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Effect of thermal annealing on grain size and phase changes in magnetron titanium oxide films

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Abstract: Thin TiO_2 films were produced on single-crystal Si-wafers by magnetron sputtering. Subsequently, they were annealed in air at different temperatures. We researched the structure, the phase composition, the morphology, and the dimensional characteristics of the films before and after annealing using X-ray diffraction, energy-dispersive and spectrophotometric analysis, scanning electron microscopy, and small-angle X-ray scattering. The analysis of the influence of annealing parameters on the characteristics of TiO_2 films is carried out. The technique for determining the qualitative and quantitative phase composition of TiO_2 during its polymorphic transformations at high-temperature heating has been developed. It was found that TiO_2 annealing at 400 °C leads to crystallization of the anatase phase, and annealing at 600 °C leads to transformations into the rutile phase. The optical band gap decreases with increasing temperature and with increasing annealing time.

Keywords: titanium dioxide, annealing, phase composition, morphology, polymorphic transformation, SEM, SAXS

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Влияние термического отжига на размер зерен и фазовые превращения в магнетронных пленках диоксида титана

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Аннотация. Объектом исследования являются тонкие пленки диоксида титана, полученные методом магнетронного распыления на подложках из монокристаллического кремния. Пленки TiO_2 отжигались на воздухе при различных температурах. Исследовались

структура, фазовый состав, морфология и размерные характеристики пленок до и после отжига. Использовались методы рентгенофазового, энергодисперсионного и спектрофотометрического анализа, сканирующая электронная микроскопия и малоугловое рентгеновское рассеяние. Проведен анализ влияния параметров отжига на характеристики пленок диоксида титана. Разработана методика определения качественного и количественного фазового состава пленок в процессе его полиморфных превращений при высокотемпературном нагреве. Установлено, что отжиг TiO_2 при 400 °C приводит к кристаллизации фазы анатаза, а отжиг при 600 °C – к превращениям в фазу рутила. Оптическая ширина запрещенной зоны уменьшается с повышением температуры и увеличением времени отжига.

Ключевые слова: диоксид титана, отжиг, фазовый состав, морфология, полиморфные превращения, СЭМ, МУРР

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Introduction

Nanostructured materials are one of the most fast-evolving areas of research. Among all the transition metal oxides, titanium dioxide nanostructures have the largest potential in modern science and technology [1]. TiO_2 can be obtained by oxidation of thin Ti films. TiO_2 has become famous because of its unique photocatalitic properties [2-4]. Active electron-hole pairs can be generated in the electronic structure of TiO_2 due to the absorption of photons with energies above 2.8 eV. When electron-hole pairs emerge on the surface, they participate in redox reactions with the formation of radical complexes. TiO_2 crystal exists in three common polymorphs, i.e., brookite, anatase (A), and rutile (R) [5, 6]. The photocatalytic activity of anatase is estimated to be higher than that of rutile. However, due to the smaller band gap, rutile can absorb a wider range of sunlight up to 450 nm [7, 8].

It is a daunting task to obtain TiO_2 films with suitable characteristics. We applied thermal annealing with trial-and-error adjustment of optimal parameters of the processing mode [9]. On the other hand, it is equally important to determine the qualitative and quantitative phase composition of TiO_2 during its polymorphic transformations at high-temperature heating. Therefore, our goal was to investigate the effect of thermal annealing on the morphology and phase composition of magnetron TiO_2 films under various processing modes.

Materials and Methods

To obtain thin TiO_2 films, we used a magnetron sputtering device, MVU TM Magna T (NIITM, Russia). The films were grown for 30 min on monocrystalline Si substrates in Ar atmosphere at magnetron discharge power of 300 W. Before deposition, the substrates were heated to 120 °C (for 1 min), then we carried out ion beam cleaning at a current of 60 mA (for 2 min). To obtain the Ti oxide, the prepared Ti films were annealed in air at 400 °C, 600 °C and 800 °C for 2, 4 and 6 hours using a Mini Lamp Annealer MILA-5050 heater.

Phase composition of the samples was analyzed by the X-ray crystallography technique. To perform measurements, we used a GBC EMMA powder diffractometer (60 kV/80 mA, 0.005%, radiation power 2.2 kW, goniometer step 0.002). First, we obtained X-ray diffraction patterns from pure Ti films, then from annealed films.

The morphological features and changes in the surface structure of the films were studied using the JEOL JSM-6610LV scanning electron microscope (SEM, 20 kV, up to 100000×). X-Max Silicon Drift Detector (Oxford Instruments) allowed getting the distribution of chemical elements in the samples.

Line-collimation small-angle X-ray scattering was also used in the characterization of the samples (diffractometer SAXSess mc^2, Anton Paar, Austria). This device is designed to find the structural features of objects with sizes from 0.1 to 100 nm. It is equipped with a typical X-ray tube with a Cu anti-cathode and monochromator, which allows obtaining X-rays with a wavelength of 0.154 nm. The measurement time was 30 s. The SAXS data were processed using GIFT software (PCG Software Package).

