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Optical Properties of TiO_2 Thin Films

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Abstract

Titanium dioxide thin films prepared by the gel process were investigated. Optical properties of the thin films were studied by the integrated optics method. Structure, morphology and the nature of the surface of TiO_2 thin films samples were studied by X-ray diffraction, electron microscopy, Fourier images and other techniques. It was shown that TiO_2-based film may have anisotropy, which can be used in many applications.

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Keywords: thin films; TiO_2; gel; process; integrated optics; birefringence.

1. Introduction

The titanium dioxide and its modified forms is of interest for its use in solar batteries [Gratzel (2003)] and its ability to generate active radicals under the action of ultraviolet radiation [Thompson and Yats jr. (2006)] which exhibit an oxidizing and bactericidal action [Miao et al. (2004)]. This is the basic photochemical methods of cleaning the air and water that are actively being developed and introduced in many countries. Titanium dioxide under UV irradiation can decompose water into molecular hydrogen and oxygen [Fujishima and Honda (1972)] and the modified (doped with various elements) TiO2 can exhibit the same effect under sunlight [Asahi et al. (2001)]. Materials based on titanium dioxide are considered as promising in the chemical sensors [Mor et al. (2004)]. Finally, in the presence of TiO2 it is possible to produce methane from water and carbon dioxide [Anpo et al. (1995)] under UV irradiation.

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However, recently, researchers pay much attention to the optical properties of films based on titanium dioxide, 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 study [van Popta et al. (2007)], 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.

Highly ordered mesoporous titania-silica (TiO_2-SiO_2) composite thin films have been prepared by spin-coating technique using poly(alkaline oxide) triblock copolymers EO20PO70EO20 (P123) as structure-directing agent. Low-angle X-ray diffraction analysis shows that the mesoporous composite thin films remain a long range periodic ordered structure even if the TiO_2/SiO_2 ratio in the thin films is as high as 80%. Wide-angle X-ray diffraction analysis reveals that the average grain size of TiO_2 increases from 2.2 to 5.1 nm as the TiO_2/SiO_2 ratio increases from 20% to 80%. The crystal structure of TiO_2 is identified to be the anatase phase. 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 band gap of the TiO_2 nanocrystals in the mesoporous titania-silica composite thin films decreases from 3.9 to 3.45 eV [Yama et al. (2009)]. Mesoporous titania-silica composite films with highly aligned cylindrical pores are prepared by the sol-gel method using a substrate with structural anisotropy. The strong alignment effect of a rubbing-treated polyimide film on a substrate provides a narrow alignment distribution in the plane of the film regardless of the fast condensation rate of titania precursors. The collapse of the mesostructure upon the surfactant removal is effectively suppressed by the reinforcement of the pore walls with silica by exposing the as-deposited film to a vapor of a silicon alkoxide. The existence of a silica layer on the titania pore wall is proved from the distributions of Ti and Si estimated by the elemental analysis in high resolution electron microscopy. 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 [Myata et al. (2011)].

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. This study focused on elucidating the effect different templating materials (Pluronic F127 and P123) have on the pore size of the final mesoporous titania film and on understanding the relation of varying the polymer concentration (taking P123 as an example) in the sol-gel solution to the pore density and size in the resultant titania film. Titania thin film samples or corresponding titanium dioxide powders were characterized by X-ray diffraction, cross-section transmission electron microscopy, nitrogen adsorption, ellipsometry, UV/vis spectrometry, and other techniques to understand the interplay between mesoporosity and optical properties [Wang et al. (2009)].

Thin films of TiO_2 and its modifications can be prepared using the sol-gel, micellar and reversed micellar sol, hydro and solvotermal, electrochemical and other methods of synthesis [Chen and Mao (2007)]. Tetrabutoxytitanium (TBT), and (poly) glycols are widely used as precursors [Negishi and Takeuchi (2005), Guo et al. (2005a), Guo et al. (2005b), Bu et al. (2004), Bu et al. (2005), Raja et al. (2007), Crippa et al. (2011)]. Polyglycols are used as templates to determine the pore size of the porous film. It is known that anatase is of the greatest interest of researchers due to the lower band gap compared with rutile and brookite. However, in practice, usually, a mixture of these crystalline forms takes place. Thus, titanium dioxide P25 (Degussa) may comprise more than 20% rutile modification. [Hidalgo et al. (2002)].

