

## TiO<sub>2</sub> - BASED NANOSTRUCTURED SOL-GEL COATINGS FOR WATER TREATMENT

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TiO<sub>2</sub> has been shown to be an excellent photocatalyst for the degradation of several environmental contaminants. Many organic compounds can be decomposed in aqueous solution in the presence of TiO<sub>2</sub> powders or coatings illuminated with near UV or sunlight. When TiO<sub>2</sub> is irradiated by UV rays there are created pairs of electrical charges-holes in the valency zone and electrons in the conductivity zone. The holes react with water molecules or with the hydroxyl ions and hydroxyl radicals are formed, which are strong oxidants of the organic molecules. TiO<sub>2</sub>-based nanostructured pure and Fe<sup>3+</sup> doped coatings, on glass and silicon wafers support have been prepared by sol-gel methods. These films have been characterized by X-ray diffraction and spectroellipsometry methods. The influence of Fe<sup>3+</sup> dopant concentration, number of coatings, and calcination temperature on the films structure was established. Studies concerning photocatalytic oxidation of organic pollutants, using these films are underway.

*Keywords:* TiO<sub>2</sub> coatings, Fe<sup>3+</sup>/TiO<sub>2</sub> coatings, Nanostructured films, Sol-gel method.

### 1. Introduction

The sol-gel process offers new approaches to the synthesis of oxide materials. One unique property of the sol-gel process is the ability to go all the way from the molecular precursor to the product, allowing a better control of the whole process and the synthesis of tailor made materials: (monolithic gels, fibers, films, powders) [1]. The chemistry of the sol-gel process based on hydroxylation and condensation of molecular precursors has been extensively studied for silica. Transition metal alkoxides appear to be much more reactive than silicon alkoxides. This is due to the lower electronegativity of the transition metals compared with silicon and the ability of transition metals atoms to exhibit several coordination states [2, 3].

TiO<sub>2</sub> has been shown to be an excellent photocatalyst for the degradation of several environmental contaminants [4, 5]. Many organic compounds can be decomposed in aqueous solution in the presence of TiO<sub>2</sub> powders or coatings illuminated with near UV or sunlight [6-8]. When TiO<sub>2</sub> is irradiated by UV rays there are created pairs of electrical charges-holes in the valency zone and electrons in the conductivity zone. The holes react with water molecules or with the hydroxyl ions and hydroxyl radicals are formed, which are strong oxidants of the organic molecules. It has been shown that the photocatalytic activity of TiO<sub>2</sub> is influenced by the crystal structure (anatase, rutile), surface area, size distribution, porosity, surface hydroxyl group density, etc. [5]. These will have an influence on the production of electron-hole pairs, the surface adsorption and desorption process and the redox process.

However, one disadvantage of TiO<sub>2</sub> is that the bandgap energy is approximately 3.2 eV; therefore UV illumination is necessary to photoactivate this semiconductor. Another disadvantage of TiO<sub>2</sub> is that charge carrier recombination occurs within nanoseconds and, in absence of promoters (e.g. Pt or RuO<sub>2</sub>), the photocatalytic activity is low. A wide range of metal ions, in particular transition metal ions (iron, chromium, cobalt), have been used as dopants for TiO<sub>2</sub>, and their effects on the

properties of the doped samples have been reported by Ranjit [9, 10], Navio [11, 12], Litter [13]. We have previously published results on TiO<sub>2</sub> pure films [14, 15] and transition metal ions (copper, cobalt, vanadium) doped [16, 17], obtained by sol-gel methods.

In the present work, TiO<sub>2</sub>-based nanostructured pure and Fe<sup>3+</sup> doped coatings, on glass and silicon wafers support have been prepared by sol-gel methods. The influence of Fe<sup>3+</sup> dopant concentration, the number of coatings and calcination temperature on the films structure was established. Studies concerning photocatalytic oxidation of organic pollutants using these films are underway.

## 2. Experimental

The reagents employed were tetraethyl orthotitanate Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (Merck) as TiO<sub>2</sub> source; Fe(acac)<sub>3</sub> – ironacetylacetonate (Merck) as source of dopant; absolute ethyl alcohol p.a. reagent (Reactivul) as solvent; nitric acid p.a. reagent (Reactivul) as catalyst. Titanium alkoxides were hydrolyzed using a small quantity of water while controlling the pH to prevent the formation of TiO<sub>2</sub> precipitates. The composition of the starting solutions and the experimental conditions are listed in Table 1.

Table 1. Solutions composition and experimental conditions.

