SYNTHESIS OF TiO_2 DIFFERENT PHASE BY DC MAGNETRON SPUTTERING

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The enhanced interest to synthesis of thin and extra-thin films using for surface materials modification continue to be quite actual up to now. A special attention is drawn to coatings having important for practical applications characteristics with costs-effective production. These may be the films of binary compounds of certain metals, particularly, titanium nitride and titanium oxide. The last compound possesses the utmost significance due to wide range of its unique physical, chemical and biological properties. Functional coatings of titanium dioxide synthesis with nanoscale thickness is of considerable interest since it allows essential economy of the material and the increase of manufacturing productivity with the decrease of production cost. To create a scientific basis of nanotechnologies researchers explore different coatings methods, including the ion-plasma methods. Among them, reactive magnetron sputtering seems to be promising: DC magnetron coating allows to deposit titania in amorphous and crystal phase and control results by variation of deposition conditions. The substrate material influences coating phase, as well as discharge characteristics. The thermal linear expansion coefficient does not influence line blue shift in Raman spectra of deposited films in our experiments. The influence of film annealing after deposition up to 800ºC on dioxide crystalline phase of the film is shown.

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INTRODUCTION

To create a scientific basis for modern nanotechnologies, researchers study various coatings deposition methods, including the ion-plasma methods. Among them, reactive magnetron sputtering seems to be promising: it uses only a metallic target and a reactive gas (N_2, O_2) as an addition to a plasma forming gas (Ar) to synthesize coatings. Absence of toxic chemical solutions and gaseous reagents makes this method maximally friendly to environment and does not require creation of deactivating facilities for recycling a waist of chemical reactions. We present the synthesis deposition method of TiO_2 nano- films in different phase by DC inverted cylindrical magnetron and influence of deposition process parameters on the result. Earlier we have shown existence of peculiarities in behavior of intensities of spectrum lines of the magnetron discharge plasma emission in presence of substances participating in the synthesis of TiO_2 nano-films [1, 2]. Existence of correlation between emission spectra peculiarities and electrophysical discharge parameters enables reliable control of operating point of titanium dioxide deposition in cylindrical magnetron, and ensures synthesis stoichiometric titanium dioxide films. It was noted [1] that at cold substrate one can obtain only amorphous titanium dioxide film in our range of the deposition parameters. At the same time, heating the substrate above 350ºC causes reliable anatase synthesis. Variations of the gas discharge parameters and the substrate temperature enable obtaining anatase films of different density, photocatalytic activity and with different crystal size [2-4].

Necessity of the substrate temperature rise above 400°C does not enable use of borosilicate glasses for the synthesis of rutile films. Due to that, we used substrates made of high temperature materials for making possible their heating up to higher temperature values. Fused silica substrate served as a test one for comparison with earlier obtained results.

1. SETUP AND METHODS

Setup in details is described in [5, 6]. The original DC inverted cylindrical magnetron is described in [7]. Films deposition was controlled with a Plazma Spec optical spectrometer, which is based on charge-coupled devices and has a resolution of 0.6 nm in the wavelength range λ=350…820 nm. The optical spectrum recording time was 5 ms, and we were able to record an entire spectrum and its selected lines [8].

The Raman spectra of the films were recorded in the backscattering geometry at room temperature. To excite vibrations, we used line 785.0 nm of an RANISHAW In Via Raman Microscope. The surface morphology and the roughness of the films we explored with a NanoScope IIIa Dimension 3000 atomic force microscope (AFM). The thickness and the refractive index of the films were measured by ellipsometry on an LEF3M1 ellipsometer at λ = 632.8 nm [1-4], and by method of [9] using optical transmission.

2. RESULTS AND DISCUSSIONS

To define the suitable conditions to synthesis of rutile films the experiments with heated substrates were carried out. For the results to be considered, the substrate was heated up to 560°C. At that, different results were obtained on different substrates. Fig. 1 represents Raman spectrum of the film deposited onto a fused silica.