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%. It is shown that in toluene and *n*-butanol these adducts under certain conditions form gels in the presence of highly ordered air humidity [Evtushenko et al. (2010), Evtushenko et al. (2011)]. This enables obtaining highly ordered films on various substrates adduct with subsequent heat treatment. In the study [Evtushenko et al. (2013)] for TiO_2 films gel method was used in which, unlike the sol-gel method, gelation occurs in true solutions. Titanium tetrabutoxide (TBT) and polyglycols as starting materials were used. Pore size depends on the nature of polyglycols that practically has no influence on the formation of the crystalline structure and the temperature of polymorphic transitions.

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 scheme shown on Figure 1.

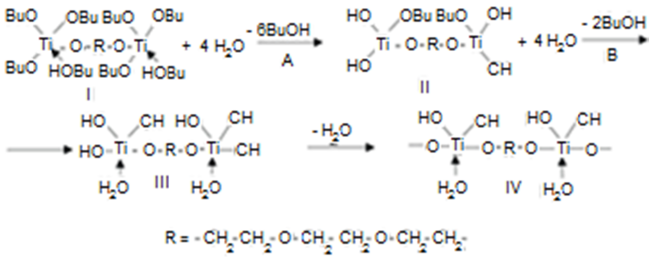

Fig. 1. The process of film formation of the adduct with TBT TEG (I).

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 eliminated butanol. Adduct (III) 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. Materials and Methods

We used tetrabutyl titanate (TBT) according to specifications TU 6-09-2738-89, threeethyllene glycol (TEG) according to specifications TU 6-01-5-88, *n*-butyl alcohol (reagent grade).

X-ray diffraction spectra of the samples were recorded on an automated diffractometer DRON 7 in step-scan mode. The range of angles 2θ of 19º to 90º, scanning step $\Delta 2\theta = 0.03^{\circ}$, the exposure time at the point – 3 s. Monochromatic CuKα-radiation with wavelenght $\lambda = 1.5418$ Å was used. The spectrum of this radiation was decomposed into Kα1 - and Kα2 - components. X-ray diffraction profile was approximated by Pseudo-Voigt function and then peak positions ($2\theta_{max}$), the position of the center of gravity ($2\theta_{cg}$), line half-width w, their maximum intensities (I_{max}), the position of the background were determined more precisely. After that integral (I_{int}) and relative (I_{rel}) intensities were calculated.

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. The study was conducted on a microscope JEOL-2100FX with an acceleration voltage of 200 keV. To determine the structural-phase state of the film the electron diffraction patterns obtained using micro-diffraction regime were analyzed. Estimates spacing and the lattice parameter of the material held on the basis of processing the Fourier images of high-resolution images. 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 (75×20×1 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 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 (Table 1).

Table 1. Study of the dependence of the refractive index and film thickness on the parameters of a technological regime using integrated optics techniques.

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

3. Results and discussion

3.1. 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 [Pavlov et al. (2011), Chekhlova et al. (2006)]. 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:

$$\frac{2\pi}{\lambda}h(T)\sqrt{n_2^2(T)-n_{eff\mathrm{TE}}^2(T)} = atan\left(\frac{\sqrt{n_{eff\mathrm{TE}}^2(T)-n_1^2}}{\sqrt{n_2^2(T)-n_{eff\mathrm{TE}}^2(T)}}\right)+atan\left(\frac{\sqrt{n_{eff\mathrm{TE}}^2(T)-n_3^2(T)}}{\sqrt{n_2^2(T)-n_{eff\mathrm{TE}}^2(T)}}\right)+\pi\cdot(\nu-1);$$

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

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; ν – 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. 2), 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 [Chekhlova et al. (2006)] at temperatures ranging from 293 to 373 K.

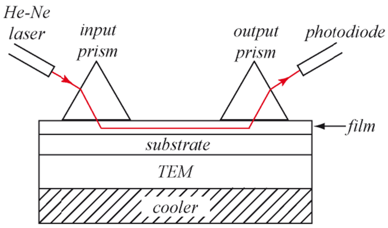

Fig. 2. Optical scheme of the measuring system.

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. 3*a* and 3*b*).

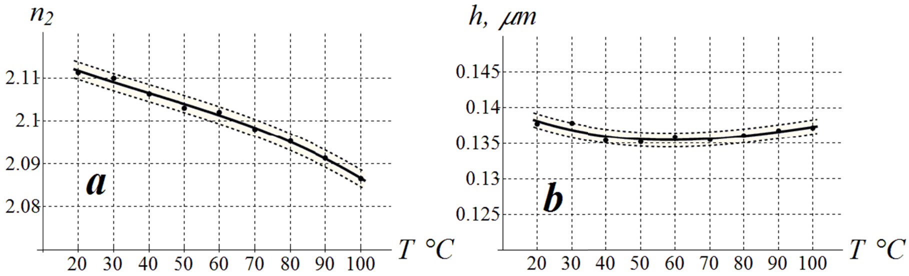

Fig. 3. The dependence of the refractive index (a) and film thickness (b) on the temperature.

