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Production of nanostructured TiO_2 films by pulsed laser deposition

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Abstract. The possibility of titanium dioxide films formation by pulsed laser deposition was studied. It was found that the titanium dioxide nanorods were formed on the surface of quartz glass under certain conditions. Craters with diameter about 40-50 μm and depth about 5-10 μm were formed on the target surface exposed with the nanosecond laser pulse. Electronic structure of the samples was studied by energy dispersive X-ray spectrum. Energy transitions of electrons determined from the energy dissipating spectra.

Introduction

The titanium dioxide (TiO_2) films have unique physico-chemical properties. In accordance with these properties the TiO_2 films are used as an element in photocatalysis devices, solar photovoltaic devices and they are widely used in optical devices [1, 2]. Titanium dioxide is different from other semiconductor materials (ZnO, SnO_2, Fe_2O_3). It has a high photosensitivity and acceptable band gap about 3.2 eV [3]. Features of the physico-chemical properties of TiO_2 films associated with its nanoscale structures. There are many methods for the synthesis of TiO_2 films. A method of pulsed laser ablation is one of the most promising methods for producing TiO_2thin films.

In this paper the results of the research the structure and energy dispersive X-ray spectra of TiO_2 films produced by pulsed laser deposition were presented.

There are two methods of laser-induced transfer of matter: direct transfer of matter and reverse transfer of matter. In the direct transfer of matter the laser beam passes through the transparent substrate evaporating material deposited on it. The evaporated material condenses on the location along the laser beam substrate. In the reverse transfer of matter laser beam passes through the transparent substrate and the acceptor focuses on the target surface. The evaporated material is deposited on substrate towards the laser radiation and condenses on the substrate. The technology of reverse transport of material was used in the present work.

Methods and Results

Universal laser technological installation was used for the deposition of TiO_2 films. Technological installation included a laser emitter ILTI-407B and vacuum universal installation VUP-4. The design of the vacuum chamber allows changing the distance from the sample to the substrate. The film thickness is controlled by changing the distance between the substrate and the sample and changing

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the duration of the laser ablation exposure. The deposition of films occurred by evaporating matter of target under the action of YAG:Nd^{3+} laser radiation with 10 ns duration, at λ = 1064 nm and a pulse repetition rate about 14 Hz. The angle between the laser beam and the sample surface was 45 degrees. The pressed cylindrical sample of titanium dioxide was used as the target. Target dimensions were 10 mm in diameter, 150 mm in length. The laser beam was focused on different parts of the target due to the translational motion of target during the ablation.

Quartz glass was used as substrate (dimensions about 10x7x1.5 mm). The substrate was placed on the resistive heater at a distance about 10 – 30 mm from the target surface. The pulse energy was 11 mJ. Power pulsed laser radiation was 10^5 – 10^7 W·cm^{-2}.

The study of the obtained films microstructure was carried out using the scanning electron microscope (SEM) JEOL JSM-5910. Its work is based on the registration of secondary electrons (SE). Space resolution in the scanning mode at voltage 15kV was 3 nm. Working distance was 8 nm. Probe current was 5 nA (analysis mode). Thermal-type Schottky electron gun was mounted into the microscope.

SEM -image of TiO_2 target surface after laser ablation is shown on Figure 1 (a). Craters formed on the surface target by nanosecond laser pulse. Craters have a diameter of 40-50 μm and a depth of 5-10 μm. The absorbed laser energy, that exceeds the critical density of the radiation flux, heated the target surface till the temperature of melting and then till the temperature of evaporation.

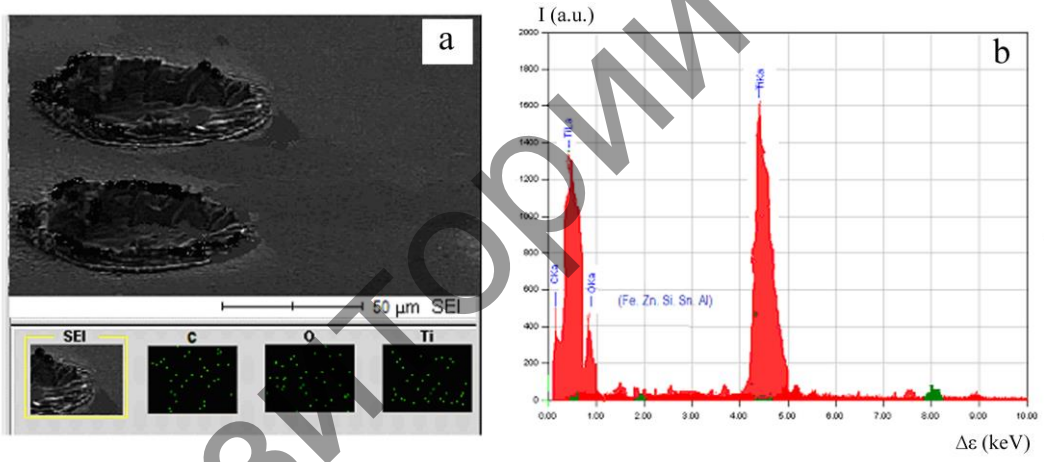

Figure 1. SEM images of the target surface (a), energy dispersive characteristic of X-ray spectrum (b).