The spectrum is separated from the substrate lines. Frequency positions of the lines in the spectrum correspond to 158.2 cm^{-1}, 413.2 cm^{-1}, 513 cm^{-1}, 645.7 cm^{-1}. Taking into account blue shift of the lines for nano-crystal anatase samples, it agrees with the data of Ohsaka et al. [10] for anatase: Eg(1) 144 cm^{-1}, Eg(2)197 cm$^{–1}$, B$_1$g 399 cm^{-1}, (A$_1$g +B$_1$g) 514 cm$^{–1}$, Eg(3) 639 cm$^{–1}$. The last enables identification of the film on fused silica substrate as one composed of anatase phase with the lines having blue shift. All the lines, with an exception of [A$_1$g +B$_1$g(2)], possess essential blue shift, which is inherent to a very fine-grain samples [11]. Half-width of **G** lines Eg(1) comprises 31.2 cm$^{–1}$, which is essentially more than the half-width **G**=8.6 cm$^{–1}$ for rough-grain anatase powder [12].

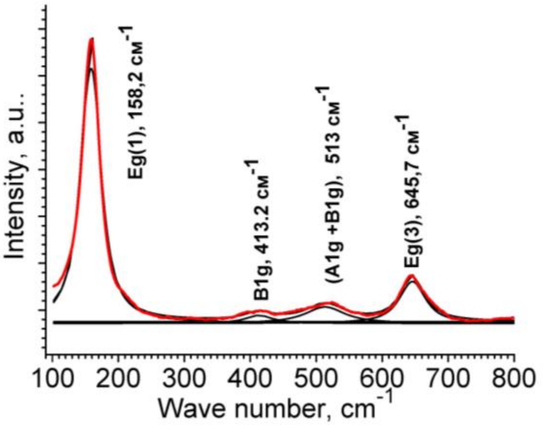

Fig. 1. Raman spectrum of the TiO$_2$ film deposited on a fused silica substrate at temperature of 560 °C and argon pressure of 3•10$^{–3}$ Torr after separating the substrate spectrum. Above the spectrum lines, their frequency positions are shown on a basis of the results of the lines approximation by Lorentzian function

The result for the film on corundum is shown in Fig. 2. The lines 378.7 cm$^{–1}$ (Eg), 427.2 cm$^{–1}$ (Eg), 643.6 cm$^{–1}$ (A1g) belong to corundum substrate. In the film spectrum one can clearly see the line 157.9 cm^{-1}, which, taking the blue shift into account, may be considered as line Eg(1) 144 cm$^{–1}$ of solid polycrystalline anatase. The other lines, which were determined for the film on fused silica as B$_1$g 413.2 cm^{-1}, (A$_1$g +B1g) 513 cm^{-1}, Eg(3) 645.7 cm^{-1} in case of corundum are masked by the bases of the substrate lines.

It is illustrated by comparison with the film spectrum on fused silica shown in Fig. 2 as dotted line. Position **ω**=157.9 cm^{-1} of line Eg(1) and its half-width **G**=29.1 cm$^{–1}$ for anatase film on corundum are close to the position and the half-width for the film on fused silica (**ω**=158.2 cm^{-1}, **G**=31.2 cm^{-1}).

Fig. 3 presents the spectrum for the film on fluorite. Line at 320 cm$^{–1}$ belongs to fluorite.

Frequency positions of the lines in the spectrum of TiO$_2$ film on CaF$_2$ substrate are, as follows: 160.2 cm$^{–1}$**,** 238.7 cm$^{–1}$**,** 377.5 cm$^{–1}$**,** 473.0 cm$^{–1}$**,** 592.3 cm$^{–1}$.

Taking into account possible shifts of the lines in nano-crystal anatase and rutile samples, these may correspond to the following lines: 159 cm$^{–1}$ – anatase line Eg (1) 144 cm$^{–1}$ with blue shift, 238.7 cm$^{–1}$ – rutile line 235 cm^{-1} (two-phonon process), 377.5 cm$^{–1}$ and 473.0 cm$^{–1}$ – are not defined, 592.3 cm$^{–1}$ – rutile line A$_1$g 612 cm$^{–1}$ with red shift.

