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Effect of the thermal treatment on the morphology and optical properties of nanosized TiO_2 films

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Thin TiO_2 films are prepared by spin coating from two types of solutions containing titanium isopropoxide with and without polyethyleneglycol. The final phase composition depends on the temperature of drying of every layer. The films obtained by drying of every layer at 120°C and 300°C contain anatase phase, while treatment of every layer at 500°C results in a mixture of anatase and brookite phase due to the diffusion of sodium from the glass substrate. The temperature of drying influences the optical properties of the films. The highest transmittance posses the films obtained after drying of every coating at 120°C and treated at 500°C. The spectra of films show a pseudo blue shift. A tendency of decreasing of the band gap energy of TiO_2 sol gel films with increasing of the drying temperatures is observed.

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1. Introduction

Titanium dioxide is an extensively studied semiconductor for photoinduced reactions, which occurs naturally and synthetically in three crystalline forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). In nature, rutile is the most common crystal phase, while brookite is scarce.

In the laboratory scale, TiO_2 is mostly manufactured using sol gel. Most of the authors, who investigate sol gel thin films, use drying of every layer at a low temperature and annealing the samples after that at sintering temperatures in the range 400-500°C [1-3]. Quite occasionally, sol gel titania films obtained by treatment of every layer at temperatures above 300°C are quite scarce. Very recently our team has proven that the titania films, prepared by spin coating and applying of two different drying temperatures to every layer, show a difference in their phase composition. If the spin-coated film is heated up to 500 C after the deposition of each layer, then a mixture of anatase and brookite is obtained [4]. The mixture of anatase and brookite phase is of special interest due to its higher photocatalytic activity than that of a single anatase phase according Yu et al [5]. Only few investigators have obtained titania of mixed anatase – brookite phase by various methods: sol gel [6-10], electrochemical oxidation of titanium electrodes [11] and pulsed laser deposition [12]. It has been revealed that various additions to the precursor solution may have a role in stabilizing of the brookite phase [8, 9, 10, 15-17].

The temperature of heating of each layer has an impact on the degree and velocity of decomposition of organic compounds in the sol as well as on the diffusion of elements from the substrate to the film .The presence of polymer additives and the thermal treatment affect the elimination of organics from the sol, which determine the final films morphology (crystalline size, formation of pores, cracks etc.) and other thin films characteristics.

Recently Kuznetsova et al. [9] have supposed that the sodium penetration from the substrate into the films probably favours the formation of brookite phase. As the diffusion depends on the temperature, the sodium concentration in films could be influenced by the drying temperatures.

The aim of this paper is to investigate the influence of solution composition and the thermal treatment on the crystallographic phases, morphology and optical properties of sol-gel TiO_2 films.

2. Experimental procedures

The ingredients of sol gel solutions were titanium isopropoxide - $Ti(OPr)_4$ (98%, Acros), acetylacetone (AcAc), isopropanol (Loba Chemie Apolda, A.R.) and distilled water.

Titanium isopropoxide, acetylacetone, isopropanol and water in the solutions were in molar ratios 1:1:50:1. The following preparation was applied: $Ti(OPr)_4$ and acetylacetone were dissolved in isopropanol. The solution was transparent and of orange colour, which is typical for a chelate complex form. The reaction of complex formation is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and isopropanol was added drop wise to the above solution (solution I). To one part of the as-obtained solution I 1 wt% polyethyleneglycol (PEG 400) (Fluka) was added under vigorous stirring for 1 h. (solution II).

The glass substrates were cleaned successively with a dichromate mixture, a mixture of hydrochloric acid and nitric acid, ethanol and acetone and finally rinsed in distilled water.

The sol was coated on glass substrates by spin coating (1500 rpm) and after that the layer was dried at different temperatures according to following three methods of heat treatment.

Method A: every coating was dried at 120°C for 15 min.

Method B: every coating was dried at 300°C for 15 min.

Method C: every coating was heated at 500°C for 15 min.

