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Properties of Titanium Dioxide Thin Films, Fabricated by Gel Methods

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Titanium dioxide films obtained by gel method are investigated. Optical properties of the fabricated films, such as thickness, refractive index and thermo-optic coefficient were studied by the methods of integrated optics which use waveguide propagation of radiation along the film. The parameters of the films fabricated by sol-gel and gel methods were compared. It was established that the pores in the films made by gel method contain smaller amounts of water and therefore have higher density. Refractive index of gel films was determined by the resonant angle of the waveguide excitation, calculated using the optical waveguide dispersion equations and amounted to 2.1–2.4. This value is higher than in the case of using sol-gel technology for fabrication of thin films (1.5–1.8).

By the reflection and transmission spectra obtained using spectrophotometer, it was found that films produced under cetrain parameters of technological regime have anisotropic properties. It was established that the presence of anisotropy is due to the structure of the film in the form of a linear oligomer.

The structure and morphology of the gel films was studied by electron microscopy. It is shown that the resulting films have a porous structure that allows their doping with substances allowing to create elements of integrated optics, such as lasers, amplifiers, etc.

Key words and phrases: thin films, titanium dioxide (TiO_2), sol-gel and gel process, integrated optics, birefringence.

1. Introduction

Recently, researchers pay much attention to the optical properties of films based on titanium dioxide, such as temperature dependence effective refractive index and, in particular to their ability to birefringence. Titanium dioxide thin films can be formed by electron-beam evaporation onto fused silica substrates using serial bideposition (SBD). The SBD technique combines rapid substrate rotation and oblique-angle physical vapor deposition (PVD) to create optical coatings that are composed of nanostructured columns which exhibit large birefringence values in the plane of the substrate. In work [1, 2], post-deposition annealing was used to crystallize amorphous TiO_2 thin films formed by SBD to improve birefringence without significantly increasing optical absorption or scattering. Birefringent thin films were fabricated at deposition angles ranging from 60° to 75° and annealed in air at temperatures ranging from 200°C to 900°C to form anatase and rutile TiO_2. Changes in the optical properties, crystallinity, and nanostructure were characterized by ellipsometry, x-ray diffraction, atomic force microscopy, and scanning electron microscopy. It was found that optical anisotropy increases strongly upon formation of anatase, yielding in-plane birefringence values that doubled from 0.11 to 0.22 in the case of TiO_2 thin films deposited at 60° and annealed at 400°C. Raising the annealing temperature to 900°C to form rutile thin films increased the thin film birefringence further but also led to low optical transparency due to increased absorption and diffuse scattering.

Transmission electron microscopy observations confirm that the mesoporous titania-silica composite thin films have a hexagonally ordered pore array nanostructure. Ultraviolet-visible absorption spectra give the evidence that the TiO_2 nanocrystals as well as the four-coordinate Ti co-exist in the silica matrix. The semiconductor TiO_2 nanocrystals in the silica matrix have an obvious blue shift phenomenon of the absorption edge. As the average TiO_2 grain size increases from 2.2 to 5.1 nm, the

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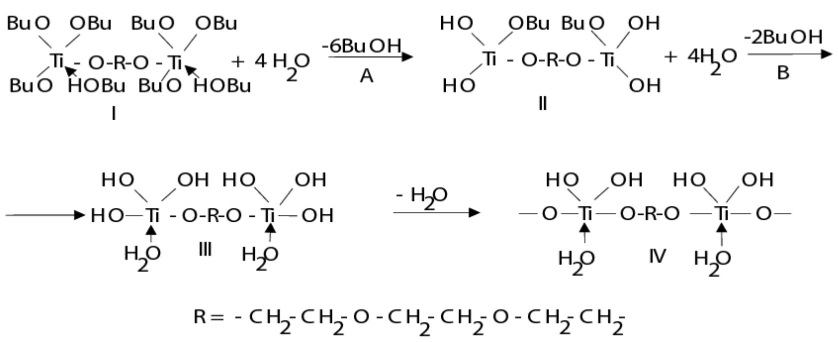
band gap of the TiO_2 nanocrystals in the mesoporous titania-silica composite thin films decreases from 3.9 to 3.45 eV [3, 4].

