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Influence of calcination temperature on optical and structural properties of TiO_2 thin films prepared by means of sol-gel and spin coating

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Abstract. In this study, ceramic TiO_2 thin films were prepared on glass substrates using sol-gel and spin-coating methods from the TNBT/AcOH/EtOH/H2O solution. The obtained coatings were subjected to drying at room temperature and were then calcined in the air at different temperatures in a range of 400–600°C in order to obtain clean TiO_2 layers. The surface morphology and chemical composition were characterized with the use of a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDX). Research has shown the presence of elements in the TiO_2 and the influence of temperatures on layer thickness. Analysis of optical properties and energy gap width of the prepared coatings was determined by means of spectra analysis of absorbance as a function of radiation energy obtained with the use of the UV-VIS spectrophotometer. The obtained spectra of the layers are characterized by a shift of absorption lines towards the visible light wavelengths and the obtained values of band gaps decrease as the calcination temperature rises. The obtained and developed results of TiO_2 thin films testify to the wide application possibilities of the layers in elements which use photocatalytic processes such as self-cleaning surfaces, solar cells, pollution removing membranes and optoelectronic components.

Key words: TiO_2 thin films, spin coating, optical properties, structural properties, calcination, sol-gel, titanium dioxide.

1. Introduction

The significant development of nanotechnology in recent years has been related to the production of oxide nanomaterials such as nanoparticles [1, 2], nanotubes [3], nanofibers [4–6], nanorods [7, 8] and nanolayers [9], which possess physical and chemical properties unprecedented among conventional materials. Simple materials, such as Al_2O_3, TiO_2, SiO_2, ZnO and Bi_2O_3 [10–16], are of particular interest to scientists, due to their worldwide availability and ease of application.

Titanium dioxide has been one of the most commonly studied and used oxides for more than two decades now. High interest on the part of both industry and science, which is enjoyed by TiO_2, is due to the multitude of applications in a variety of fields, e.g. cosmetic, construction, medical, electrical or chemical ones. In scientific research, its popularity is due to to its very good catalytic properties, relatively low price, high physical and chemical stability and non-toxic nature [17]. It is currently considered one of the most interesting photochemical materials [18–20]. In nature, titanium dioxide occurs in the form of three polymorphic minerals, including the most common one, tetragonal anatase, rutile and rather rare rhombic brucite. TiO_2 is an n-type semiconductor and has a large energy difference between the valence and conduction bands. For each of the polymorphic types, the value of the band gap is different and it stands at 3.32 eV for anatase, 3.03 eV for rutile and 2.96 eV for brucite, respectively [21]. An important and often used feature of TiO_2 is its high refractive index, which varies from 3.8 for rutile to 2.5–3.0 for anatase. Thanks to all of its properties, TiO_2 nanostructures can be used in various industries as self-cleaning layers or corrosion inhibitors, solar cells, pollution removing membranes [22, 23] as well as optical and optoelectronic components [24].

Thin films of titanium dioxide are one of the most interesting structures in terms of optical properties. It is important to choose the constituting method of the coating because it has a significant influence on its properties. There are various methods of applying thin layers on pre-prepared substrates. They include sol-gel, chemical vapor deposition (CVD) [25], electron beam evaporation and cathode sputtering [26]. The sol-gel method, associated with a series of chemical reactions occurring in a sol liquid, which through slow dehydration turns into a semi-solid gel, combined with spin coating, has found its greatest use in obtaining thin films. The reason for this is the easy application of the coating on large surfaces, the low cost of gel production and the control of the homogeneity of the structure of the obtained layer by selecting appropriate process parameters (solution viscosity, rotation speed, calcination temperature) and solution chemical composition [18, 24, 29–32].

In this paper, the results of studies on the effect of calcination temperature on optical properties for TiO_2 thin films obtained by combining two methods: sol-gel and vortex deposition on laboratory glass slide are presented. The studies of morphology and chemical composition of the obtained coatings were based on microscopic examination (SEM) and X-ray analysis and microanalysis (EDX). The influence of the calcination conditions on the optical properties of the layers obtained

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was determined on the basis of the absorbance spectrum as a function of the radiation wavelength obtained using a UV-VIS spectrophotometer. In addition, based on the optical spectra, the values of energy gaps produced by thin TiO_2 ceramic layers were calculated.