It is known from published data [13] that in rutile with crystallite dimensions less than 25 nm, lines Eg (447 cm$^{–1}$) and A$_1$g (612 cm$^{–1}$) exhibit red shift with decrease of the dimensions. Besides, the lines are broadened, and their intensity decreases. In [14] also were determined red shift of rutile line A$_1$g (612 cm$^{–1}$) and blue shift of rutile line 235 cm^{-1} with the decrease of crystal dimensions. On a basis of all said above, on can consider the film as one of rutile and anatase mixture. At that, blue shift of line Eg(1) 159 cm$^{–1}$ is practically analogous (a bit more) to those for the films on corundum (up to 157.9 cm$^{–1}$) and on fused silica (up to 158.2 cm$^{–1}$)**.**

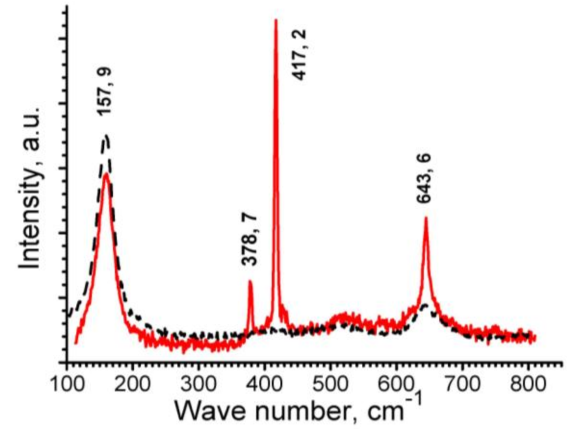

Fig. 2. Raman spectrum of the TiO$_2$ film deposited on a corundum substrate at temperature 560°C and argon pressure 3•10$^{–3}$ Torr. Frequency positions are shown above the lines. The dotted line shows the spectrum of TiO$_2$ film from Fig. 1 deposited on the fused silica substrate under the same conditions

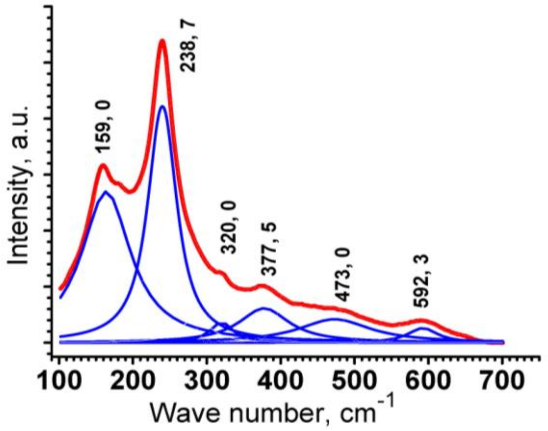

Fig. 3. Raman spectrum of the TiO$_2$ film deposited on a CaF$_2$ substrate at temperature 560°C and argon pressure of 3•10$^{–3}$ Torr. Spectral lines were fitted by a Lorentzian function. Above the lines, their frequency positions are shown

It should be notes that for Al$_2$O$_3$ (corundum), thermal linear expansion coefficient (TLEC) at 300 K equals 5,6 x 10^{-6}/K parallel and 5 x 10^{-6}/K perpendicular to optical axis, which is close to anatase TLEC (4,47×10$^{–6}$/K parallel to **a** axis and 8,43×10$^{–6}$/K parallel to **c** axis [15]). For SiO$_2$ (fused silica) TLEC at 300 K comprises 0.55×10^{-6} /C [16], which is almost an order of magnitude less than that for anatase. It means that anatase films deposited onto fused silica at higher substrate temperature, and after that cooled down to room temperature, are in stretched state. For CaF$_2$ (fluorite) TLEC comprises 18.9 ×10^{-6}/K at 300 K [17], which is 3 to 4 times more than that for anatase. Thus, anatase films after deposition onto heated fluorite, and subsequent cooling down to room temperature, are in compressed state.

