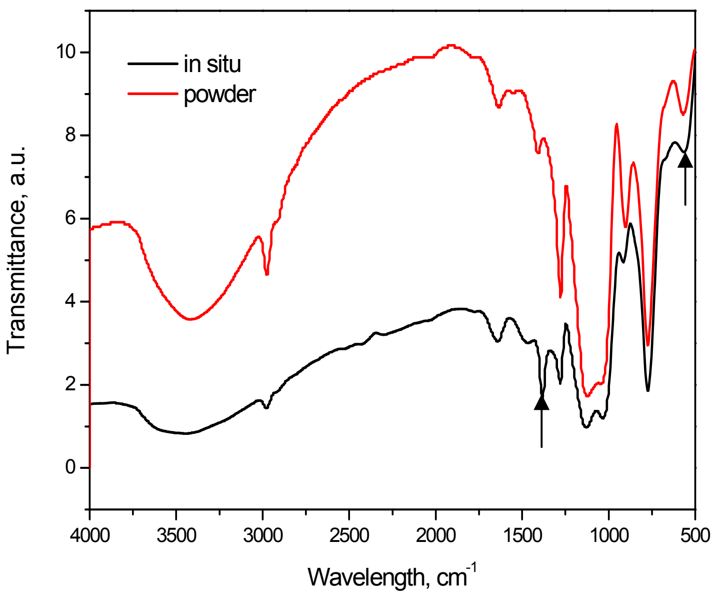
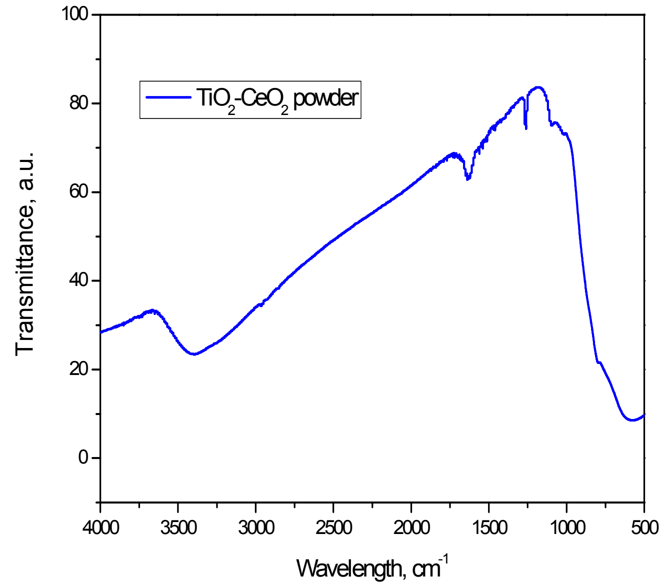
Results and discussions: Gels characterization



a)



b)

Figure 6. IR spectra of the SiO_2-TiO_2-CeO_2 gels obtained by in situ generation of the nanoparticles (a) and embedment of the pre-synthesized (TiO_2-CeO_2) particles (b)

- ***for the coating obtained by the dispersion of the pre-synthesized particles*** a classical IR spectrum of MTEOS based gel is observed; the presence of the (TiO_2-CeO_2) nanoparticles could be noticed by the vibration bands at the 540 cm^{-1}
- ***for the coating obtained by "in situ" generation of the nanoparticles*** a more disordered Si-O-Si network and supplementary vibration bands are observed (1380 cm^{-1}, ν NO_3^-)

Results and discussions: Gels characterization

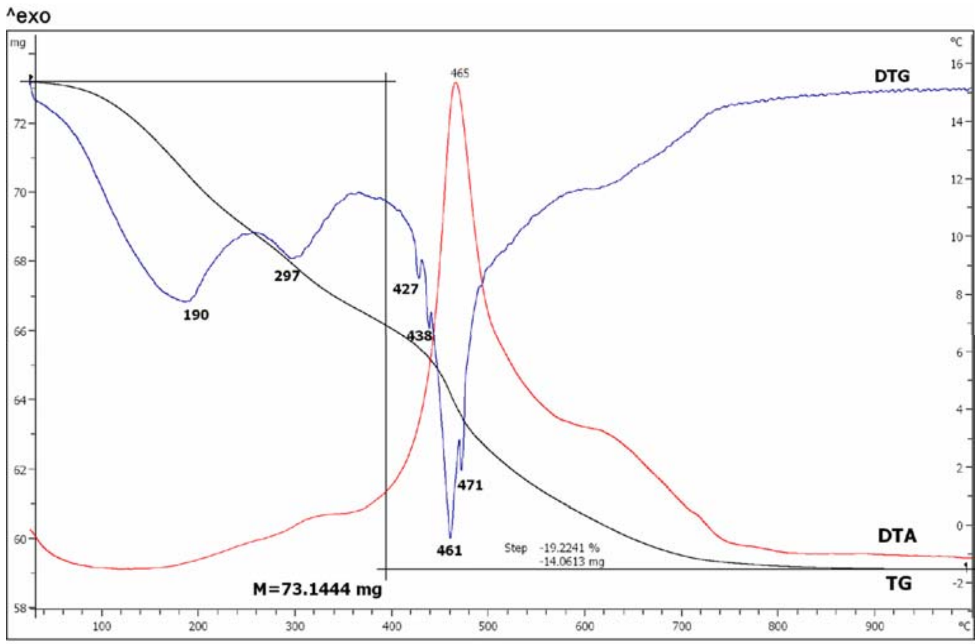


Figure 7. DTA/TGA curves for the gels obtained with pre-synthesized particles dispersion

- The hybrid gel obtained by pre-synthesized oxide nanoparticles decomposes at 465^0C that is the temperature of undoped MTOS gel decomposition
- The low temperature weight losses could be assigned to the dehydration of the particles included in the hybrid matrix