The flux density of the laser radiation q can be represented as a function equivalent to multiplication function of time and the functions of the surface coordinate [4, 5]. The flux density of the laser radiation given by following formula (1):

$$q = A\varphi(t)q^*(x,y), \quad (1)$$

where A – the absorptivity that depends on the surface state and its temperature. The function $\varphi(t)$ describes the temporal structure of the pulse. The function $q^*(x,y)$ is the spatial distribution of the flux density of the laser radiation.

Form of melted area of sample changes during laser irradiation continuously and depends on the pulse duration. X-ray diffraction spectroscopy was used to study the chemical composition and elemental microanalysis of TiO_2 films and targets.

Energy dispersive X-ray spectroscopy technique is based on electron beam excitation of the sample followed by detection of the X-ray characteristic [6]. Energy dispersive characteristic X-ray spectra were obtained by X-ray spectrometer JXA-8200 with the energy dispersion and wave dispersion. This

spectrometer was installed in the SEM microscope. Type of detector was EX54133MUK. The electron energy probe was 25 keV. The probe current was 1 nA. The measurement time was 30 seconds. Working distance was 10 mm.

Energy dispersive characteristic of X-ray spectrum of elemental constituents of the film are shown on Figure 1, (b). The spectrum has the peaks corresponding to all the chemical elements of the film. Quantitative determination of elements was performed using analytical signals OK_α, TiK_α. OK_α spectrum line was formed at the transition between atomic states $2p_{3/2} \rightarrow 1s_{1/2}$, for $TiK_\alpha - 2p_{3/2} \rightarrow 1s_{1/2}$, $TiL_\alpha - 3d_{5/2} \rightarrow 2p_{3/2}$, taking into account the dipole selection rules [7].

OK_α line shows the distribution of 2p states of oxygen atoms. TiL_α lines show information about d-electrons and the distribution of 3d states of titanium atoms primarily. This is due to the smallness of the contribution to the intensity of the s-electrons. Energy electron transitions corresponding analytical lines determine from the energy dissipating spectra: $\Delta\varepsilon(OK_\alpha) = 0.525$ keV; для $\Delta\varepsilon(TiL_\alpha) = 0.46$ keV; $\Delta\varepsilon(TiK_\alpha) = 4.54$ keV. The experimental data of the transition energy $\Delta\varepsilon$ correspond to quantum-mechanical calculations using Moseley's law on the theory of atomic spectra [7].

Concentration of TiO_2 films elements were determined by mathematical processing of energy dispersive spectra. Mathematical processing was made by the program PHI-RHO-Z using the method of Bence and Albee binary oxide systems. Comparison of atomic (*At.%*) and the weight (*G,%*) elemental concentrations at various elementary areas of the objects shows that the samples are chemically homogeneous.

The films were prepared at different repetition frequencies of the laser radiation. These films don't differ in the percent abundance of atoms and mass. The value x for TiO_x is close to 2 in all cases. It corresponds to the stoichiometric composition of TiO_2.

Images of the microstructure of titanium dioxide films are presented on Figure 2.

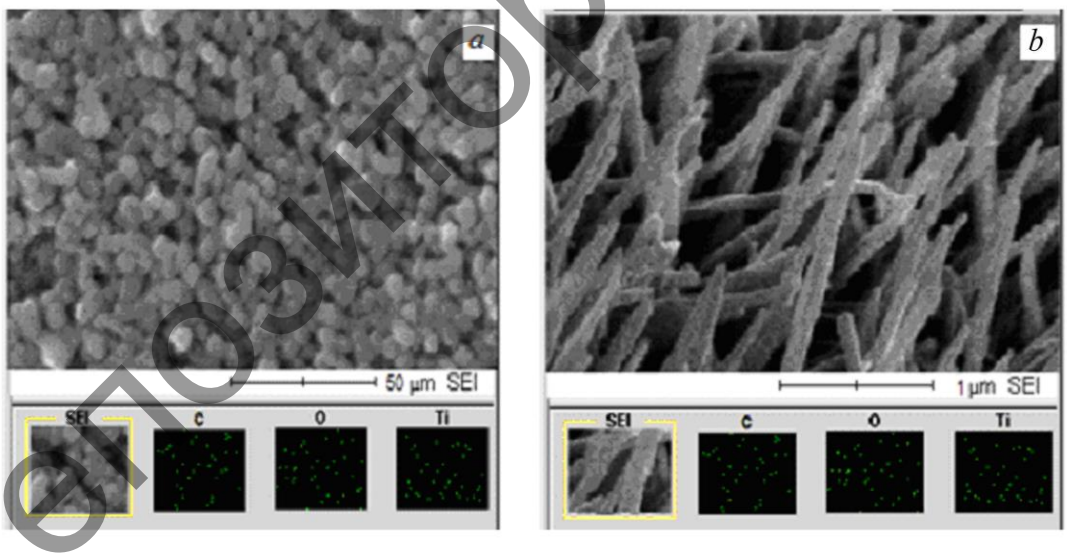

Figure 2. Microstructure of titanium dioxide film (a), a cross section of film (b).

The film has a mesoporous structure, as can be seen from the figure 2. Regularities aren't observed in the arrangement of the grains and their spatial orientation.

The average grain size is 5-8 microns. Direct forms of walls are observed for the tubes. Most of the surface of the film is smooth with a small roughness of 10-15 nm. The diameter of the tubes is about 190 nm in average. A series of experimental measurements carried out using SEM show that the film thickness and stoichiometry of TiO_2 don't depend on the parameters of laser radiation. The thickness of the film increases with deposition time.

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