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Preparation and characterisation of TiO_2 thin films with special optical properties

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Thin films of TiO_2 were coated onto optical glass substrate from a medium containing metal alkoxide precursors, chelating agent and solvents. In order to prepare TiO_2 films with controllable porosity or special optical properties, polyethylene glycol and europium nitrate were added into the coating bath. Multiple TiO_2 layers were deposited by dip-coating method and they were annealed in air, at 550ºC. Thermal analysis, FT-IR spectroscopy and surface area measurements were used to characterise the precursor powders. The optical properties of TiO_2 films were studied by UV-Vis absorption/reflection spectroscopy and photoluminescence measurements while the film morphology was evaluated by scanning electronic microscopy (SEM).

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1. Introduction

Titanium dioxide (TiO_2) is a large band-gap semiconductor with many interesting properties. It is transparent to visible light, has high refractive index and excellent chemical stability over a wide pH range and in a large number of solvents [1].

TiO_2-films can be prepared by various techniques such as sol-gel, chemical vapour deposition, pulsed laser deposition or sputtering. Dip-coating based on sol-gel process is one of the most useful methods to obtain uniform thin titanium oxide films, and the metal alkoxides are commonly used as the starting materials [2]. Sol-gel technique offers many advantages over other preparation methods such as the precise control of the film composition and doping level, the simplicity and also, the low temperature processing.

Titanium dioxide thin films are special materials with a broad spectrum of applications in the field of optoelectronic devices, photocatalytic systems and protective anti-reflection coatings. Numerous studies have been performed in order to improve the film special properties by depositing noble metals, introducing surface modifiers and dopants [3,4]. TiO_2-films could become valuable light emitting materials if they are doped with highly luminescent rare earth ions [4-6]. Moreover, the luminescence study of the rare earth elements hosted in several crystalline matrices such as metal oxides and a variety of semiconductor materials are strongly motivated because of their technological applications in optoelectronic devices and flat panel displays.

The present paper presents our results referring to the synthesis of transparent and porous TiO_2 thin films on glass substrates. The luminescence properties of TiO_2 thin films are also discussed.

2. Experimental part

2.1 Preparation of dip-coating bath

TiO_2-films have been prepared on optical glass substrates by dip-coating method. The coating bath was prepared using tetraisopropyl ortotitanate Ti $(^iOC_3H_7)_4$ – TIPO, ethanol C_2H_5OH-EtOH, acetic acid CH_3COOH – AcOH, Acetilacetone $CH_3COCH_2COCH_3$ –acac, polyethylene glycol (PEG 200 and PEG 600) and/or europium nitrate $Eu(NO_3)_3.5H_2O$.

The coating bath was obtained by dissolving TIPO in two thirds of the total ethanol volume while stirring under nitrogen atmosphere. After addition of glacial acetic acid and PEG, the solution was magnetically stirred for 15 minutes; the stirring continued for another 90 minutes with the remaining ethanol being added. In order to obtain europium-doped TiO_2 thin films, europium nitrate $Eu(NO_3)_3.5H_2O$ was added to the mixture. The white precipitate formed was dissolved by drop wise addition of acetylacetone, during the stirring.

The coating bath composition correspond to the following reagents volume ratio: TIPO: acac: EtOH: AcOH: PEG= 1.250:1.000:19.000:0.006:1.000

2.2 Preparation of TiO_2 films

Prior the coating, optical glass platelets (45mm x 30mm x 1mm) were ultrasonically cleaned with acetone/ethanol mixture and dried at 110^0C. The dipping process was carried out at room temperature under air atmosphere (approx. 25^0C). The substrates were put in a vertical position, tightly held by a dipping holder. Both sides of substrates were immersed and rapidly pulled out with a rate of 4 cm/min. A thin, uniform and stable film was due to the partial hydrolysis of TIPO with ambient humidity without inert gas protection. The solvent was

allowed to evaporate for 30 min and then the samples were thermally treated at 550^0C. In order to obtain multilayer thin films with controllable thickness, four-six TiO_2 layers were successively coated and then thermally treated as described above.