To evaluate the influence of heating rate on the films properties ,the methods A, B and C were applied at a heating rate of 4°C.min^{-1}.To obtain the desired film thickness, the spin coating and drying at different temperatures were repeated four times and the final forth coating the sample was heated at 500°C for 1 h after final forth coating. The samples were characterized by X-ray diffraction (XRD), Ultraviolet-visible spectroscopy (UV VIS) and X-ray photoelectron spectroscopy (XPS). The size of crystallites was estimated by XRD-LB measurements. The XRD patterns were obtained on a Philips PW 1050 diffractometer (Cu K_α radiation)

The XPS analyses were carried out by ESCALAB II system (vacuum generator) using Al Kα radiation (hυ=1486.6 eV). To estimate the reflectance of films the ultraviolet-visible spectra were measured on a Beckman 5720 UV-VIS spectrophotometer equipped with an integrating sphere. A $BaSO_4$ disc was used as reference. All spectra were recorded under ambient conditions. Spectroscopic analysis was performed by using a UV VIS double beam spectrophotometer Cary 100at a wavelength range 300-800 nm. IR spectroscopic study of the powder samples was performed by Nicolet Avatar 320 in a pastille of KBr.

3. Results and discussion

3.1. IR study

As the influence of thermal treatment is the object of this paper, it is interesting to obtain more information about the behaviour of initial sol during the drying. For this reason, we have prepared powder samples from solution $Ti(OPr)_4$:acetylacetone:isopropanol:water in molar ratios 1:1:50:1 and PEG400-1 wt% (solution II) which was dried at 120°C for 15 min. The powder is analysed by IR spectroscopy (Fig 1).As it is seen from the figure, there is a series of narrow bands with a maximum at 1031, 1282, 1360, 1425, 1535, 1574 and 2919 cm^{-1}, and a broad band with maxima at 3360 cm^{-1}. Taking into account the data available in literature, the band at 1031 cm^{-1} can be attributed to bridging Opr^i ligands of titanium isopropoxide TTIP [17-19]. The broad intense band with maximum at 3360 cm^{-1} is due to (O–H) vibrations of the hydroxyl groups [17, 19-21]. The bands at 2919 and 2860 cm^{-1} are related to the stretching vibration of C-H bonds of organic compounds [22]. It is seen that such compounds are still present in the sample even after drying (sample AcAc-T0). The interpretation of other detected bands is the following: 1282 cm^{-1} corresponds to the combination frequency of ν(C-C) + ν(C–CH_3); 1360 cm^{-1} to symmetric deformation δ(CH_3), while 1425 cm^{-1} corresponds to the combination of ν(C=O) + δ(C–H) [23].The characteristic bands at 1574 and 1535 cm^{-1} correspond to intermediate acetylacetonate complexes [24].

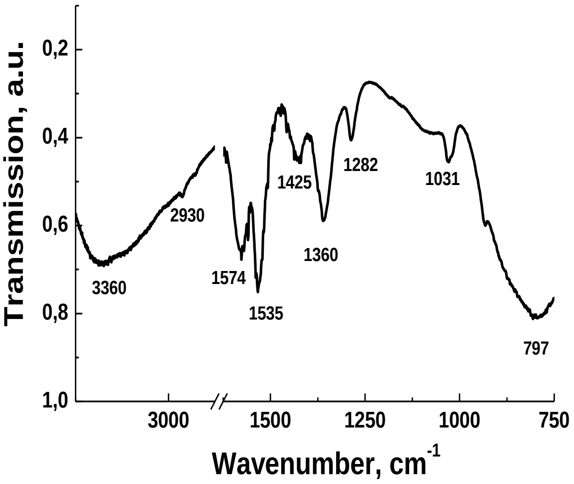


Fig. 1. IR spectrum of the powder sample subjected to stepwise thermal treatment up to 120°C and then dried at this temperature for 30 min. Precursor from solution $Ti(OPr)_4$: acetylacetone :isopropanol water in molar ratios 1:1:50:1.