To study the optical properties of the annealed films, we used an SF-2000 spectrophotometer (OKB Spectr, Russia). Its wavelength range is 190–1100 nm. The obtained reflection spectra were converted to absorption spectra using the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}. \quad (1)$$

Here K and S are the absorption and back-scattering coefficients, R_∞ is remission fraction of an infinitely thick layer. The absorption spectra were used to determine the value of band gap.

Results and Discussion

Scanning electron microscopy (SEM) revealed that all our TiO_2 films were polydisperse (scan for 800 °C, 2 hours is shown in Fig. 1,*a*). The grain sizes grow with an increase in annealing time. The minimum grain sizes found on SEM scans are listed in Table 1.

According to SEM results, the thickness of the films varied from 0.95 to 1 μm (Fig. 1, *b*). During the experiment, the samples were placed at an angle of 89° to the horizontal plane.

To gain insights into the integral characteristics of TiO_2 grains, we considered the samples using SAXS. The scattering intensity data (Fig. 2, *a*) were used for plotting the pair distance distribution functions (PDDF) shown in Fig. 2,*b*). The configuration of these functions clearly shows that TiO_2 grains have an irregular shape and different sizes. The Guinier approximation applied at the very beginning of the scattering curves give the minimum dimension of grains, amounting to 20–25 nm.

The phase composition of the annealed films was determined using powder diffractometer. As evident from the obtained spectra, the TiO_2 anatase phase is formed at a temperature of 400 °C, while at 600 °C it transforms into a rutile phase (Fig. 3).

Each peak of the diffractograms was approximated by a Gaussian curve using OriginPro software:

$$y = y_0 + e^{\frac{-(x-x_C)^2}{2w^2}}. \quad (2)$$

a) *b*)

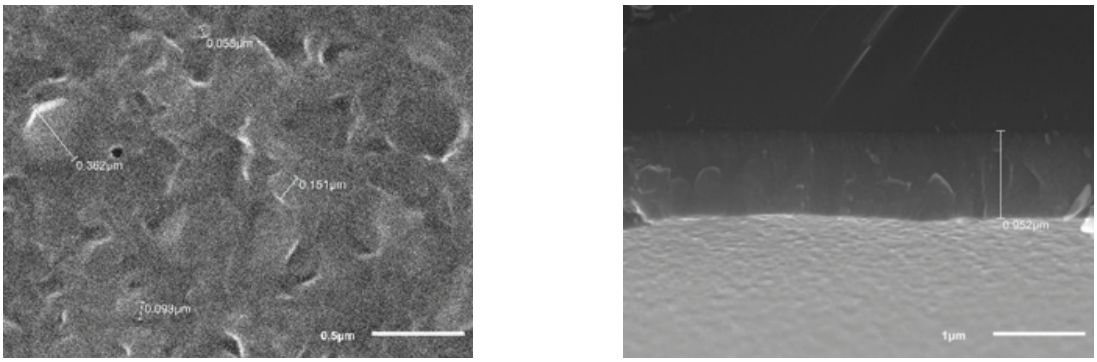

Fig. 1. SEM results: front view (*a*); cross-sectional view (*b*)

Table 1

Minimum grain sizes found in SEM scans

Time	Temperature		
	400 ºC	600 ºC	800 ºC
2 hours	25 nm	25 nm	> 100 nm
4 hours	35 nm	30 nm	
6 hours	40 nm	50 nm	

The concept of the coherent scattering region (CSR) was also used to research TiO_2 films. The CSR size is generally 10–15% smaller than the size of grains identified using electron microscopy, while coherent scattering region corresponds to the inner (ordered) region of grain and does not include severely distorted boundaries [10]. CSR sizes were calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\delta \cos\theta}, \tag{3}$$

where $k = 0.95$ is the dimensionless shape factor; δ is the line broadening at half the maximum intensity; θ is the Bragg angle; $\lambda = 0.154$ nm is the X-ray wavelength. The estimation gives the average size of crystallites is from 3 to 11 nm.

In order to research the influence of the size factor on the width of band gap, we studied the optical absorption spectrums of TiO_2 nanofilms. We obtained the reflection spectrums of the annealed films and then calculated absorption spectrums using Kubelka–Munk equation (1).

According to quantum-mechanical calculations, in the case of intrinsic absorption of semiconductors and dielectric materials, transitions of electrons from valence band to conduction band are determined through the sum of the probabilities α_P for all states of electrons:

$$\alpha_P = \left(2\frac{m_e m_p}{m_e + m_p}\right)^{\frac{3}{2}} \frac{q_e^2}{ncm_e}\left(h\nu - E_g\right)^{\frac{1}{2}}, \tag{4}$$

where m_e and m_p are effective electron and hole masses; q_e is elementary charge; n is refraction coefficient.