For rutile film on three chosen substrate types, the same tendencies for tensions in the films take place since rutile TLEC at 300 K comprises 7.14 $\times 10^{-6}$/K parallel to **a** axis and 9.19 $\times 10^{-6}$/K parallel to **c** axis [18].

Thus, difference in thermal linear expansion coefficients for the substrates has no significant influence on blue shift value for line Eg(1) in Raman spectra of anatase films, although average TLEC for polycrystalline anatase (5.79×10^{-6}/K) is almost an order of magnitude more than that for fused silica, and 3 to 4 times less than that for fluorite.

After annealing of the films in air subsequently for 3 hours at 700°C temperature and for 3 hours at 800°C**,** Raman spectra for the films on fused silica and corundum did not show presence of rutile. Blue shift of the lines decreased, which is considered by us as a consequence of grain dimensions growth after the annealing. Intensity of the lines increased, which can be attributed to improvement of the substance order due to annealing of the defects and decrease of contribution of grain boundaries.

For the film on CaF_2 substrate another situation occurs (Fig. 4). Changes in Raman spectrum are observed after the annealing. Frequency positions of the lines now are: 154 cm^{-1}, 238 cm^{-1}, 321 cm^{-1}, 395 cm^{-1}, 520 cm^{-1}, 649 cm^{-1}, which, taking the shifts into account, may correspond to: 154 cm^{-1} – anatase line Eg(1) 144 cm^{-1} with blue shift, 238 cm^{-1} – rutile line 235 cm^{-1}, 395 cm^{-1} – anatase line 399 cm^{-1} B1g, 649 cm^{-1} – anatase line Eg. (3) 639 cm^{-1} with blue shift. Line at 321 cm^{-1} belongs to fluorite.

Thus, we again have the film with anatase and rutile mixture. At the same time, for anatase line Eg. (1) the blue shift decreased from 160.2 to 154 cm^{-1}), the intensity increased, and the half-width decreased.

Anatase line 649 cm^{-1} is clearly visible. Observed changes can be due to growth of the crystallites and annealing of the defects.

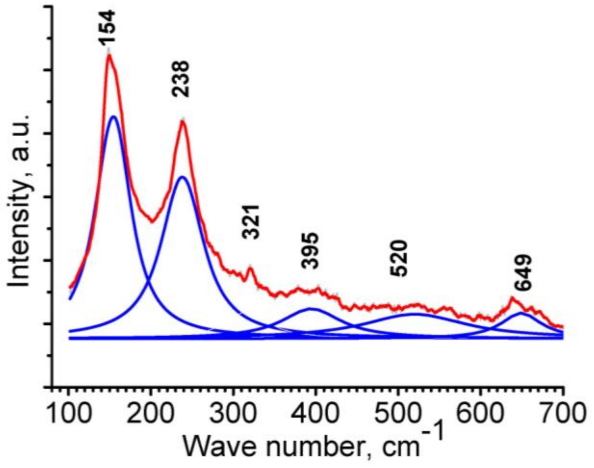

Fig. 4. Raman spectrum of the TiO_2 film deposited on a CaF_2 substrate at temperature of 560°C, under an argon pressure of $3{\bullet}10^{-3}$ Torr, and then annealed in air at 700 C for a 3 hours. Above the spectrum lines, their frequency positions by results of approximation are shown

Rutile appearance at annealing of the samples only on CaF_2 can be due to both appropriate influence of the substrate material, and presence of contraction tension in the film due to different TLEC values for the substrate and the film. As it is known, rutile is titanium dioxide modification with higher density.

We study the surface states of the deposited samples with atomic force microscope (AFM). The results are presented in Table. Ra value are calculated with exponent q = 1 and absolute values of the data (zero mean), as for the Rms this exponent is q = 2. S is the area of scan window, S_n – the area of film surface.