2. Materials and methodology

2.1. Materials. In order to prepare the spinning solution, the following were used: tetra N-butyl titanate (TNBT, 97%), ethanol (EtOH, 99.8%), acetic acid (AcOH, 99.8%) and purified water. All reagents were supplied by Sigma-Aldrich.

2.2. Methodology. In the first step of sol preparation, a solution of tetra N-butyl titanate and acetic acid was prepared by adding 2 ml of the substrates to the tube, which was then stirred using a magnetic stirrer for 30 minutes. At the same time, 1.5 ml of demineralized water and 10 ml of ethanol were added to the second tube, which was subjected to stirring under the same conditions as the first one. After this time, the solutions were combined and left for stirring for 1 hour until a clear mixture was obtained. TiO_2 layers were deposited on previously prepared glass substrates, which were microscope slides bathed in ethanol and dried. Constant parameters were used during the coating application process: rotation speed of 3000 bpm and rotation time of 30 s. Directly after the samples were produced, they were left to dry at room temperature and then calcined in a tube furnace (Czylok PRC75) at the following temperatures: 400°C, 500°C and 600°C, with a heating rate of 10°C/min for 2 hours.

In order to analyze the morphology and chemical composition of the obtained coatings, a scanning electron microscope (Zeiss Supra 35) with the energy dispersive X-ray spectrometer (Trident XM4) was used. In addition, the optical properties of the obtained materials were analyzed using the Thermo Scientific UV / VIS spectrophotometer (Evolution 220). The wavelength used was in the range of between 200 and 600 nm. Energy band gaps of the layers produced were determined using the method previously described by the authors [33, 34, 36].

3. Results

3.1. Analysis of structure, morphology and chemical composition. The structure and morphology of TiO_2 sol-gel coatings applied to the glass substrate were analyzed by means of scanning electron microscopy and atomic force microscopy. Figure 1 shows the surface topography of the thin oxide layers observed with the use of atomic force microscopy. The results obtained show the difference between the individual morphologies of the samples tested. For a non-calcined sample (Fig. 1a), a smooth surface of amorphous structure is observed. It takes the shape of the substrate. For samples calcined at 400°C and 500°C, the stalks of sharp-tipped TiO_2 crystals are visible. On the surface of the coating calcined at 600°C there are numerous