Solution	Solutions composition	Molar ratio
TiO <sub>2</sub>	[C <sub>2</sub> H <sub>5</sub> OH]:[Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	55
	[H <sub>2</sub> O]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	1.5
	[HNO <sub>3</sub> ]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	0.173 (pH = 4.1)
	Gelling time:	180 h
Iron source: Fe(acac) <sub>3</sub> Fe <sup>3+</sup> /TiO <sub>2</sub> =0.5%w	[C <sub>2</sub> H <sub>5</sub> OH]:[Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	57.75
	[H <sub>2</sub> O]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	1.5
	[HNO <sub>3</sub> ]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	0.15 (pH = 4)
	[Fe <sup>3+</sup> ]:[Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	0.0063
	Gelling time:	336 h
Iron source: Fe(acac) <sub>3</sub> Fe <sup>3+</sup> /TiO <sub>2</sub> =1.0%w	[C <sub>2</sub> H <sub>5</sub> OH]:[Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	57.75
	[H <sub>2</sub> O]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	1.5
	[HNO <sub>3</sub> ]: [Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	0.15 (pH = 4)
	[Fe <sup>3+</sup> ]:[Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	0.0126
	Gelling time:	312 h
Experimental conditions		
Reaction time (min) / Reaction temperature (°C)		60/50
Withdrawal speed (cm/min.)/Withdrawal temperature (°C)		5/20
Numbers of coatings		1-3
Thermal treatment of the film		
Temperature (°C)/Time (h)		300/1

The vitreous film was deposited by dip-coating on a sheet of carefully cleaned soda-lime-silica glass and silicon wafer substrates. The densification of the films was realized by thermal treatment for 1 hour at 300°C. For multi-layered films after each deposition, the same thermal treatment was applied.

Characterization of films obtained was performed using X-ray diffraction and spectroellipsometric measurements. The vitreous films formed after thermal treatment and their tendency to crystallize were characterized by X-ray diffraction using a TuR M-62 apparatus, equipped with an HZG-3 diffractometer, using CoK $\alpha$  radiation.

The optical properties of  $\text{Fe}^{3+}/\text{TiO}_2$  amorphous films were determined by SE measurements in the 300-700 nm wavelength range. The optical constants were obtained from the best fit of the SE experimental data with a multilayer and multicomponent Bruggemann-EMA [18] model. The optical gap ( $E_g$ ) was obtained by fitting the refractive index dispersion with the Wemple Di Domenico equation [19]:

$$n^2(\omega) - 1 \cong E_d E_o / (E_o^2 - E^2) \quad (1)$$

where  $E_d$  is the dispersion energy and  $E_o$  is the oscillation energy. The first parameter measures the average strength of the interband optical transitions, associated with the changes in the structure of the material. The second one, can be correlated with the optical gap ( $E_g$ ) by the empirical formula:  $E_o = 1.7E_g$ .

### 3. Results

Continuous, homogeneous and nanostructured films resulted from initial solutions and experimental conditions presented in Table 1. X-ray diffraction confirmed the amorphous character of films thermally treated at 300°C. In all the unsupported gels thermally treated at 300°C, poorly crystallized anatase is present.

The values of oscillation energy ( $E_o$ ) and optical gap ( $E_g$ ) are presented in Table 2.

Table 2. Oscillation energy ( $E_o$ ) and optical gap ( $E_g$ ).

Sample	Number of deposition	$E_o$	$E_g$ -direct (eV)
$\text{TiO}_2$ [10]			3.200
$\text{TiO}_2$			3.180
$\text{TiO}_2$ -0.5% $\text{Fe}^{3+}$ , fresh	1	10.138	3.167
$\text{TiO}_2$ -0.5% $\text{Fe}^{3+}$ ; annealed	1	11.854	3.115
$\text{TiO}_2$ -0.5% $\text{Fe}^{3+}$ , annealed	2	12.900	3.084
$\text{TiO}_2$ -1% $\text{Fe}^{3+}$ ; fresh	1	9.868	3.105
$\text{TiO}_2$ -1% $\text{Fe}^{3+}$ ; annealed	1	11.449	3.059
$\text{TiO}_2$ -1% $\text{Fe}^{3+}$ ; annealed	2	11.355	2.770

The values of thickness and refractive index of the obtained films are presented in Figs. 1 and 2.

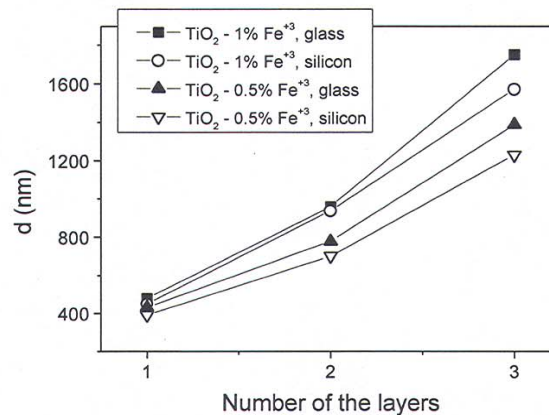


Fig.1. The influence of the  $\text{Fe}^{3+}$  content and of the substrate nature on the thickness of the films.