The obtained mesoporous titania-silica composite film exhibits a remarkable birefringence reflecting the highly anisotropic mesoporous structure and the high refractive index of titania that forms the pore wall. The Δn value estimated from the optical retardation and the film thickness is larger than 0.06, which cannot be achieved with the conventional mesoporous silica films with uniaxially aligned mesoporous structure even though the alignment of the pores in the films is perfect. These inorganic films with mesoscopic structural anisotropy will find many applications in the field of optics as phase plates with high thermal/chemical/mechanical stabilities [5, 10].

The optical properties of spin-coated titanium dioxide films have been tuned by introducing mesoscale pores into the inorganic matrix. Differently sized pores were templated using Pluronic triblock copolymers as surfactants in the sol-gel precursor solutions and adjusted by varying the process parameters, such as the polymer concentration, annealing temperature, and time. The change in refractive index observed for different mesoporous anatase films annealed at 350, 400, or 450°C directly correlates with changes in the pore size. Additionally, the index of refraction is influenced by the film thickness and the density of pores within the films. The band gap of these films is blue-shifted, presumably due to stress the introduction of pores exerts on the inorganic matrix.

The study adducting tetrabutoxytitanium (TBT) and ethylene glycol (EG), diethylene glycol (DEG) and triethylene glycol (TEG) has established that at an equivalent ratio of TBT: TEG linear adducts are formed, which, after appropriate heat treatment create anatase, the content of which is close to 100% [6, 7].

The film formation by the reaction occurred in TBT and compounds with TEG, gelling the solution, and the resulting compound TEG TBT-n-butanol and the subsequent transformation of the air during the annealing. The process of film formation of the adduct with TBT TEG (I) in a thin layer, excluding the polycondensation reaction can be represented by the following scheme:



In the fast step (A) of adduct (I) are removed (eliminated) 6 molecules of butanol and 4 water molecules align to form an adduct (II). In the slow step (B) to the adduct (II) are attached four water molecules and two molecules of butanol are eliminated. Adduct (III) is capable of forming a polymeric structure (IV) by condensation with elimination of water under normal conditions.

The aim of this work is to prepare TiO_2 thin films by gel method with the use of TBT and TEG as precursors and to study their optical properties.

2. Methods and Results

2.1. Fabricating of Thin Films

Thin films were prepared by deep coating method. The mixture of TBT and TEG (1:1) of different concentration in n-butyl alcohol was used.

Sodium glass plates ($75 \times 20 \times 1$ mm) were used as substrate. After deep coating procedure the samples were dried at room temperature for 30 min, then 1 h at 373 K and 4 h at 723 K.

The experimental samples of thin films were prepared using gel technology with parameters of a technological regime shown in Table 1.

Table 1

The parameters of a technological regime used for formation of thin films

Samples	1	2	3	4	5	6	7	8	9
Temperature of solution, K	296	296	298	283	296	296	283	296	283
Drying	+	+	+	+	–	–	–	–	–
Calcination temperature, K	723	723	723	723	753	753	753	873	873
Calcination time, h	8	8	8	8	6	6	6	2	2

The properties of the films were regulated by concentration of precursors in n-butyl alcohol, varying the components in the feed solution and speed of deep coating procedure.

Transmission and reflection spectra in the visible range were recorded on a Lambda 950 spectrophotometer (Perkin–Elmer) with a resolution of 1 nm. The reflectance spectrum was measured at an incident angle of 8 degrees with respect to the normal.

X-ray photoelectron spectra of the samples were obtained using UHV analysis module electron-ion spectroscopy platform based Nanofab 25. Further XPS spectra were obtained by irradiating X-ray source SPECS X-ray Source XR 50 with dual anode Al/Mg (1486.6 eV/1253.6 eV).

Micrographs of films were obtained by atomic force in the unit Integra. Scanning was performed in the tapping mode.

The structure of the film samples was examined by transmission electron microscopy of high resolution.