Statistic data on surface characteristics of the test films

Substrate type	Ra, nm	Rms, Nm	S_n/S
Fused silica	3.6	4.55	1.4
Corundum	5	6.4	1.6
Fluorite	10	13.5	1.7

One can see from the table that the maximum roughness is observed for the films on fluorite. High substrate temperature at deposition of the films promotes formation of larger grains and developed surface [2]. In general, usual stochastic relief is formed without specific peculiarities.

CONCLUSIONS

Presented results enable to conclude that the substrate material influences the formation of particular polymorphic modification of titanium dioxide at magnetron-based deposition of the films. Chemical elements contained in the film can shift boundary temperature of anatase-to-rutile transition. TLEC of the substrate in a wide range does not have essential effect on the shift of anatase Raman spectrum lines. The shift and the half-width of the lines can be used for an estimation of crystallite dimensions, similarly to that in case of powders. Synthesis of amorphous titanium dioxide and its polymorphic modifications anatase and rutile are possible in direct current magnetron at proper choice of the substrate material and the synthesis conditions.

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СИНТЕЗ РАЗЛИЧНЫХ ФАЗ TiO_2 В DC-МАГНЕТРОНЕ

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В настоящее время продолжает сохраняться значительный интерес к созданию тонких и сверхтонких пленок, модифицирующих поверхностные свойства материалов. Особое внимание уделяется покрытиям, имеющим важные для практического применения характеристики при невысокой себестоимости процесса их синтеза. К таким можно отнести пленки бинарных соединений некоторых химически активных металлов, например, нитридов и оксидов титана. Последние имеют особое значение в силу широкого спектра уникальных физико-химических и биологических характеристик. Отдельный интерес представляет получение функциональных пленок диоксида титана наноразмерной толщины, что позволяет существенно экономить материал и ускорять осаждение покрытий при снижении их себестоимости. В процессе создания научных основ современных нанотехнологий используются различные методы осаждения покрытий, в том числе и ионно-плазменные. Среди них перспективными являются методы реактивного магнетронного осаждения. Осаждение в DC-магнетроне позволяет синтезировать покрытия из диоксида титана в аморфной и кристаллической фазах в зависимости от условий осаждения. Материал подложки оказывает влияние на возможность получения рутила наряду с условиями осаждения. Изменение в широких пределах линейного коэффициента термического расширения подложки не оказывает существенного влияния на сдвиг линий рамановского спектра пленок анатаза. Показано влияние отжига в воздухе до 800ºС после осаждения на полиморфную модификацию диоксида титана в пленках.

СИНТЕЗ РІЗНИХ ФАЗ TiO_2 У DC-МАГНЕТРОНІ

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Останнім часом зберігається підвищена увага до створення тонких та надтонких плівок, що змінюють поверхневі властивості матеріалів. Особлива увага приділяється покриттям, що демонструють характеристики, важливі для практичного застосування. До таких можна віднести плівки бінарних сполук деяких хімічно активних металів, наприклад, нітридів та оксидів титану. Останні мають особливе значення через широкий спектр їх унікальних фізико-хімічних та біологічних характеристик. Окрему зацікавленість викликає одержання функціональних плівок двоокису титану нанорозмірної товщини. Це дозволяє суттєво економити матеріал та пришвидшити осадження покриттів з одночасним зменшенням їх собівартості. У процесі створення наукових основ сучасних нанотехнологій використовуються різні методи осадження покриттів, зокрема й іонно-плазмові. Серед них перспективними є методи реактивного магнетронного осадження. Осадження в DC-магнетроні дозволяє синтезувати покриття з двоокису титану в аморфній або кристалічній фазах у залежності від умов осадження. Матеріал підкладки впливає на можливість утворення з рутилу на рівні з умовами осадження. Зміни в широкому діапазоні лінійного коефіцієнта термічного розширення суттєво не впливають на зсув ліній раманівського спектра плівок анатазу. Показано також вплив відпалювання в повітрі до 800ºС після осадження на поліморфну модифікацію двоокису титану в плівках.