The influence of the substrate and thermal treatment on the films properties is presented in Fig 2.

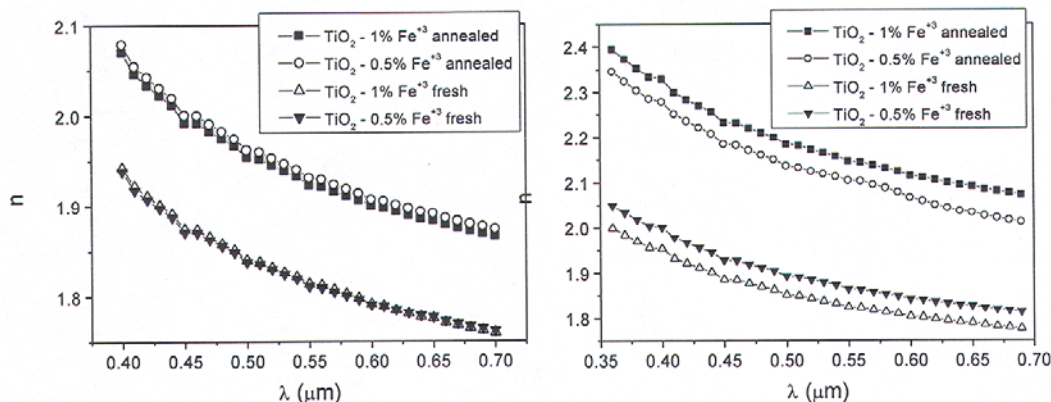


Fig. 2. The influence of the substrate nature and of the thermal treatment on Fe<sup>3+</sup>/TiO<sub>2</sub> coatings - one deposition - (top - the substrate is glass; bottom - the substrate is silicon wafer).

#### 4. Discussion

In the presented paper the influence of different parameters on the optical properties of the TiO<sub>2</sub> based films were determined on mono- and multi-layered films.

As resulted form the data in Fig. 1, the thickness of a multi-layered films obtained by several depositions and subsequent several thermal treatments represents roughly the thickness of the film obtained by one deposition, multiplied by the number of depositions;

The main factors which influence the optical properties of the sample are: the composition of the film (which in its turn depends on the technological parameters of the deposition process and of the subsequent thermal treatments) and the nature of the substrate.

##### a) The influence of Fe<sup>3+</sup> content

It is obvious that the introduction of iron in TiO<sub>2</sub> film lowers the E<sub>g</sub> values the more so the higher the Fe<sup>3+</sup> content (Table 2). The doping with iron may enhance the photoactivation of the semiconductors by UV.

The thickness of the films increases with the Fe<sup>3+</sup> content of the film irrespective of the substrate used (Fig. 1).

##### b) The influence of the substrate

It is known the substrate topography influence the crystallization of the film. On a crystalline substrate the film itself is more liable to crystallize [20].

Our results are in good agreement with the data mentioned above. The films (with 0.5% and 1% Fe<sup>3+</sup> content) deposited on glass are more porous (with smaller refractive index-Fig. 2) and thicker than those deposited on silicon wafers.

##### c) The influence of the thermal treatment

The lowest temperature which allows formation of continuous dense oxide films free of organic traces is 300°C. All films obtained below this temperature exhibit variations of optical constants with the thermal treatment [16].

After a thermal treatment (1h at 300°C) the films are densified lowering in thickness with 20-30% (depends on the type of substrate used and the quantity of the Fe<sup>3+</sup> introduced in film) and lowering also the porosity around 10%, which leads to a remarkable growing of the refractive index (Fig. 2). The films with higher Fe<sup>3+</sup> content present a higher densification.

Concerning the porosity of the multi-layered films the results are not so clear, due to the fact that in this case two phenomena occur:

- a higher number of depositions means a higher number of thermal treatments, which lead to a densification, followed by porosity decrease;
- in the same time, multiplied thermal treatments lead to changes in the crystallite size and their re-arrangement in the network is possible to determine the voids formations, which increase the porosity of the film. The final result could be either an increasing or decreasing of the porosity of the film.

## 5. Conclusions

TiO<sub>2</sub> –based nanostructured pure and Fe<sup>3+</sup> coatings doped, on glass and silicon wafers support have been prepared by sol-gel methods. The influence of Fe<sup>3+</sup> dopant concentration, the number of coatings and calcination temperature on the films structure was established.

The thickness of the films increases with the Fe<sup>3+</sup> content of the film irrespective of the substrate used.

The films deposited on glass are more porous and thicker than those deposited on silicon wafers.

The films with higher Fe<sup>3+</sup> content present a higher densification.

Studies concerning photocatalytic oxidation of organic pollutants using these films are underway.

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