2.3 Sample characterisation

Precursors i.e. gels-powders obtained by slowly drying the coating-sol, were characterised by thermal analysis, FTIR spectroscopy and surface area measurements. Thermal analysis was carried out using a Mettler Toledo TGA/SDTA851 thermal analyser (heating rate of 5^0C /min; nitrogen flow). FT-IR spectra of the gels-powders before and after the thermal treatment at 550°C were recorded in the 500-4000 cm^{-1} range, on a JASCO 610 Spectrometer (KBr pellets technique). Surface area was measured from kripton absorption isotherms (nitrogen temperature), by Brunauer- Emmett –Teller (BET) analysis.

TiO_2 films were characterised by absorption/transmission and reflection properties as well as by photoluminescence measurements. An UNICAM Spectrometer UV4 (with RSA-UC-40 integrating sphere accessory) was used to investigate the optical properties of TiO_2 thin films. A JASCO FP-6500 Spectrofluorimeter Wavel was used to evaluate the photoluminescence characteristics of films. The morfology of the TiO_2-films was evaluated by scanning electron microscopy (SEM) with a JOEL-JSM 5510LV microscope.

3. Results and discussion

Titanium dioxide is known to be a stable and transparent material in the form of thin films**.** Formation of TiO_2-based films could be generally described by the following processes of hydrolysis (1) and condensation (2):

$$Ti\,(O\,{}^{i}C_3H_7)_3 + H\text{-}O\text{-}H \rightarrow HO\text{-}Ti(O\,{}^{i}C_3H_7)_3 + {}^{i}C_3H_7\text{-}OH \quad (1)$$

$$({}^{i}C_3H_7O)_3Ti\text{-}OH + {}^{i}C_3H_7O\text{-}Ti(O\,{}^{i}C_3H_7)_3 \rightarrow$$
$$\rightarrow ({}^{i}C_3H_7O)_3Ti\text{-}O\text{-}Ti(O\,{}^{i}C_3H_7)_3 + {}^{i}C_3H_7\text{-}OH \quad (2)$$

Metal alkoxides are susceptible to nucleophilic attack and are highly reactive due to the electronegative OR groups stabilizing the metal in its highest oxidation state. However, owing to their high reactivity, some modifiers or stabilizers have been used to stabilize the sols derived from the alkoxides[7,8].

TiO_2-film growing rate is regulated by the presence of acetylacetone as chelating agent that stabilizes the sol by decreasing the alkoxide reactivity. The alkoxy groups R are displaced by the acetylacetone molecule (3) in order to form a stabilized chelate coordination compound [9,10].

$$Ti(O\,{}^{i}C_3H_7)_4 + 2acacH \rightarrow Ti(O\,{}^{i}C_3H_7)_{4-x}(acac)_x + x\,{}^{i}C_3H_7OH \quad (3)$$

In this case, the formed complex (3) will take part to the processes (1) and (2).

TiO_2 films were prepared by dip-coating method from sol containing tetraisopropyl ortotitanate, ethanol, acetic acid, acetilacetone and polyethylene glycol. General characteristics of the TiO_2 –films samples are presented in Table 1.

Table 1. General characteristics of TiO2 films.

Code	Structure	Modifier or Eu-Doping	Layer number	Remarks
Ti1	TiO_2/ glass/ TiO_2	0	1-5	Good adherence Good optical uniformity; Translucent;
Ti2	TiO_2(Eu)/ glass/ TiO_2(Eu)	3 mol Eu/ 100 mol Ti		Good adherence Good optical uniformity;
Ti3	TiO_2/ glass/ TiO_2	PEG600	4	Good adherence; Good optical uniformity;
Ti5	TiO_2/ glass/ TiO_2	PEG200	4	Good adherence Good optical uniformity;
Ti6	TiO_2(Eu)/ glass/ TiO_2(Eu)	10 mol Eu/ 100 mol Ti	4	Good adherence; Good optical uniformity; Translucent;

Where: PEG-polyethylene glycol.