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 $\approx - 3 \cdot 10^{-4}$ °C^{-1}. This value is close to the TOC of the films prepared by the sol-gel method [Chekhlova et al. (2006)].

3.2. 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 possibility of anisotropy property investigation transmission and reflection spectra of the films was made. 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 (< 0.1μm) (Fig. 4a) are isotropic. But at certain parameters of a technological regime and with increasing thickness the films become anisotropic (Fig. 4b).

Analyzing the above data one can conclude that TiO_2 films can have significant birefringence in all visible spectrum. The value of this birefringence which is the difference between refractive indices if two orthogonal polarizations of light wave, is equal tp 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, scanning electron microscopy and X-ray photoelectron spectroscopy. Analyzing data X-ray diffraction spectrum of the degradation products of the adduct TBT-TEGs after heat treatment at 723 K (Fig. 5) one can define cell parameters. 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 Å3. Theoretical data had values: a=3.7845 Å, c = 9.5143 Å, V = 136.27 Å3. It can be seen that experimental and theoretical data are in good correspondence.

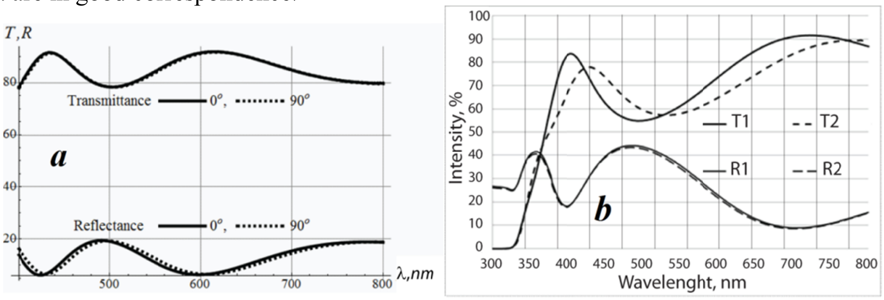

Fig. 4. The transmission and reflection spectra of films: a – film thickness 0.08 μm; b – film thickness 0.21 μm.

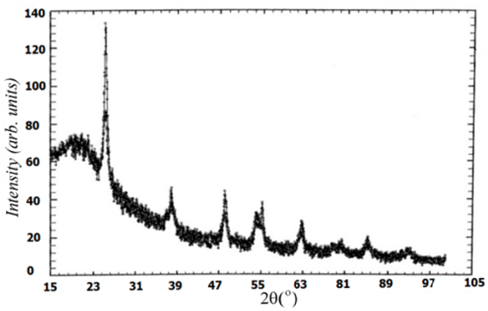

Fig. 5. X-ray diffraction spectrum of the degradation products of the adduct TBT-TEGs after heat treatment at 723 K.

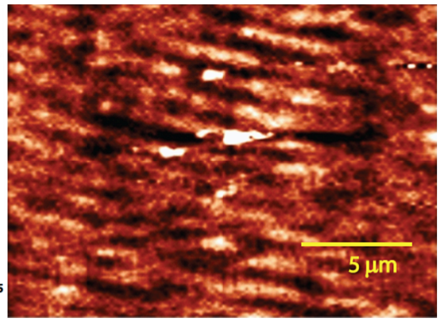

Fig. 6. Micrograph of the surface of TiO_2 thin film.
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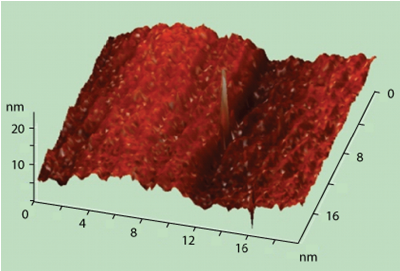
Figure 6 is a micrograph of the film TiO_2. According to [Mezhenny et al. (2003)], such films were obtained from partially reduced titania where ordered light band assigned to the polycrystalline titania, and bridges between the strips bright spots - to oxygen vacancies. The photomicrograph of the same film of a three-dimensional mode (Fig. 7) showed that the surface topography of the film is composed of ridge-like protuberances and depressions there between. 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. Water does not wet the surface and exists in the form of droplets. M. Ĉaploviĉová and coworkers [Ĉaploviĉová et al. (2012)] studied the morphology of the anatase films obtained by heat treatment composition $TiOSO_4 \bullet 2\ H_2O$ - Na_2CO_3 at 973 K. The most characteristic of anatase TiO_2 nanocrystals are in the form of a bi-pyramid and its derivatives (truncated and distorted forms). According to TEM of the films three types of nanocrystals (bipyramid, truncated bipyramid and distorted bipyramid) also found. Consequently, the formation of anatase films with precursors based on TBT and glycols is possible at lower (450 K) temperature. The film is a structure in the form of clusters of crystallites of titanium dioxide (Fig. 8). Typical dimensions of the crystallites lie in the range from 5 to 15 nm.