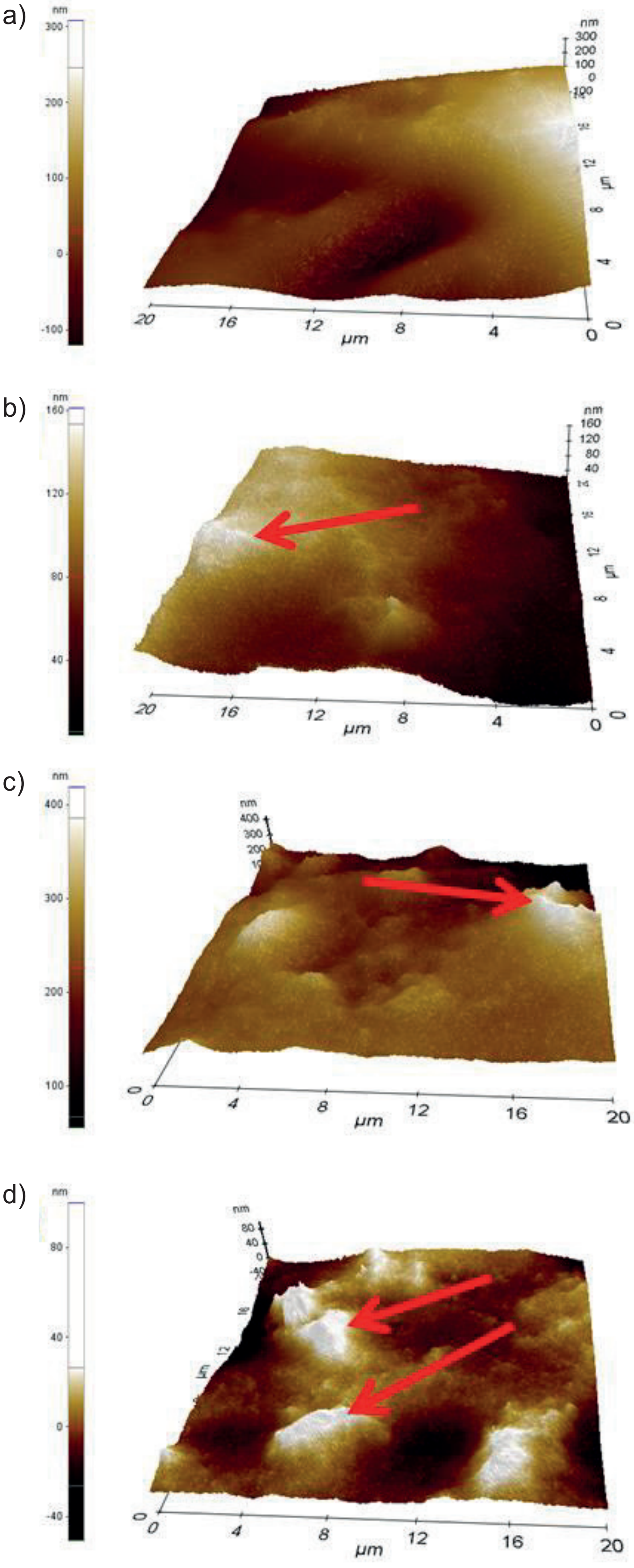

Fig. 1. Images of surface topography obtained from the atomic force microscope: a) pre-calcined layer b), c), d) layers calcined successively at 400°C, 500°C and 600°C

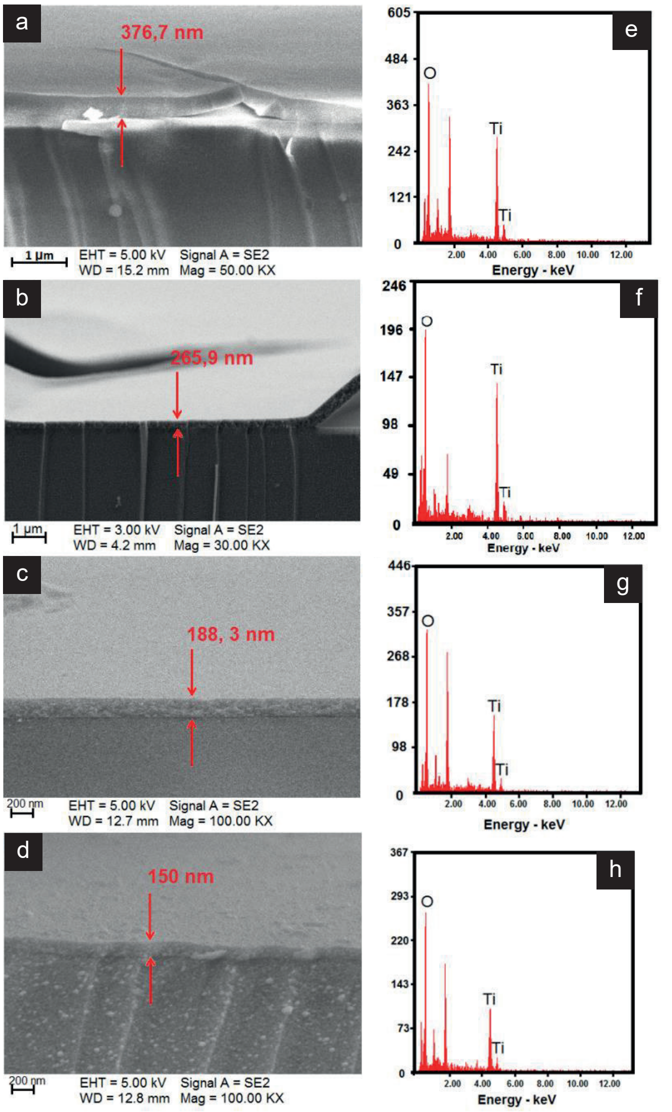

Fig. 2. SEM image of the TiO2 thin films studied: a) pre-calcined layer b, c, d) layers calcined successively at 400°C, 500°C and 600°C, and structural and chemical composition analysis: e) EDX spectrum of pre-calcined layer f), g), h) EDX spectra of layers calcined successively at 400°C, 500°C and 600°C

coniferous crystallites of similar dimensions. This results in highest surface roughness.