The surface state of the films, their morphology is evaluated by scanning electron microscopy. Fig. 1 presents the SEM images of TiO_2 films obtained from coating bathes with different compositions. Sample Ti1 (TiO_2) shows an inhomogeneous surface. The presence of europium nitrate into the coating bath seems to ameliorate the surface state of the film while the addition of PEG into the coating bath generates TiO_2 films with rather rough surface. Doping substances and modifiers influence the morphology of the films.

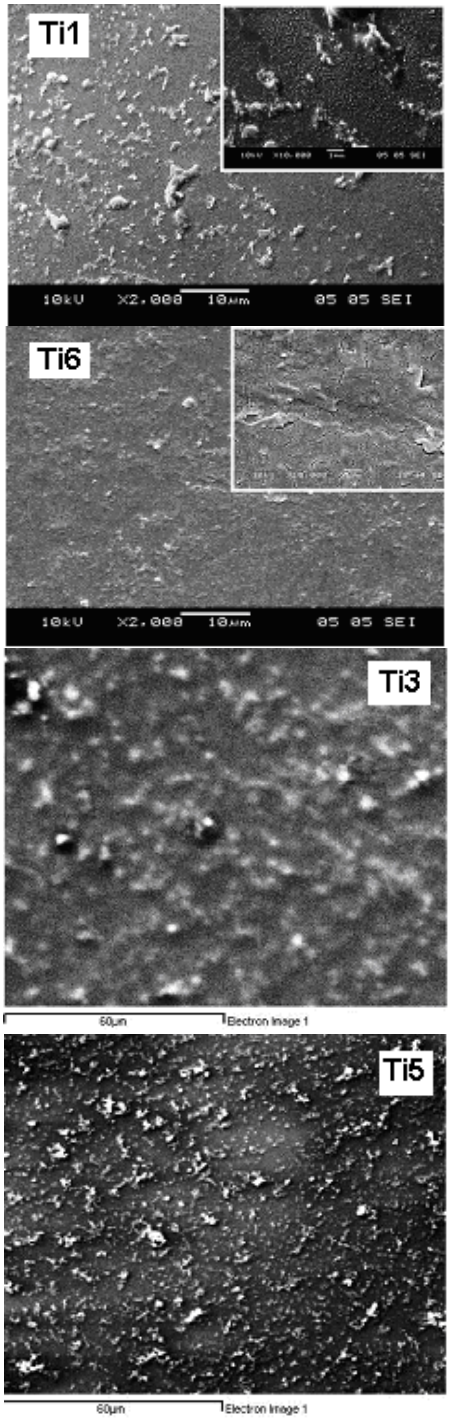


Fig. 1. SEM images of TiO_2 films obtained from coating bathes with different compositions

3.1 Characterisation of the precursors

In order to establish the optimum thermal treatment for the TiO_2 films, thermal analysis and FTIR measurements on the dried gel-powders (precursors) were performed. The thermal behaviour of TiO_2- and TiO_2: Eu-precursors is indicated by the thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves depicted in Fig. 2.

The total weight loss of TiO_2 and TiO_2:Eu precursors is about 37 – 41 % . For both samples, the thermal decomposition of gel-precursors is almost finished at about 400ºC. Up to this temperature, the weight loss is associated with water and organic compounds removal. The weight loss observed at about 900ºC could be associated with some oxygen eliberation from the TiO_2 lattice. DTA curves indicate a strong endothermic effects correlated with the precursor/organic compounds thermal dissociation and water evaporation.A small exothermic effects (at about 400°C) associated with the self-burning (in nitrogen flow) of organic compounds, in the nitrate presence can be noticed.

Taking into account the nature of the substrate (glass) and the need for an organized host lattice to generate good special optical properties, the recommended annealing treatment is of 500ºC- 550ºC.