2.2. Investigation of Dependence of the Effective Refractive Index and the Film Thickness on the Parameters of Process Conditions and the Ambient Temperature

One of the promising methods for the study of the films is a waveguide-optical method [8, 9]. In this method, light propagates through the film, which has refractive index greater than the refractive index of the substrate. The dependence of the effective refractive index (ERI) for propagating waveguide modes (TE and TM), on the film thickness at a given wavelength was calculated using the dispersion equations that define this relationship, which had a view:

$$\frac{2\pi}{\lambda}h(T)\sqrt{n_2^2(T)-n_{\mathrm{eff\,TE}}^2(T)} = \arctan\left(\frac{\sqrt{n_{\mathrm{eff\,TE}}^2(T)-n_1^2(T)}}{\sqrt{n_2^2(T)-n_{\mathrm{eff\,TE}}^2(T)}}\right) + \\ + \arctan\left(\frac{\sqrt{n_{\mathrm{eff\,TE}}^2(T)-n_3^2(T)}}{\sqrt{n_2^2(T)-n_{\mathrm{eff\,TE}}^2(T)}}\right) + \pi(m-1),$$

$$\frac{2\pi}{\lambda}h(T)\sqrt{n_2^2(T)-n_{\mathrm{eff\,TM}}^2(T)} = \arctan\left(\frac{n_2^2(T)\cdot\sqrt{n_{\mathrm{eff\,TM}}^2(T)-n_1^2(T)}}{n_1^2\cdot\sqrt{n_2^2(T)-n_{\mathrm{eff\,TM}}^2(T)}}\right) + \\ + \arctan\left(\frac{n_2^2(T)\cdot\sqrt{n_{\mathrm{eff\,TM}}^2(T)-n_3^2(T)}}{n_3^2\cdot\sqrt{n_2^2(T)-n_{\mathrm{eff\,TM}}^2(T)}}\right) + \pi(m-1),$$

where λ — is the wavelength of the radiation source, n_{eff} — is the effective refractive index of the waveguide mode, n_1, n_2, n_3 — the refractive indexes of air, waveguide film and the substrate, m — number of waveguide mode.

Experimentally measuring the ERI for two propagating waveguide modes, e.g. TE_1 and TM_1 one can determine the thickness and refractive index of the film at a predetermined temperature. Besides, the described method can be used to determine the losses in the film. The measurements were carried out using the measuring system (Fig. 1), consisting of He-Ne laser as the source of radiation, an optical waveguide with an input and output prism coupler devices, the thermo-electrical module (TEM) as a heater, and a goniometer for measuring the angles of resonance excitation of the waveguide. Measurements were carried out [9] at temperatures ranging from 293 to 373 K.

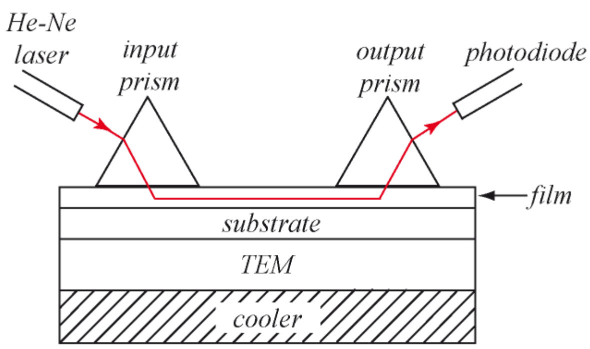
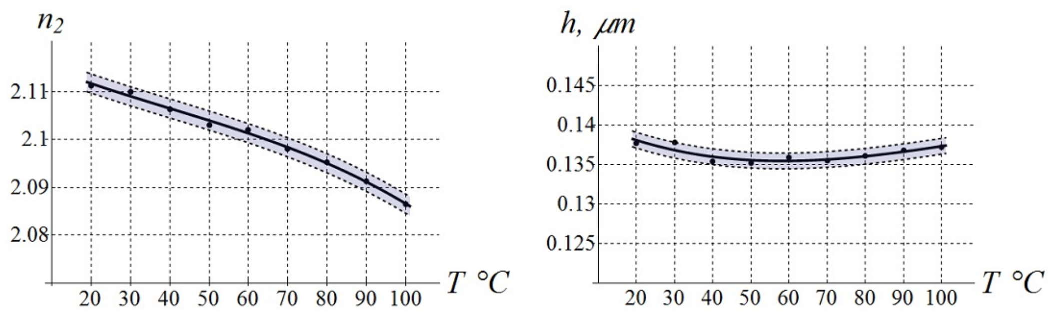


