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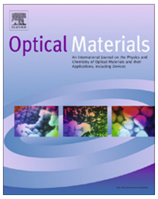

Porous titania films fabricated via sol gel rout – Optical and AFM characterization

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ABSTRACT

Mesoporous titania films of low refractive index ~1.72 and thickness within the range of 57–96 nm were fabricated via sol–gel rout and dip-coating technique on a soda–lime glass substrate. Tetrabutylorthotitanate $Ti(OBu)_4$ was used as a titania precursor. High porosity and consequently low refractive index were achieved using the polyethylene glycol (PEG 1100) as a template. Based on transmittance, using Tauc's relations, the optical energy band gaps and the Urbach energy were determined. The research shows that in the fabricated titania films there are two types of optical energy band gaps, connected with direct and indirect electron transitions and brought about by the presence of amorphous and crystalline phase respectively. Based on the quantum size effect, the diameters of nanocrystals versus film thickness were determined. AFM studies of the titania films have demonstrated that there are changes of surface morphology taking place with the change of thickness. We have demonstrated that the surface morphology of titania films has influence on wettability.

1. Introduction

Thin oxide layers are commonly applied as coatings in various optical and optoelectronic structures. Through the application of oxide layers we can improve the mechanical properties of the surface of a structure or to modify its optical, electrical or chemical properties. One of the most commonly applied oxide material is titanium dioxide TiO_2, which is a wide energy band gap *n*-type semiconductor. Titanium dioxide films are very versatile from the view point of its potential applications such as antireflection [1,2] or high reflection coatings [3,4], photocatalyst [1,5–7], self-cleaning glasses [2,5,8], electrochromic films [9], solar cell [10,11], transparent conductors [12], and gas sensitive films [13]. Many different technological procedures for the fabrication of thin films of titania have been reported, such as: *e*-beam evaporation [14], RF sputtering [4], ultrasonic spray pyrolysis [15], chemical vapor deposition CVD [6], metal organic chemical vapor deposition MOCVD [16], pulsed laser deposition PLD [7], and sol–gel method [1–3,5,8,9,17,18]. In contrast to the other, the sol–gel method is very efficient and does not require expensive technological equipment. The sol–gel method has advantages, such as low temperature processing, easy coating of large area, and being suitable for preparation of porous films and homogeneous multicomponent oxide films. The most important advantage of sol–gel over other coating methods is the ability to tailor the microstructure of deposited films, so using the sol–gel method the titania films of controlled structure can be produced. These properties of sol–gel method we used in the fabrication of the mesoporous titania films presented here. The mesoporous titania films of low refractive index (~1.72) we have fabricated using tetrabutylorthotitanate $Ti(OBu)_4$ as a titania precursor. High porosity and consequently low refractive index we have achieved using the polyethylene glycol (PEG 1100) as a template.

The main goal of our research study was to determine possible correlations between the thickness of the mesoporous titania film and the surface morphology, optical properties as well as nanocrystal diameters and wettability.

The paper is organized as follows. Section 2 presents the basis of sol–gel method, the procedure of sol preparation and the

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procedure of titania films fabrication. Section 3 is devoted to the instruments and measurement methods used in our investigation study. The obtained results and their discussion are presented in Section 4.

2. Technology

2.1. Sol preparation

The processes of sol–gel technology are described in detail in a comprehensive book; "*Sol–Gel Science*" by Brinker and Scherer [17]. The chemical compounds used to preparation of a sol were: tetrabutylorthotitanate ($Ti(OC_4H_9)_4$ ($Ti(OBu)_4$, purchased from Aldrich Chem Co.), water H_2O, nonequeous ethyl alkohol C_2H_5OH (EtOH, purchased from POCH, Poland), diethanolamine $NH(CH_2CH_2OH)_2$ (DEA, purchased from Aldrich Chem Co.) and polyethylene glycol $HOCH_2(CH_2OCH_2)_nCH_2OH$, molecular weight 1100 (PEG_{1100}, purchased from Aldrich Chem. Co). The DEA bring about restrain the rapid hydrolysis of $Ti(OBu)_4$. The procedure of a sol preparation used in this study were similar to reported in Ref. [19]. At the beginning 3.5 g of DEA was dissolved in 20 ml of EtOH, then to these solution were added next 20 ml of EtOH and 10.7 ml of Ti $(OBu)_4$. Obtained solution was ultrasonically stirred in a closed glass vessel at temperature of 40 °C. After 60 min of stirring to the solution was added drop by drop of 17 ml of EtOH (96%) and after next 30 min 3 g of PEG_{1100} was incorporated into the solution. Then the solution was still stirred ultrasonically for 30 min.

