GAS MAGNETRON DEPOSITION OF STRUCTURED TiO_2 NANOFILMS

A.M. Dobrovolskiy[1], A.A. Goncharov[1], E.G. Kostin[2], E.K. Frolova[1]
[1]Institute of Physics, NASU, Kiev, Ukraine;
[2]Institute for Nuclear Research, NASU, Kiev, Ukraine
E-mail: dobr@iop.kiev.ua

The paper describes the peculiarities of deposition nano-sized titanium dioxide coatings in the cylindrical inverted gas magnetron. It is shown the influence of the main parameters magnetron sputtering, like as working gas pressure and temperature of substrate, on film grain size, porosity and optical properties of deposited TiO_2 nanofilms. The investigations were carried out with films up to 200 nm of thickness.

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INTRODUCTION

It is known that titanium dioxide (TiO_2) thin films offering unique electro physical, optical, chemical, and bactericidal properties have high usage for today's high technologies, primarily, in nanotechnology. TiO_2 films are synthesized by different techniques, among which magnetron ones stand out, since they can be easily adapted to synthesis films of nano size of reactive binary metal compounds [1, 2]. The TiO_2 thin films in rutile or anatase form demonstrate [3] one of the highest values for non-linear refractive index. Other oxides, this value is the third after PbO ($185\cdot10^{-14}$) and Sb_2O_3 (134, $4\cdot10^{-14}$), and at least an order of magnitude larger than the nonlinear refractive index [4] all other oxides. This high value in conjunction with their optical properties and resistance to adverse environments makes titanium dioxide in the first position in the application for the use of films in nonlinear optical devices.

Earlier [5, 6], a gas discharge initiated in an inverted cylindrical dc magnetron was used for synthesis of titanium nitride thin films. In [6] the plasma spectrums in the range of 350…820 nm was recorded with a Plasma Spec portable spectrograph with a resolution of 0.6 nm and define work point for deposition of exactly TiN film. In work [7] this ideas applies to TiO_2 thin film synthesis.

In this work, we study the influence of discharge parameters in a cylindrical inverted magnetron [8] used to deposition titanium dioxide films on morphology, structure and optical properties of the films.

1. METHODS AND SETUP

The magnetron used in experiments consists of a hollow cylindrical titanium cathode, a rotational set of permanent magnets, and rod anodes. The magnets produce an arched magnetic field with a tangential component of 0.03…0.05 T near the anodes. The magnetic field is closed at the cathode and forms a meander. An erosion zone on the cathode has the same form. Because the magnets rotate, the erosion zone rotates following the field, thus providing the uniform cathode material utilization to 80%, which is an advantage over planar magnetron. Another advantage is the stability of parameters during process. In planar magnetron the discharge current should be adjusted to the degree of cathode erosion during operation.

When stoichiometric films of binary metal compounds are deposit by reactive deposition [9], the stability of discharge parameters is high importance, since the film parameters must be reproduced in narrow intervals of the discharge voltage and reactive gas flow rate. These intervals depend, in particular, on the geometry of the magnetron and discharge power [8].

The third advantage of the inverted magnetron over the planar one is that its geometry provides a denser flux of the material sputtered from the cathode toward the substrate. The design of the magnetron chamber described in detail in [5, 7, 8]

Argon and oxygen served as working and a reactive gas, respectively. Both gases were supplied through a separate channel with a precision (≈ 1%) adjustable mechanical valve.

We made ellipsometry, Raman spectroscopy, AFM and optic spectroscopy tests to characterize our films. Also we used traditional optic methods to determine properties of transparent films.