Figure 1. Optical scheme of the measuring system

The excitation of the waveguide was carried out on the TE_1 and TM_1-modes. ERI was calculated from the measured angles. Measurement accuracy of ERI was $2 \cdot 10^{-5}$, and is determined by the accuracy of the measurement of the angle of the resonance excitation of the waveguide through the prism coupler device.

Then, using the dispersion equation, the temperature dependences of the refractive index and the thickness of the film were calculated (Fig. 2a and 2b).



a b

Figure 2. The dependence of the refractive index (a) and film thickness (b) on the temperature

It can be seen that with increasing temperature within the considered range the film thickness changes insignificantly, and the refractive index of the film decreases with increasing temperature, that is, the film has a negative thermo-optical coefficient (TOC), the value of which was $\approx -3 \cdot 10^{-4}\,{}^{\circ}\mathrm{C}^{-1}$. This value is close to the TOC of the films prepared by the sol-gel method [9].

3. Investigation of Transmission and Reflection Spectra, Structure and Morphology of the Films

As the hydrolyzed product created in the film is an oligomer of a linear structure, there is the likelihood of anisotropy in these films. The degree of anisotropy depends on shape, size and mutual orientation of the crystallites. To explain the possibillity of anisotropic properties of the films the transmission and reflection spectra of these films were investigated.

The transmission and reflection spectra of films in visible range were obtained using the Lambda 950 spectrophotometer (Perkin–Elmer) with the resolution of 1 nanometer. It was shown that films with small thickness (< 0.1 μm) (Fig. 3a) are isotropic. However with increasing thickness the films become anisotropic (Fig. 3b).

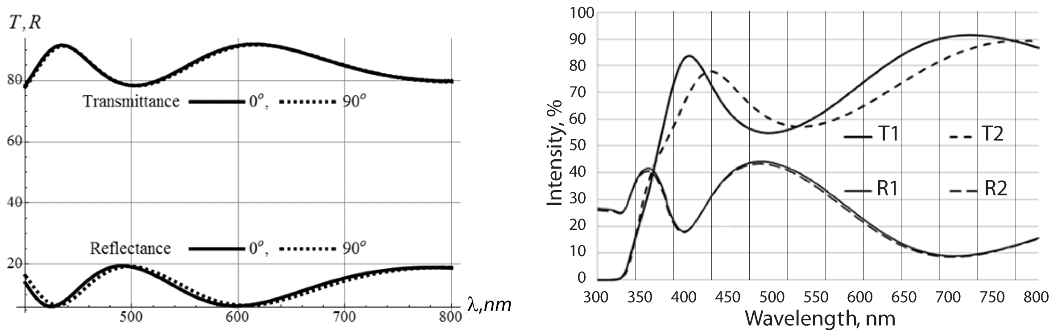


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Figure 3. The transmission and reflection spectra of films: (a) — film thickness 0.08 μm; (b) — film thickness 0.21 μm

Analyzing the above data one can conclude that TiO_2 films can have significant birefringence in all visible spectrum. The value of this birefringence is equal approximately 0.1. This value is comparable to the values for the known nonlinear optical materials, such as $LiNbO_3$, KDP, etc.

Structure and morphology of the films were investigated by transmission electron microscopy and scanning electron microscopy. If the samples are heated to 723 K and hold for 5 hours a crystalline film in anatase form is created. Crystal cell parameters were the following: $a = 3.7881$ Å, $c = 9.5227$ Å, volume $V = 136.63$ Å^3. Theoretical data had values: $a = 3.7845$ Å, $c = 9.5143$ Å, $V = 136.27$ Å^3. It can be seen that experimental and theoretical data are in good correspondence.

