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In this work spectral behaviour of complex refractive index of thermal oxidized titanium films deposited onto Si (100) substrate were investigated by spectroscopic ellipsometry in the range of 1.5-4.77 eV. The films were subjected to annealing in air at temperature 750 °C for 7 and 25 hours. As it follows from our studies, air oxidation of titanium resulted in coexisting of different phases in the film, and dependence of their optical and structural properties upon z-coordinate (upon film depth). The spectral dependences of complex refractive index and the changing of film thickness due to cumulative annealing were determined from pseudodielectric function (PDF) - ε(E) spectra, for which data acquisition was performed by Spectroscopic Phase Modulated Ellipsometer (SPME). Complicated phase composition of films was revealed by using multi-layers conception of investigated film and applying oscillator's model and EMA approximation for description of spectral dependence of dielectric function of film or its separate layers. Raman spectra were used to distinguish phase components in the films.

1 Introduction Thin film titania (TiO_2) is an interesting wide band-gap oxide transparent in visible region, possessing both high refractive index and mechanical and chemical stability, can be used in a number of applications: in dynamic-random-access-memory, in electroluminescent devices, as protective and antireflection coatings, color filters, laser mirrors and others. Titanium dioxide occurs in three crystalline polymorphs: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). It is well known that rutile is most stable phase at all temperatures, while anatase and brookite exist as metastable phases below ~800°C. Titanium is in octahedral coordination with O as TiO_6 units in all polymorphs which have yet different Ti-O bond length and angle. In additional to the stoichiometric polymorphs, nonstoichiometric forms a series of daughter structures with the general formula Ti_nO_{2n-1} where $4 \leq n \leq 10$ can coexist as titania film constituents. So far electrical, magnetic, optical properties of the bulk crystalline titania and film TiO_2 has been the subject of theoretical and practical interest. Their properties were investigated by Raman spectroscopy, resistivity, Hall-effect, photoconductivity, photoluminescence, spectrophotometry (optical absorption), and ellipsometry. Bragg-Brentano x-ray diffraction was successfully used for phase identification of TiO_2. As reported in the literature [1-3], properties of TiO_2 depended on conditions of film depositions, such as reactive triod sputtering, reactive rf magnetron sputtering, or reactive electron beam evaporation of various starting materials (Ti, TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7). Furthermore, TiO_2 films have structural complexity which means a) bond flexibility giving rise to polymorphs with the same chemistry and/or similar free energy of formation and b) mixed valence compounds [1]. As a rule, properties of titania films were investigated by authors considering films as homogeneous ones.

The goal of this work is to study changing of film properties due to annealing at 750 °C for 7 hours and 25 hours using ellipsometric spectra of given samples measured in the range of 1.5-4.77 eV.

2 Experimental

2.1 Instrumentation Metal titanium films were evaporated in vacuum 6.7×10^{-4} Pa from W-boat on Si (100) substrate. Ti/Si structures were heated up to 750 °C

in Pt-container in air atmosphere for formation of titanium oxides. Evaluation of Ti thickness was carried out by the resistivity monitoring *in situ* as about 70 nm using quartz satellite. Durations of cumulative annealing were for 7 hours and 25 hours. Measurements of ellipsometric spectra were carried out by SPME in the range of 1.5-4.77 eV. Our experiments had been aimed at a finding of correlation between fundamental optical properties ε(E) and the presence of several phases in titania films, and a finding of film thickness alteration due to the annealing time. Raman spectra with excitation of 488 nm were recorded for our samples and rutile.

2.2 Measured and calculated quantities In this work two kinds of TiO_2 films were taken into account: the films of the first kind were exposed at 750 °C in air for 7 hours (1, 2, 3), and the films of the second kind were additionally exposed for another 25 hours at same conditions (1ox, 2ox, 3ox, respectively); and their PDF - ε (E) spectra are shown in Fig. 1. Spectra 1, 2, 3 are distinguished from each other, and are fundamentally distinguished from 1ox, 2ox, 3ox, respectively. Interference effect was present in all spectra and it allowed roughly evaluating film thickness. The former distinctions can be explained by deposition of metallic films with different thickness, suggesting other factors being the same, but the latter distinctions can be related both with formation of new or additional bandings O-Ti-O and a changing of film thickness due to annealing.