High-resolution images were obtained by Fourier transform. The Fourier image has distinct reflexes corresponding to array of planes of type {101} (Fig. 9). Typical forms and shapes of crystal are presented on Figure 10. Fourier analysis of the images showed that the lattice parameter is equal to 0.35 nm, which was confirmed by X-ray diffraction analysis. The data do not allow us to make definite conclusions about the nature of the porosity of the films, although for 3d image (Fig. 7), the film is fairly uniform, swings at a height of not more than 10 nm, and the porosity of the film may be due to the presence of cavities on the surface.



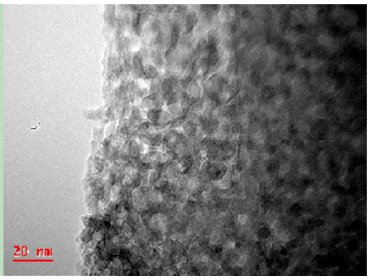


Fig. 7. Micrograph of the surface of TiO_2 films of a 3d image.

Fig. 8. Morphology of anatase nanocrystals.

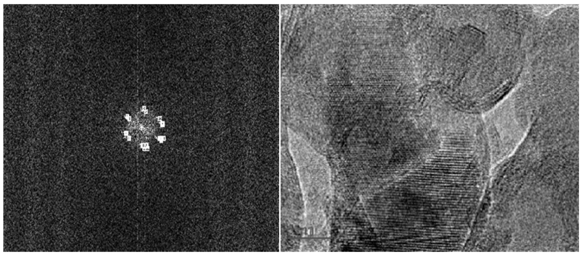


Fig. 9. Fourier image of TiO_2 crystal.

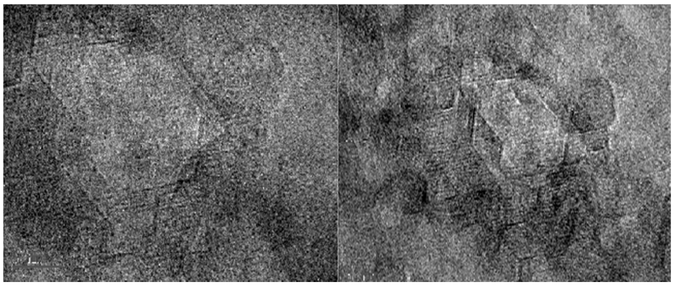


Fig. 10. Structure and shapes of TiO_2 crystallites.

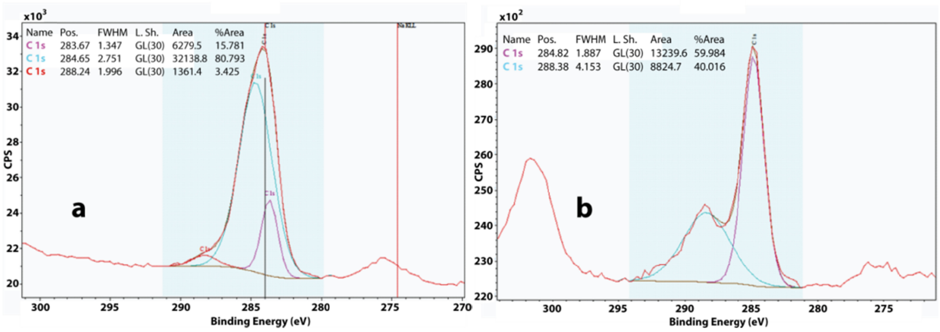


Fig. 11. C 1s lines in XPS of the samples annealing at 373 K (a) and 723 K (b).

According to X-ray photoelectron spectroscopy spectrum contains two lines of C 1s, corresponding to the binding energy of 284.8 and 288.6 eV (Fig. 11). The peak at 284.8 eV is related to elemental carbon and the peak at 288.6 eV - to C – O bonds [Ren et al. (2007)].

4. Conclusion

In this work homogeneous and transparent optical film 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 integrated optics (IO) applications. 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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