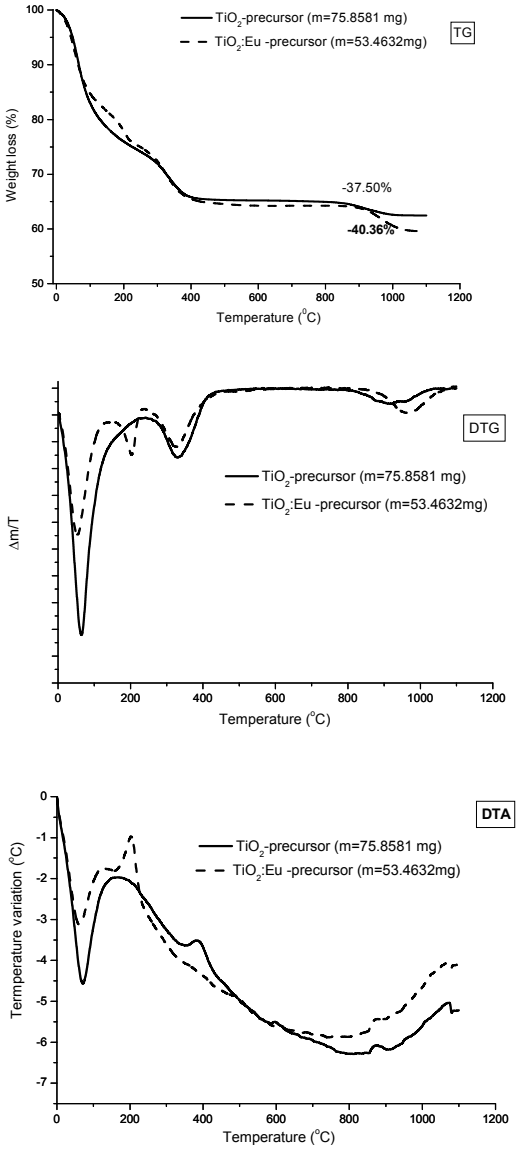


Fig. 2. TG-DTG-DTA curves of gel-powders T1 (for TiO_2) and Ti2 (for TiO_2:Eu).

Mention has to be made that, for gel-powders separated from coating sol containing PEG, the total weight loss is about two times larger than in the case of simple bath, as follows: 65.9% (Ti3) and 73.6% (Ti5) as compared with 37.5% (Ti1).

The infrared absorption spectra of dried powders (gel-precursors) before and after the thermal treatment at 500ºC are showed in Fig. 3. There are presented spectra of gel-precursors obtained from simple coating bath (Ti1) and PEG containing coating bath (Ti3), respectivelly.

FTIR spectra put in evidence the good conversion of precursors into TiO_2- thin films. The specific vibration bands of PEG from precursors disappear in gel-powders obtained by thermal treatment at 550°C.