3.2. XRD and XPS studies

Figs. 2 and 3 present XRD **s**pectra of TiO_2 films from solution I, obtained at different temperatures of drying. The films, obtained after drying of every coating at 120°C (method A), contain pure anatase phase (Fig 2a). The method B also leads to the growth of pure anatase crystallites (Fig2b). In the films heated by method C anatase is the main phase; small amounts of brookite phase and traces of nonstoichiometric Ti^{3+} (Ti_4O_7) are registered as well.(Fig 2c)**.** The addition of PEG does not affect significantly the crystalline phase composition (Fig 3). Therefore, the final phase composition depends on the temperature of drying of every layer. The average size of crystallites is about 25 nm for all films**.** It could be proposed that during the heating at low temperatures (up to 300°C) after every layer deposition a thicker film is formed due to the incomplete destruction of complexes. When every layer was annealed at 500°C (method C), a full decomposition of the acetylacetonate complex with titanium is realized. Madarasz et al. [25] have carried out evolved gas analysis of titanium oxo-acetylacetonate complexes and have proven that the organic residues are burned out totally below 500°C. As a result a thinner film is formed when method C is applied. Some authors have established that the concentration of Na in titania films decreases with increasing of the film thickness [26, 27, 28].

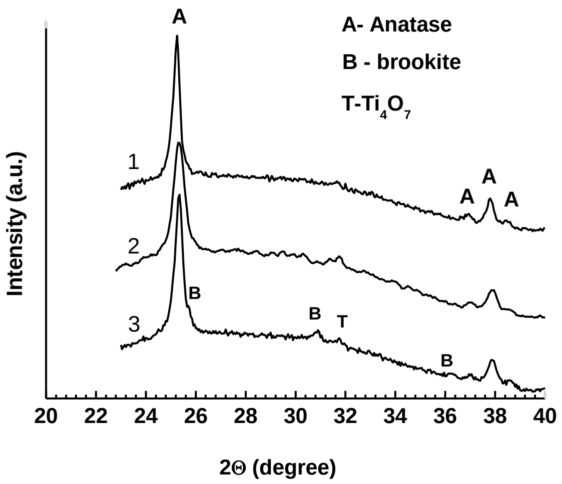


Fig. 2. XRD spectra of TiO_2 films obtained from solution I (without polymer). Every coating was dried at 120°C (1), 300°C (2) and 500°C (3) for 15 min. After the forth drying, a final heating at 500°C is applied.

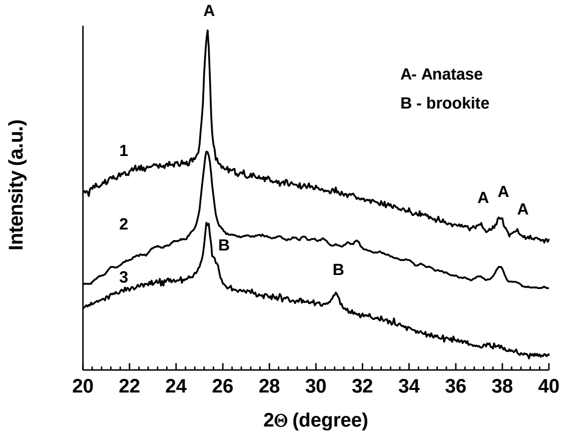


Fig. 3. XRD spectra of TiO_2 films obtained from solution II (with polymer) Every coating is heated at 120°C (1), 300°C (2) and 500°C (3) for 15 min. After the forth drying, a final heating at 500°C is applied.

This supposition has been proven by XPS analysis of the films, deposited from solutions with and without PEG and heated by different methods (Fig. 4). The peak positions for lines Ti $2p_{3/2}$ and O 1s (458 eV and 529 eV) registered by X-ray photoelectron spectroscopy agree well with the literature values for titania. XPS peaks for Na are observed in the spectra of TiO_2 films, thus implying the occurrence of some chemical reactions on the interface between the films and glass substrate, and migration of sodium from the glass substrate into the films. As was proven from XPS analysis of the chemical composition, the temperature of thermal treatment influences the Na diffusion from the substrate. For the samples obtained by methods A and B, the sodium concentration is about 7 at%, irrespective on the type of precursor solution (Fig. 4a) registered by X-ray photoelectron spectroscopy.