2.3 Modelling As expected, films had complex compositions. The modelling was carried out for fitting of PDF spectra a) by using multi-layer conception of description of inhomogeneous TiO_2 film; b) by using well known from [4] spectral dependences of dielectric function (DF) of anisotropic rutile, anisotropic anatase, {o-Anatase and o-Rutile for ordinary beam (E ⊥ **c** crystal axis) and e-Anatase and e-Rutile for extraordinary beam (E ∥**c** crystal axis) }; c) by using Bruggeman EMA model for description of DF of film composed by two components; and d) by using classical oscillator's model for description of DF (Eq. (2)) for some modified phases, derived from above four ones.

The first attempt of the modelling of titania film by one of four TiO_2 components only was unsuccessful. It could be predicted if we have paid attention to Fig. 2 where real and imaginary part of PDF for any sample did not coincide with any spectrum of four TiO_2 crystal phases from Ref. [4] in range of strong absorption (when E > 3.8 eV), where film could be considered as semi-infinite medium; in other words, where film thickness was greater than penetration depth of light and influence of the bottom layers on reflected light could be completely neglected.

For reference, spectral dependences of penetration depth of light for rutile and anatase (for extraordinary beam) are shown in the insert into Fig. 2, where penetration depth is equal to $d = 1/\alpha = \lambda/4\pi k_e$. Therefore it is necessary to use more complicated model for description of PDF for our structures. Moreover, films oxidized for longer time had less complicated model; this phenomenon was found in the result of modelling. Here the questions related with oxygen diffusion and its limiting processes based on oxidation theory have been not taken to consideration.

Unfortunately we could not find more adequate model describing structure of sample 1 and get lesser value of objective function than the shown in Table 1. The attempts of using more complicated model with greater layers number did not give more best fitting.

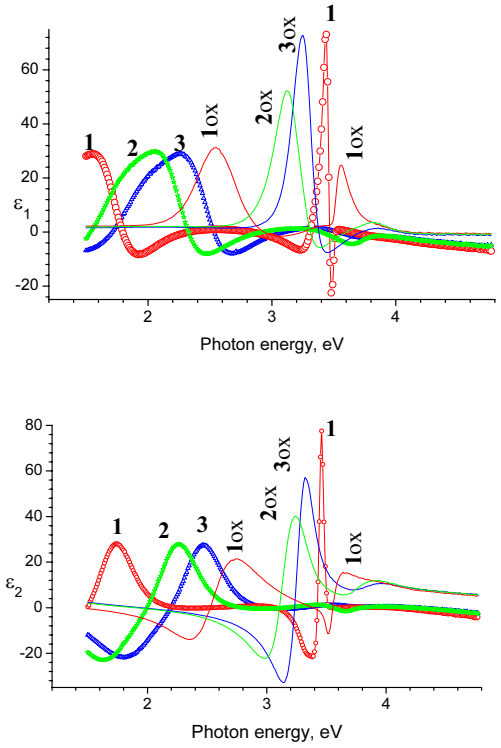

Figure 1 Real and imaginary parts of pseudodielectric function of Si-Ti samples exposed in air at 750 °C for 7 hours (1, 2, 3) and for 25 hours (1ox, 2ox, 3ox), via photon energies.

2.4 Calculation procedure Interface layer on boundary of Ti/Si, likely formed as result of mutual diffusion of titanium and silicon atoms was used in all cases. Properties of layers, noted as Rutile-Modified and Anatase-Modified were determined by transformation of oscillator's model parameters describing crystal rutile or anatase with high accuracy in the same energy range, respectively. Objective function χ^2 was presented by following sum:

$$\chi^2 = \frac{1}{2N}\sum_N \left(\frac{\varepsilon_1^{calc} - \varepsilon_1^{\exp}}{\sigma_1} + \frac{\varepsilon_2^{calc} - \varepsilon_2^{\exp}}{\sigma_2} \right) , \qquad (1)$$

where subscripts *1* and *2* relate to real and imaginary parts of PDF and superscripts *calc* and *exp* relate to calculated and experimental values of PDF; and σ_1, σ_2 are normalizing coefficients.