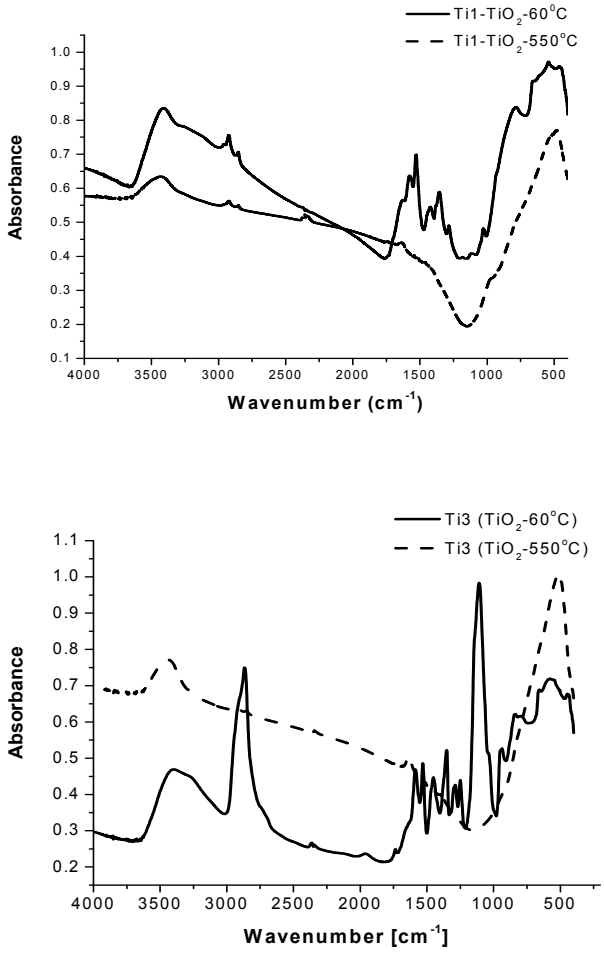


Fig. 3. FT-IR spectra of gel- powders (precursors) before and after the thermal treatment

The strong vibration bands at about 2870 cm^{-1}, correlated with CH_2 groups, and vibrations in the 1600-100 cm^{-1} range, assigned to C=O groups, desapear in thermally treated samples. The thermal treatment at 550°C leads to the partial or complete removal of polyethylene glycol and acetilacetone.

The porosity of these materials was evaluated by measuring the surface area of gel-powder samples containing different PEG type, after a thermal treatment at 550ºC.

Table.2 Specific surface area of gel- powders (precursors) prepared with different modifiers.

Code	Modifiers	Thermal treatment	Surface area S_σ (m^2/g)
Ti1	0	550ºC (30 min)	9.9
Ti3	PEG600	550ºC (30 min)	37.3
Ti5	PEG200	550ºC (30 min)	16.7
Ti6	$Eu(NO_3)_2$	550ºC (30 min)	18.8.

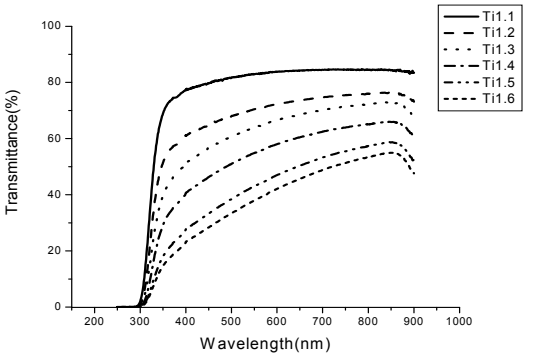
One note that, the porosity of the thermally tretaed gel-powders increases when PEG is added into the coating bath; the higher the molecular weight, the larger the surface area. Moreover, the use of europium nitrate causes also the increase of the surface area. In all cases, the thermal decomposition of nitrate and PEG results in the porosity increasing.

3.2 Thin films characterization

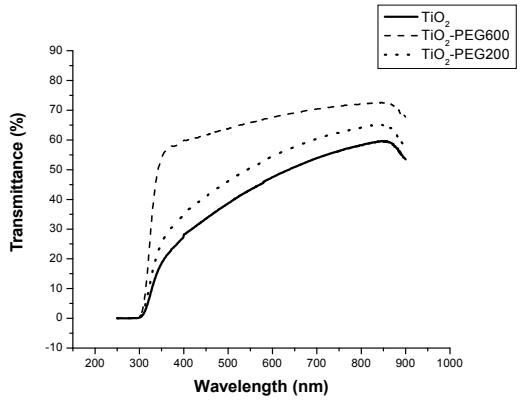
In order to determine the special optical properties, rather thick films of TiO2 films has to be prepared by using the multilayer coating technique. In this respect, films were prepared by successive deposition of multiple layers using 4-6 dip-coating steps. One can be note that density packing of the films increases with number of layers. UV-Vis absorption and reflection spectra illustrate the optical behaviour of TiO_2 film samples (Figs. 4 –5).

The optical properties of TiO_2 films are strongly dependent on thickness and porosity of the films. The porosity of the films can be adjusted by introducing PEG in the sol-gel process.