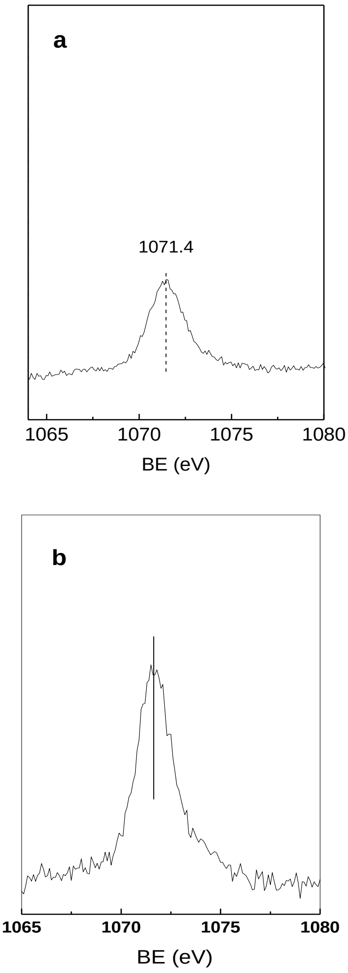


Fig. 4. Na 1s photoelectron spectrum of the surface of TiO_2 films obtained from solution without polymer. Every coating is heated at 300°C (a) and 500°C (b)

In the samples obtained by method C the content of Na is higher - 11 at % for the films obtained from solution I and 11.5 at % for the films obtained from solution II (Fig 4b).

It has been recognized that the interaction of sodium oxide from soda glass substrate with the TiO_2 films produces a brookite phase [9, 14-16]. Probably in our case the high content of Na in the films, obtained by method C regardless the heating rate promotes the formation of a brookite phase. This result is in agreement with the XRD data. Recent research of Li Y. et al. [29], who have obtained brookite using aged wet gels reveals that the sodium diffusion is not the only factor that can affect the brookite phase formation.

3.3. Investigation of the morphology by SEM

The SEM photographs of TiO_2 films, obtained from solutions I and II and treated by different methods, are shown on Figs 5-7.

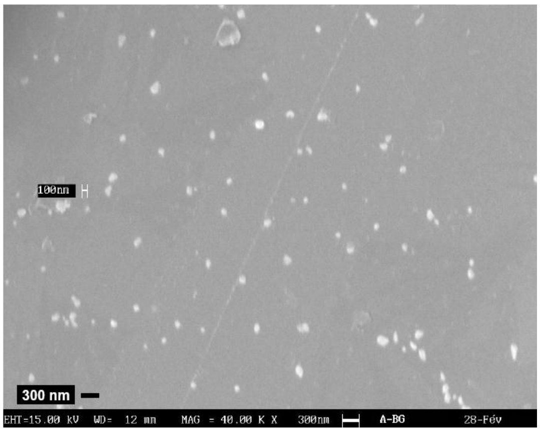
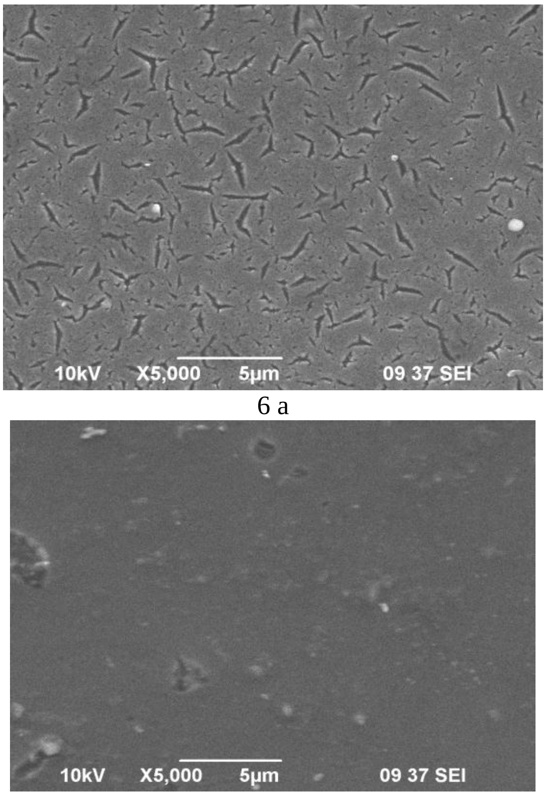