In accordance with the Classical dispersion model, dielectric function is equal to the sum of high frequency

value of ε_∞ and a few single oscillators, the number of which is determined by the number of critical points in reflectance or in transmittance spectra [5]. We took a sum of four items here:

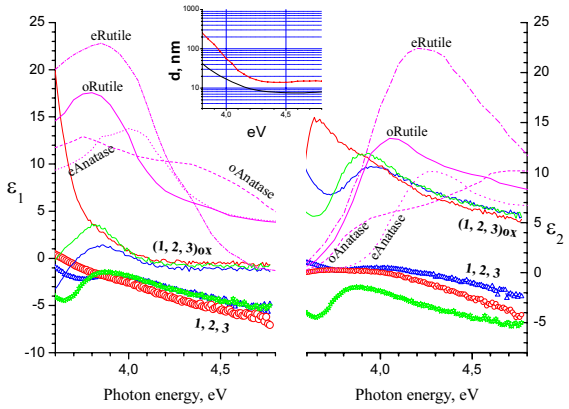

Figure 2 Pseudodielectric function of Si-Ti samples exposed in air at 750 °C for 7 hours (1, 2, 3) and for 25 hours (1ox, 2ox, 3ox) via photon energies in the range of strong absorption. Real and imaginary parts of ε of anatase and rutile for ordinary (E⊥**c** crystal axis) and extraordinary (E||**c** crystal axis) beams [4] are shown for comparison. The insert shows dependence of d = 1/α via photon energies in the same region for the same anatase and rutile

$$\varepsilon = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_T^2}{\omega_T^2 - \omega^2 + i\Gamma_0\omega} + \sum_{j=1}^{2} \frac{f_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j\omega}\,, \qquad (2)$$

where ε_∞ and ε_s are high frequency and static dielectric constants, respectively; Γ_0, γ_j are positive damping factors; f_j is the oscillator's strength; ω_{0j}, ω_T are the oscillator's, and transverse energies, respectively, in eV. The results of minimization of χ^2 (in according with Eq. (1)) and calculated model parameters: number of model's layers, their thickness separately and in sum, layer's composition and values of objective function χ^2- are displayed in Table 1. Note that numbering of layers were listed starting from substrate. Experimental parameters:- number of Ti layer evaporations and duration of annealing at 750 °C- are shown in the same Table 1.

3 Results and discussion It is necessary to note the following changes of samples after additional oxidation for 18 hours: a) considerable decrease of general thickness of films; and b) interface's thickness enlarging in about two times in all cases; and c) formation of crystal phase (1ox) or their mixtures (2ox, 3ox); d) alteration of film composition along layer depth; and e) difference of upper layer composition from any of four components of TiO_2 which were taken for calculation; and at last, f) the getting of the best fitting. Taking into account duration and temperature exposure, the reasons of the thickness decrease of oxide layer after additional oxidation can be explained by formation of oxide which is less porous and less structural disordering hence having great density and less thickness. Moreover, if thickness decrease was not taken into account then wrong absorption coefficient α [cm^{-1}] would have been got from transmittance and reflectance, for example, in [1].

Optical properties of crystal rutile (extra-ordinary beam) and optical properties of top layer named Rutile-Modified and used in fitting procedure of samples (1ox, 2ox, 3ox), which were cumulatively oxidized for 7+18 hours, are shown in Fig. 3. Spectra of Rutile-Modified (for 1ox, 2ox, 3ox samples) are characterized by smaller absorption magnitude and by shift to the lower energy for both critical points and the absorption edge. These energy shifts are implicit functions of the mode of cumulative annealing, because steps of cumulative annealing and film thickness for each of samples were individual. By extra-

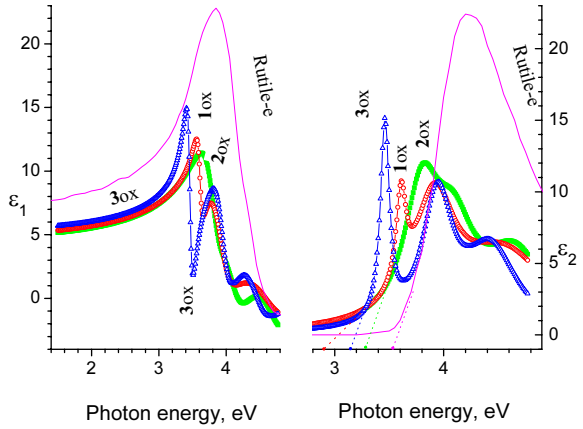

Figure 3 Optical properties of rutile (e beam) and Rutile-Modified used in the fitting of ε(E) spectra of 1ox, 2ox, 3ox samples, as shown in Table 1.