Figure 2a shows a layer of TiO_2 obtained from a solution formed by a mixture of titanium (IV) tetrabutanol, acetic acid, ethyl alcohol and demineralized water, not calcined. The layer has a homogeneous structure and thickness of up to 360 nm. Visible cracks and damage to the coatings in Fig. 2a–d were caused by sample breaking to accurately measure the thickness of the obtained TiO_2 layers. The titanium dioxide layer calcined at 400°C, made from a solution with a percentage of substrates identical to that of pre-heat layers, has a smaller thickness of about 260 nm. The downward trend in thickness values is also observed in the layers obtained with the same parameters and solution concentration as the coatings shown in Fig. 2a–b but calcined at temperatures of 500°C and 600°C, where the thickness was approximately 180nm and 150 nm. Thickness measurements were made in 5 places in order to obtain average values (Table 1). The reason for changing the thickness of the coatings can be to reduce the amount of water molecules in the structure.

Table 1
Thickness measurements

	pre-calcined [nm]	calcined at 400°C [nm]	calcined at 500°C [nm]	calcined at 600°C [nm]
1	371.5	258.3	184.3	147.8
2	381.9	271.2	180.7	154.1
3	378.5	263	191.2	150.4
4	373.9	264.1	187	148.8
5	376.7	274.9	198.3	146.9
$\bar{x}$	376.5	266.3	188.3	149.6

In order to analyze the chemical composition of the TiO_2 thin films produced, research was carried out using the X-ray EDX spectrometer. The obtained EDX spectrum from the areas presented in Fig. 2a–d showed that the layers obtained from the solution of 2 ml TNBT doped with acetic acid, ethanol and purified water corresponded to the chemical and stoichiometric composition of the TiO_2 compound – this is demonstrated by oxygen and titanium peaks, while the remaining peaks are derived from the substrate material on which the coating was applied (Fig. 2e–h).

3.2. Optical properties analysis. UV-VIS spectra were recorded for the pre-calcined TiO_2 layer and for layers calcined at 400°C, 500°C and 600°C. This is shown in Fig. 3 as absorbance spectra as a function of wavelength. All of the layers are characterized by high absorption in the ultraviolet region of wavelength and its decrease at the range close to visible light. This is related to the transition of the electron from the valence band to the conduction band and formation of the pair of electron (e^-) and hole (h^+). As the calcining temperature increases, the tendency of the absorption line to move towards the VIS wavelength with higher energy can be observed. The UV-VIS spectrum for a titanium dioxide sample calcined at 600°C is characterized by a higher amplitude of wave interference [35] in the range of 200–350nm, and maximum absorption is in the wavelength of 246 nm. Most likely, this is due to a lower layer thickness in comparison to non-calcined samples and samples calcined at 400°C and 500°C as well as the influence of smaller crystallites and the appearance of rutile phase. The worst absorption, in the range of 352–600 nm, is manifested by a non-calcined TiO_2 layer which is influenced by the presence of water particles and the amorphous titanium dioxide phase. The obtained spectral characteristics of the samples calcined at 400°C, 500°C and 600°C show a strong increase of absorp-