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Results and discussions: Gels characterization

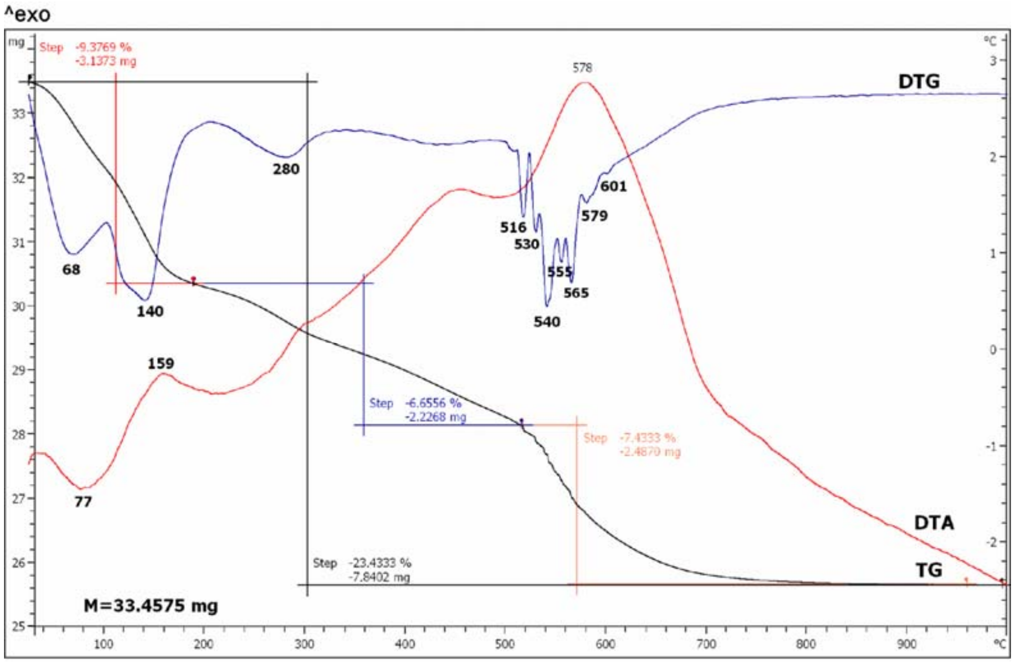

Figure 8. DTA/TGA curves for the gels obtained by "*in situ*" generation of the nanoparticles

- For the gels obtained by "in-situ' generation of the nanoparticles a higher number of thermal effects were noticed
- The thermal decomposition of the matrix ***is displaced to higher temperatures with about 100⁰C***, probably due to interaction of the precursors for nanoparticles generation with the silica matrix

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Application

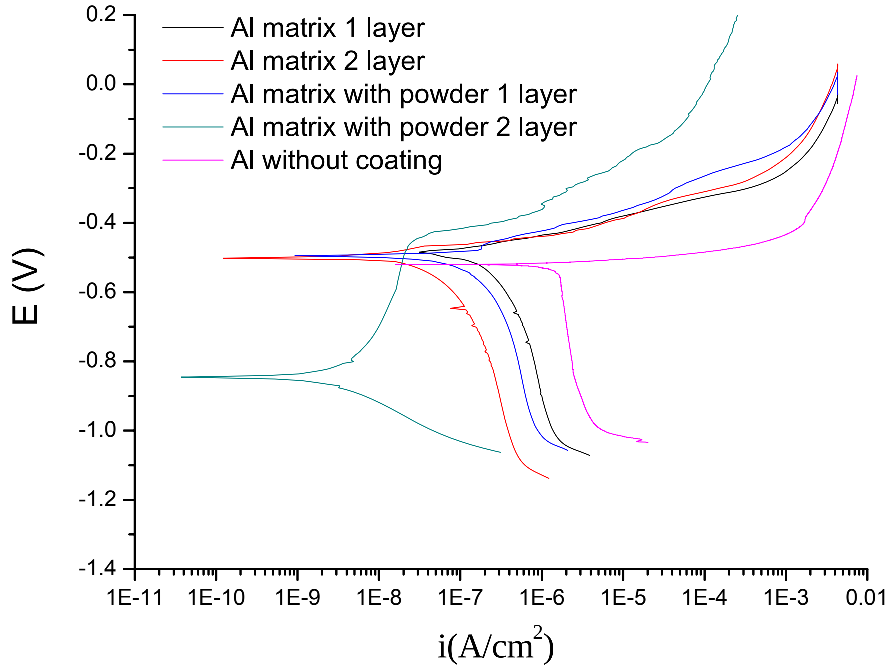

Figure 8. Polarization curves obtained for Al 2024 alloys covered with SiO_2 matrix and SiO_2 matrix + powder imersed in NaCl 0.05 M for compared with the uncovered substrate.

→ A pasivation of substrate alloy given by the sol-gel coatings is observed
→ This coatings can provide a partial barrier for blocking the electrochemical process.

Conclusions

- Sol-gel hybrid coatings on silicon wafers doped with TiO_2-CeO_2 nanoparticles have been produced by *"in situ"* particles generation or by pre-synthesized particles embedment in a hybrid matrix

- The coatings obtained by *"in situ"* generation of the particles allow a more homogeneous distribution in the coating, but chemical interaction with the silica hybrid matrix may occur

- When pre-synthesised particles were used their tendency to aggregate in the hybrid hydrophobic silica matrix was observed but the interaction with the matrix is much less evident

- The doped coatings have shown a higher anticorrosive action as compared with the undoped coatings

- The presented results are preliminary and further studies are required to bring more information on the matter

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