Fig. 4 presents the transmittance spectra of TiO_2 films with different number of layers (left) and also, of TiO_2 films obtained from coating bathes with different compositions (right). An increase in the number of layers leads to the decrease of films transparency. A low number of maxima and minima could also be identified. In addition, the PEG content clearly modifies the films transmission in the UV-vis region. The optical quality of TiO_2 films decreases when the PEG molecular weight increases.



a



b

Fig. 4. Transmittance spectra of TiO_2 films with different number of layers (a) and of TiO_2 films obtained from coating bathes with different compositions (b)

Reflectance spectra of TiO_2 films with different PEG types measured at 8º incidences illustrate that the adding of polyethylene glycol increases the film diffuse reflectance (Fig.4). The higher reflectance is observed for film prepared from coating bath with PEG600 that probable, during the thermal treatment, generates larger pores then PEG200.

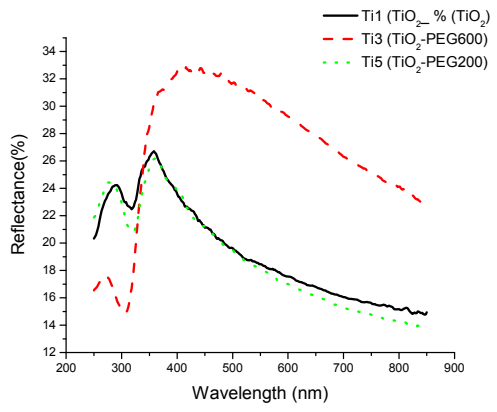


Fig. 5. Reflectance spectra of TiO_2 films with different PEG type measured at 8º incidence

The photoluminescence behaviour of europium doped TiO_2-film is illustrated by the emission spectrum depicted in Fig. 6, in comparison with the spectrum of the un-doped TiO_2-film.

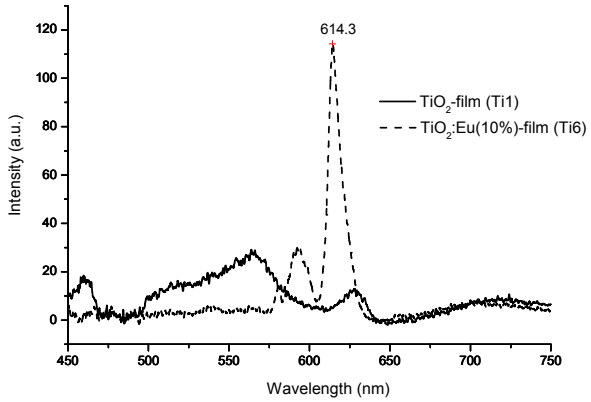


Fig. 6. Emission spectra of TiO_2 /glass/ TiO_2 structures under UV radiation (λ_{exc}=260 nm).

Under ultraviolet excitation, the heterostructure TiO_2(Eu)/glass/TiO_2(Eu) shows a specific luminescence in the red spectral domain that is generated by the electronic transitions $^5D_o \rightarrow {}^7F_J$ taking place inside the Eu^{3+} ion. In our case, the strongest emission band is situated at ~ 614 nm ($^5D_o \rightarrow {}^7F_2$). In comparison, the film obtained without europium (Ti1) shows a weak luminescence in the blue-green domain due to TiO_2 itself.

4. Conclusions

Thin films of TiO_2 were coated onto optical glass substrate from a medium containing titanium tetraisopropoxide, acetilacetone, acetic acid, ethanol and polyethylene glycol or europium nitrate as surface modifier or dopant. Both the modifier, PEG and the dopant, $Eu(NO_3)_3$ influence on the optical properties of films, i.e. transmittance and diffuse reflectance of the films in the UV-Vis region. The optical quality of TiO_2 films decreases when the PEG molecular weight increases. Moreover, as shown by surface area measurements, the films porosity can be adjusted by introducing PEG with variable molar weight in the coating bath.

Under excitation with ultraviolet radiation, the red luminescence of Eu^{3+} ions could be observed for the as-prepared TiO_2:Eu thin films.

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