Fig. 4 is a micrograph of the film TiO_2. According to [2], such films were obtained from partially reduced titania where ordered light band assigned to the polycrystalline titania and bridges between the strips bright spots — to oxygen vacancies.

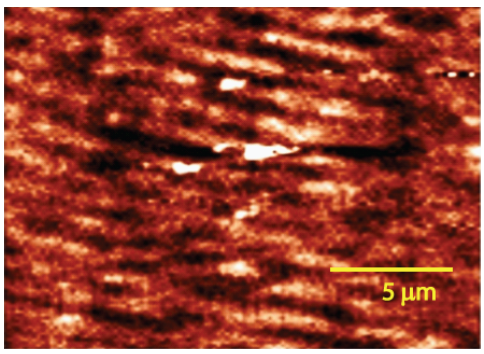

Figure 4. Micrograph of the surface of TiO_2 thin film

The photomicrograph of the same film of a three-dimensional mode (Fig. 5) showed that the surface topography of the film is composed of ridge-like protuberances and depressions therebetween. The nature of the surface of the film is similar to the lotus effect, when the existence of ordered bulges is the cause of manifestation of hydrophobic surface properties [4]. Water does not wet the surface and exists in the form of droplets.

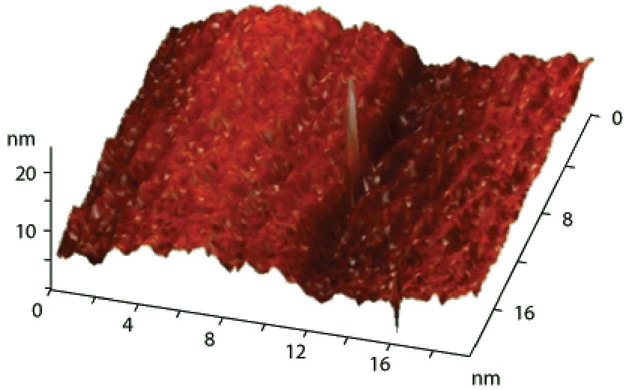

Figure 5. Micrograph of the surface of TiO_2 films of a 3D image

4. Conclusion

In this work homogeneous and transparent optical films of titanium dioxide were obtained by gel method. Manufactured films have a negative thermo-optic coefficient, the value of which is determined by the parameters of technological process, including changing the ratio of the components of the solution. The changing of the film thickness is less pronounced than in the case of the sol-gel method, which is caused by a smaller amount of water contained in the pores of the film. It shows that TiO_2-based film may have anisotropy, which can be used in many applications of integrated optics (IO). It is shown that the films have a porous structure that allows doping them with substances, allowing to create IO active elements such as lasers, amplifiers, etc.

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Свойства плёнок диоксида титана, изготовленных по гель-технологии

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Исследованы плёнки диоксида титана, полученные гель-методом. Проведено изучение оптических свойств изготовленных плёнок, таких как толщина, показатель преломления и термооптический коэффициент, с помощью методов интегральной оптики, использующих волноводное распространение излучения вдоль плёнки. Проведено сравнение параметров изготовленных плёнок золь-гель и гель методами. Установлено, что поры в плёнках, изготовленных гель-методом, содержат меньшее количество воды и поэтому обладают большей плотностью. Показатель преломления гель-плёнок был определён по резонансному углу возбуждения волновода, рассчитан с помощью дисперсионных уравнений оптического волновода и составил 2,1–2,4. Это значение выше, чем в случае золь-гель-технологии получения тонких плёнок (1,5–1,8).

По спектрам пропускания и отражения, полученных с помощью спектрофотометра, было установлено наличие анизотропии в плёнках, изготовленных при определённых параметрах технологического режима. Установлено, что наличие анизотропии связано со структурой плёнки в виде линейного олигомера.

Строение и морфология гель плёнок была исследована методами электронной микроскопии. Показано, что полученные плёнки имеют пористую структуру, что допускает легирование их веществами, позволяющими создавать элементы интегральной оптики, такие как лазеры, усилители и др.

Ключевые слова: тонкие плёнки, диоксид титана (TiO_2), золь-гель и гель технология, интегральная оптика, двулучепреломление.

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