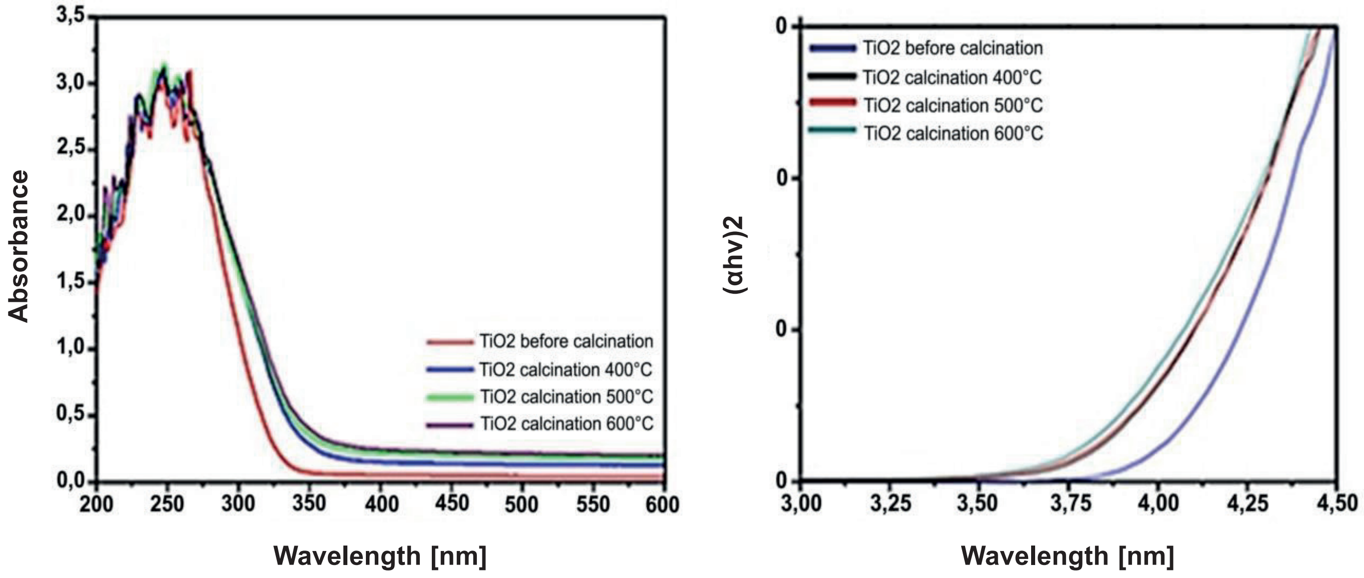

Fig. 3. UV-VIS spectra of absorbance as a function of radiation length

tion from about 2.5 to 3 times in comparison to spectra of the non-calcined layer, with the edges corresponding to 350 nm wavelengths. This fact demonstrates increased photocatalytic activity, which creates the application potential of the TiO_2 layers produced by with the use of sol-gel and spin coating. Based on the analyzed characteristics, it can be seen that the increase in the tempering temperature has an influence on the optical properties and absorption in the UV-VIS range of titanium dioxide.

In order to determine energy gaps in the materials generated, the analysis was based on the method presented in [31, 32]. The dependence of the absorption coefficient of the investigated material as a function of radiation is taken as:

$$\mathrm{A}h\nu = \mathrm{A}\left(h\nu - \mathrm{E}_g\right)^{\rho}. \qquad (1)$$

Where α is the absorption coefficient, h is the Planck constant, ν is the frequency of the incident radiation, A is the constant depending on the probability of electron passing and E_g is the energy gap of the material studied. Depending on the type of electron transitions type between valence and conduction bands, the factor ρ may be given as 1/2 or 3/2 for sequentially accessible and inaccessible straight transitions, and 2 or 3 for oblique allowed and forbidden transitions [36]. Due to the results obtained for the calculation, the value of 1/2 has been assumed.

In order to find a dependence between the α coefficient and radiation wavelength, spectra of the generated titanium dioxide layers that were pre-calcined and heat-treated at temperatures of 400°C, 500°C and 600°C as well as spectra registered with the UV-VIS spectrophotometer were used. Energy gap of the pre-calcined TiO_2 layer was 4.15eV and energy gaps of ceramic thin layers of titanium dioxide calcined at 400°C, 500°C and 600°C were 4.01 eV, 3.91 eV and 3.86 eV, respectively. These values are approximately the same as those described in [37–39]. The probable reason for the increase in the energy gap, as compared with the values for the anatase ($E_g = 3.32$ eV) and rutile ($E_g = 3.03$ eV), is the layer thickness of up to 376nm for the non-calcined layer and 150nm for the layer calcined at 600°C along with the layer density and grain size [37–39]. On this basis, it can be inferred that the increase in the temperature of calcining affects reduction of the energy gap. The results obtained indicate the wide application potential of TiO_2 thin films obtained by means of sol-gel and spin coating in photocatalytic processes.

4. Conclusions

The TiO_2 sol-gel layers obtained from the TNBT/AcOH/EtOH/H_2O solution, applied by the spin coating technique, were examined in terms of structure, morphology, chemical composition, optical and photocatalytic properties. The physical properties of titanium dioxide thin layers closely depend on calcination temperature. The greater it is, the better the properties are. It has also been observed that layers processed at higher temperatures have a finer structure and smaller thickness of about 150 nm. The obtained and calcined layers are also characterized by the shift of absorption lines towards the wavelength of visible light and the reduction of energy gap. The results obtained demonstrate the wide applicability of the layers in photocatalytic elements such as self-cleaning surfaces, solar cells, pollution removing membranes as well as optical and optoelectronic components.

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