2.2. Films fabrication

Presented in this paper titania films, were deposited on ultra clean soda–lime glass substrates (microscope slides, Menzel-Glaser) using dip-coating technique. The procedure for preparing ultra clean substrate we were described in our previous work [23]. For a general case, the dependence of final film thickness d on the substrate withdrawal speed v can be expressed in the following form [18]:

$$d = a_0(\xi v)^{\chi} + d_0 \tag{1}$$

The proportionality index a_0 depends on sol viscosity, its density and on the surface tension on the surface sol-environment, whereas $\xi = (1\ \mathrm{cm}^{-1}\ \mathrm{min})^{-\chi}$ is a unit scaling factor of the dimension of speed inverse. The exponent χ is referred to as slope index, and its value for Newtonian liquid is within the range from 0.50 to 0.66. Detailed expressions on the dependence of film thickness on substrate withdrawal speed can be found in Refs [17,20]. For a given technological process, the proportionality index a_0 and slop index χ can be determined empirically. The fabricated structures were annealed at the temperature of 500 °C for 1 h. The annealing temperature is sufficient to remove the residual organic matter from titania films, DEA and PEG. DEA is completely eliminated at 500 °C [21] and PEG is eliminated below 500 °C [22].

TiO_2 exists in three main phases: anatase, brookite and rutile. As a bulk material the most stable is rutile. However, when TiO_2 is produced with solution-phase methods, then principally anatase is obtained [21]. With a very small size of nanoparticles, their surface energy accounts for a considerable part of the total energy, and the surface energy of anatase is lower than that of rutile or brookite [22]. We assume that in the films presented here, which were annealed at the temperature of 500 °C, only anatase [24] and the amorphous phase are present. Rutile shows up in titania dioxide films annealed above 600 °C [24,25].

3. Measurement methods and instrumentation

The thicknesses and refractive indices of the manufactured titania films were measured using monochromatic ellipsometer Sentech SE400 ($\lambda = 632.8$ nm, Sentech, model 2003, Germany). The measured refractive indices were applied to determination the porosity of titania films. For this purpose, the Lorentz–Lorenz equation was applied:

$$\frac{n^2-1}{n^2+2} = \left(1 - \frac{P}{100\%}\right)\frac{n_d^2-1}{n_d^2+2} \tag{2}$$

where n_d is the refractive index of anatase ≈ 2.52.

Reflectance R and transmittance T as well as the absorption of glass substrate A_{gs} were measured with application of UV–vis spectrophotometer AvaSpec-ULS-TEC ($\lambda = 200–1100$ nm, Avantes), and light source AvaLight-DH-S-BAL ($\lambda = 200–2500$ nm, Avantes). The recorded transmittance spectra were used to determine the optical energy band gap E_g of the titania films, and then the quantities ΔE of blue shift of the energy band gap were used to determination of the nanocrystallites diameter D. The optical energy band gap were determined by analyzing the relationship between absorption coefficient α and photon energy hv using Tauc's relation [26]:

$$\alpha \cdot hv = B(hv - E_g)^r, \tag{3}$$

where B is a constant which does not depend on hv, and r is the power coefficient which value determines the type of optical transition. The power coefficient r takes the value 2 for an indirect allowed transition and the value 1/2 for a direct allowed transition. The linear dependence of $(\alpha \cdot hv)^{1/r}$ on photon energy and its extrapolation to $(\alpha \cdot hv)^{1/r} = 0$, give the values of E_g^{ind} ($r = 2$) or of E_g^{dir} ($r = 1/2$), respectively. The transmittance for the symmetrical structure TiO_2/glass/TiO_2 can be written in the approximated form as [18]:

$$T = (1-R)(1-A_{gs})(1-A)^2 \tag{4}$$

and the formula on absorption coefficient of titania is as follow [18]:

$$\alpha = -\frac{1}{2d_{eff}} \ln\frac{T}{(1-R)(1-A_{gs})}, \tag{5}$$

where $d_{eff} = (1-P)d$, and d is a film thickness.

The quantity ΔE of blue-shift of the energy band gap is connected with diameter D of nanocrystallites. For parabolic energy band near the band-gap, the average value of D may be estimated from the formula [27–29]:

$$\Delta E = \frac{2\pi^2\hbar^2}{m^* D^2} - \frac{0.893e^2}{\pi\varepsilon\varepsilon_0 D} - 0.248E^*_{Ry} \tag{6}$$

where $\hbar = 1.0545 \times 10^{-34}$ Js is the reduced Planck's constant, $m^* = m_e m_h/(m_e + m_h)$ is the reduced effective mass of the electron–hole pair, m_e is the effective mass of the electron, m_h is the effective mass of the hole, ε_0 is the permittivity of free space, ε is the dielectric constant of anatase TiO_2, $E^*_{Ry} = (m^*/(2\hbar^2)) \cdot (e^2/4\pi\varepsilon_0\varepsilon)^2$ is the effective Rydberg energy. In the calculations we have been taken into account the parameters as follow; effective masses of the electron $m_e = m_0 = 9.11 \times 10^{-31}$ kg and the hole $m_h = 0.65m_0$, dielectric constant of anatase $\varepsilon = 31$.

The surface morphology of the fabricated titania films were tested with the application of the atomic force microscope (AFM), Ntegra Prima (NT-MDT). The AFM experiments were performed with semi-contact mode AFM. In AFM measurements the HA_NC (NT-MDT) silicon cantilever with nominal curvature radius of a tip 10 nm and resonance frequency of 250 kHz was used. The AFM image analysis was carried out using commercial NOVA 1.0.26.1644 (NT-MTD) software procedures to determine Root-Mean-Square (RMS) parameter.