Fig. 5 SEM image of TiO_2 films from solution of $(TiOPr)_4$:AcAc : isopropanol: H_2O = 1:1:50:1 with 1wt% PEG400 and treated at 120^{o}C and finally at 500^{o}C (method A)



6 a

6 b

Fig. 6. SEM image of TiO_2 films from solution of $(TiOPr)_4$:AcAc:isopropanol:H_2O = 1:1:50:1. Every layer is treated at 300^o (a) and 500^{o}C (b)

The drying of every layer (methods A and B) affects the films morphology in different manner depending on the solution composition (the presence of polymer additive-polyethylene glycol). When method A is applied the PEG addition promotes the formation of a smoother film surface (Fig 5), while by using a solution without polymer (solution I) is impossible to deposit a continuous film. The increase of drying temperature (300^{o}C, method B) results in a better film morphology with very small cracks (Fig. 6a). Method C leads to the formation of a smooth nonporous film surface (Fig 6-b). Figure 7 shows that the film deposited from a polymer containing solution (solution II) and treated by method C is slightly porous due to the presence of PEG additive.

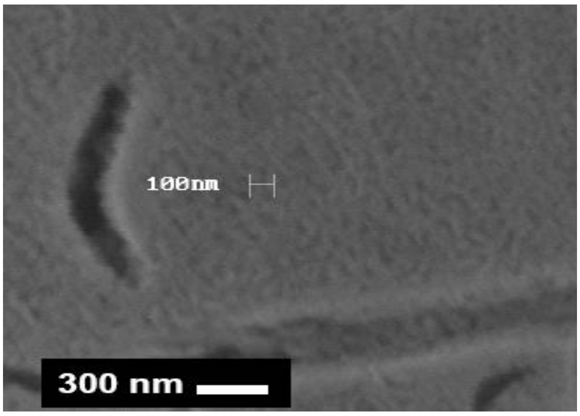


Fig. 7 SEM image of TiO_2 films from solution $(TiOPr)_4$:AcAc:isopropanol:H_2O = 1:1:50:1 with 1wt% PEG400 and treated at 500^{o}C (method C).

According to the studies of Guo et. al. [30], polyethyleneglycol decomposes completely below 400^{o}C. Consequently the polymer fully decomposes, under thermal regime C, volatilizes and causes the formation of pores.

3.4. Optical properties

Reflectance spectra of the samples obtained by methods A, B and C are shown in Fig. 8. The reflectance peaks in the UV region become more prominent with increasing of the temperature of drying which is accompanied with the films crystallization.

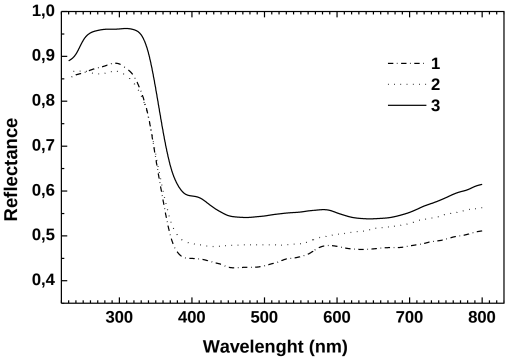


Fig. 8. Optical reflectance spectra of TiO_2 films from solution $(TiOPr)_4$:AcAc:isopropanol:H_2O = 1:1:50:1 and treated by methods A, B and C – curves 1, 2 and 3, respectively.