For all samples, the band gap E_g was obtained by extrapolating the linear part of the square of absorption spectrum at $(\alpha(h\nu))^2$. The dependence of the band gap values on the annealing time at each temperature appears linear (Fig. 4).

The optical band gap decreases with increasing temperature from 3.10 eV (at 400 ºC) to 3.02 eV (at 800 ºC). It also decreases with the annealing time growing. SEM and SAXS data prove that the higher the annealing temperature, the larger the crystallite size, which is accompanied by a decrease in the band gap E_g.

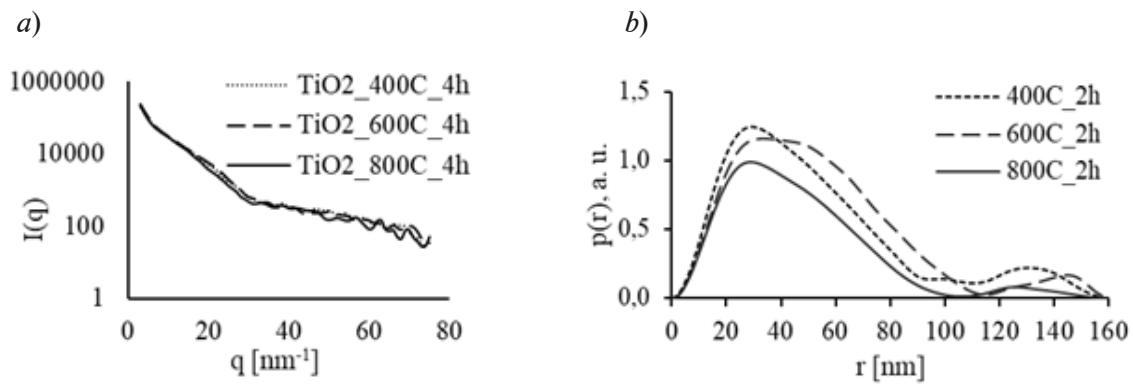

Fig. 2. SAXS results: scattering intensity data (*a*); pair distance distribution functions (*b*)

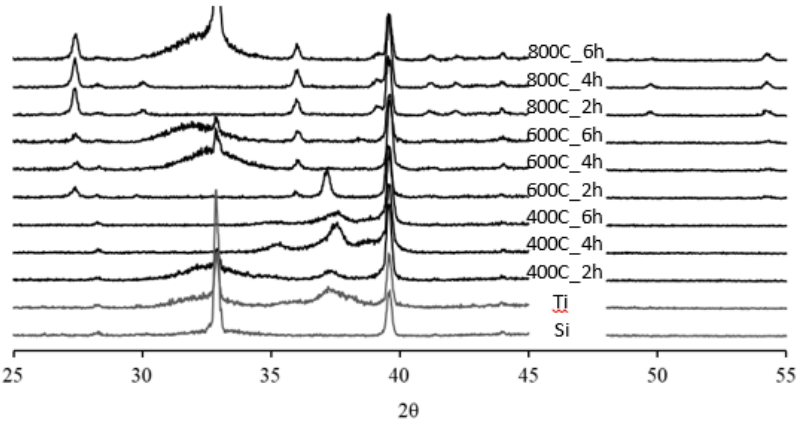

Fig. 3. X-ray diffractograms of TiO_2 films, pure Ti, and pure Si

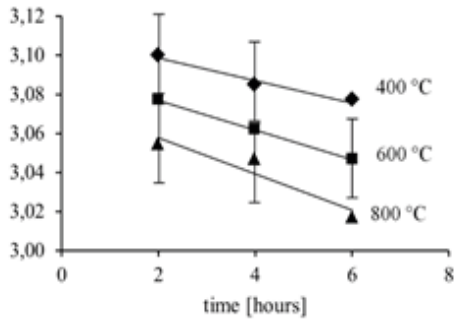

Fig. 4. Dependence of the band gap value on the annealing time

Conclusion

Titanium oxide films were obtained by magnetron Ti sputtering and subsequent annealing in air for 2, 4, and 6 hours at 400 °C, 600 °C and 800 °C. The thickness of the obtained TiO_2 films is ~1 μm. According to SEM and SAXS data, all studied TiO_2 films are polydisperse. The grains have an irregular shape, and their size grows with increasing of temperature and the duration of annealing.

The phase analysis shows that TiO_2 annealing at 400 °C leads to crystallization of the anatase phase, and annealing at 600 °C leads to the transformations into the rutile phase. According to our estimations of coherent scattering region, the average size of crystallites is in the range from 3 to 11 nm. Optical absorption spectra were used to obtain the band gap for each sample. The value of the band gap decreases with increasing annealing time and with increasing temperature. It is 3.10 eV at 400 °C and 3.02 eV at 800 °C. To summarize, it is evident that an increase in the annealing temperature leads to an increase in the crystallite size, which is accompanied by a decrease in the band gap.

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