polation of linear parts of ε_2 it was possible to receive values of energy close to band gap E_g, which were equal to 3.53 eV, 2.89 eV, 3.28 eV and 3.14 eV for rutile-e, 1ox, 2ox, and 3ox samples, respectively. Shifts to the lower energies with respect to 3.53 eV for rutile-e could be explained by presence of amorphous phase if we would follow results of analytical work [6] where parameters characterizing the absorption tail breadth were introduced to relate the optical absorption spectrum with amorphism degree of semiconductors.

To reveal presence of different TiO_2 phases in our films, Raman spectra of 2 and 2ox samples and crystal rutile (for comparison) were recorded. Table 2 shows Raman modes of anatase film [7], crystal rutile, and our 2 and 2ox samples. Except of two Raman modes (104 and 609 cm^{-1}), the rest modes of 2 and 2ox samples differed from crystal rutile modes for about 10 cm^{-1} and from anatase one (640 cm^{-1})– for about 30 cm^{-1}, this fact did not contradict results of ellipsometric model calculations. On one hand, samples 2 and 2ox were enough similar to rutile excepting presence of anatase-like mode ~ 670 cm^{-1} as shown in Table 2. On the other hand, unfortunately Raman spectra did not give convincing information about different compositions of

samples oxidized for 7 hours and 25 hours although it was clearly indicated by SE spectra in Fig. 1.

Table 1 The experimental data and model parameters of TiO_2 films obtained by air oxidation at 750 °C.

Experimental data			Model parameters			
Sample number	Number of Ti evaporation	Annealing time in hours	Layers	Thickness in nm	Layer's composition	χ^2
1	1 +2	5 +7	1 2 3 4 Σ	7.4 81.1 +45.5 +25.1 =151.7	85.41%Ti+14.59%Si 75% Rutile-o +25%Anatase-e Rutile-Modified Anatase-Modified	41.15
1ox	1 +2	5 +7 +18	1 2 3 Σ	12.4 51.1. +21.0 =72.1	86.15%Ti+13.85%Si Rutile-e Rutile-Modified	0.895
2	1	7	1 2 3 4 Σ	6.1 62.5 +20.5 +23.8 =106.8	76.84%Ti+23.16%Si Rutile-o Rutile-Modified Anatase-Modified	13.14
2ox	1	7 +18	1 2 3 Σ	16.0 25.1 +24.2 =49.3	98.13%Ti+1.87%Si 97.3% Rutile-e+2.7%Anatase-o 99%Rutile-Modified+1% Anatase-Modified	1.176
3	1	7	1 2 3 4 Σ	4.7 63.6 +13.4 +23.5 = 100.5	96.18%Ti+3.82%Si 74.5% Rutile-o +25.5%Anatase-e Rutile-Modified Anatase-Modified	15.83
3ox	1	7 +18	1 2 3 Σ	12.3 25.7 +21.3 = 47.0	98.13%Ti+1.87%Si 71.1% Rutile-e +28.9%Anatase-o 99%Rutile-Modified +1% Anatase-Modified	2.035

Table 2 Raman modes of film anatase [7] and of crystal rutile and our samples 2 and 2ox.

Samples	Raman shift , cm^{-1}						
Anatase film	145		399	516	640		
Rutile crystal	104	232		443	609		816
2	106	223	302	434	609	666	821
2ox	106	224	303	436	610	670	826

4 Conclusion In this study was found that TiO_2 films possessed oxidation profile under given mode of fabrication, in other words, films composition depended upon transverse coordinate (upon layer depth), and the latter in its turn depended upon conditions of evaporation and the oxidizing. Our modelling revealed that some layers could be represented by crystal form of rutile, though upper layer always had different composition and hence other properties. One should keep in mind that air oxidizing might result in not isotropic films. To get isotropic TiO_2 film it is necessary to select suitable oxidation mode.

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