The broad and not well distinct band in the UV region could be attributed to the ligand metal charge transfer (LMCT) from the oxygen to the free orbital of Ti^{4+}.This peak can be decomposed into two Gaussians with maxima at 260 and 320 nm, respectively**.** The band at 320 nm is assigned to the octahedral coordinated Ti^{4+} and the band at 260 nm is attributed to the hydrated tetrahedral coordinated titanium [31]. The optical reflectance spectra reveal that the drying temperature affects the intensity of broad band in the UV region. The highest peak intensity is registered for the samples, obtained by method C and the maximum band edge value is observed for the same samples. This phenomenon could be explained with the crystallization of films. [32, 33].The spectra of films, obtained by drying at 120 and 300°C (methods A and B) containing relatively small crystallites, show a pseudo blue shift. It is known that the blue shift is caused by quantum size effects that are observed in semiconductors as the particle size decreases.

The band gap energy E_g of titania films is estimated by the following equation:

$$\alpha=(h.\nu - E_g)^{1/2} \qquad (1)$$

where α is the absorption coefficient, h is the Plank's constant, and ν is the frequency of incident photon. According to Eq.(1) the band gap energies of the titania films are 3.19 eV(method A), 3.11 eV (method B) and 3.04 eV (method C). Madhusadan et. al. [34] have reported band gap energies of nanosized TiO_2 particles in the range 3.03-3.17 eV which is close to our results. Jimenez-Gonzalez et. al. [35] have revealed the same tendency of decreasing band gap energy of TiO_2 sol-gel films with increasing of treatment temperatures. Similar relationship is observed by Kang et. al. [36] for sol gel ZnO films.

Fig. 9 presents the UV-VIS spectra of TiO_2 films, obtained by heating methods A, B and C.

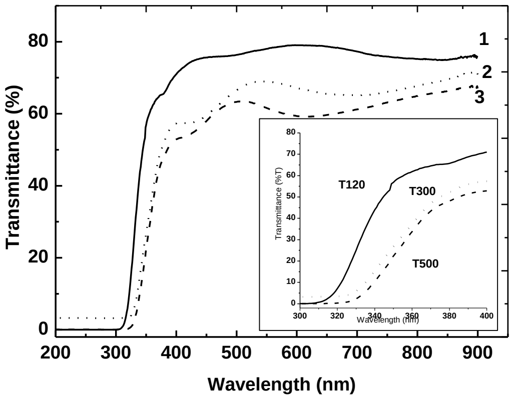


Fig. 9. UV -VIS spectra of TiO_2 films obtained by the sol gel method. Every coating is dried at 120 (1) 300 (2) and 500°C (3) (method

It is seen that the increase in drying temperature of the films leads to decrease in transmittance, due to the presence of non stoichiometric phase (Ti_4O_7) in the films, heated at 300 and 500 °C.

4. Conclusions

Nanosize TiO_2 thin films are prepared using the sol gel technique. The influence of the thermal treatment on the phase composition and optical properties of the films is investigated. It is established that the phase composition of the obtained films, depends on the drying temperature. At low drying temperatures (120-300°C), a pure anatase phase is registered. The films dried at higher temperatures consist of a mixture of anatase and brookite phases. The existence of brookite phase is attributed to the enhancement of sodium content in the films, due to the interaction of films and glass substrate.

The films obtained from polymer free solution and dried at low temperatures (up to 300°C) have visible cracks on the surface, while heating of every layer at 500°C results in homogeneous and crack free morphology of the films obtained from both types of solutions. The addition of polyethylene glycol leads to the formation of small pores in the films.

The reflectance and transmittance of the films are also affected by the drying temperature. The increase of drying temperature leads to a decrease of the film transmittance due to the presence of non stoichiometric phase (Ti_4O_7). The small dimensions of crystallites (25 nm) results in a "blue shift" of the optical spectra. Quantitatively, the band gaps for the samples dried at 120, 300 and 500°C amount to 3.19, 3.11 and 3.0 4 eV, respectively.

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