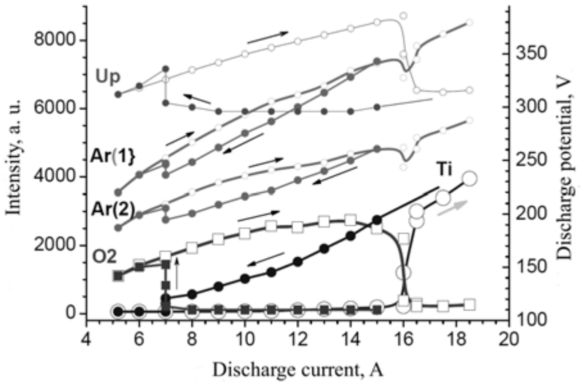


Fig. 1. The typical view for intensity changing of lines Ti – 465. 6 nm, oxygen atom O – 777. 2 nm, and Ar(1) – 812.9 nm, Ar(2) – 753.7 nm; also shown discharge potential U_d from discharge current I_d for fixed oxygen flow. Filled symbols on curves – for directing downward I_d, empty symbols – for direction increasing I_d. The direction of current changes also indicated by the arrows

To monitor the synthesis of the films, we used a Plasma Spec advanced portable spectrometer, which allows real time observation of the discharge plasma optical spectrum. The full spectrum was recorded for 5 ms. The spectrum was recorded with a CCD array and then processed with a dedicated program. Both the full spectrum and lines of interest in the wave length range 350…820 nm were recorded with a resolution of 0.6 nm. The "working point" of the TiO_2 synthesis is controlled with intensity of lines of oxygen and titanium simultaneously with control of magnetron supply power as shown on Fig. 1. Here the working point correspond to 16 A of discharge current area. In our experiments, the deposition start with oxygen flow when intensity of O line (777, 2 nm) increases sharply and after maximum of discharge potential passed for all pressure of argon. With these conditions in process of deposition you can obtain exactly TiO_2 film. All films thickness was about 200 nm.

2. RESULTS AND DISCUSSIONS

It's shown in Fig. 2 Raman spectra for TiO_2 films obtained for temperature of substrate 400°C and pressure $3\cdot10^{-3}$, $5\cdot10^{-3}$, $9\cdot10^{-3}$ Torr. We present the part of spectra in area of Eg. (1) line of anatase.

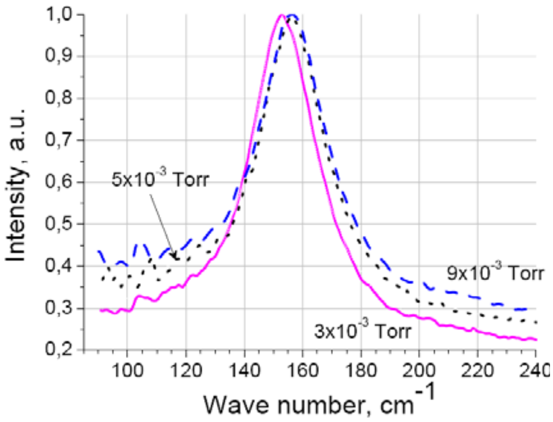


Fig. 2. The Intensity of lines in Raman spectra of deposited films in area of Eg. (1) line of anatase for pressures $3\cdot10^{-3}$, $5\cdot10^{-3}$, $9\cdot10^{-3}$ .Torr and substrate temperature 400°C (a.u.)

From spectra you can see clear anatase lines and influence of pressure on structure of films. The comparisons of the film spectra with spectra of bulk anatase showed the presence of «blue» shift in all lines position and are characteristic for small crystallites. With pressure decreasing the blue shift decreases simultaneously with background level. The background decreasing note decreasing amorphous phase in volume of film and shift decreasing can be connected with increasing of crystallites size.

The place of ω and G of Eg. (1) line change as:

$P_{Ar} = 3\cdot10^{-3}$ Torr, ω =153.3 cm^{-1}, G = 26.9 cm^{-1};
$P_{Ar} = 5\cdot10^{-3}$ Torr, ω =156.5 cm^{-1}, G = 27 cm^{-1};
$P_{Ar} = 9\cdot10^{-3}$ Torr, ω =156.5 cm^{-1}, G = 27.3 cm^{-1}.

So, significant decreasing of ω with decreasing of pressure and increasing of crystallites size in film observed with decreasing P_{Ar} from $5\cdot10^{-3}$ to $3\cdot10^{-3}$. In the same time, the decreasing pressure from $9\cdot10^{-3}$ to $5\cdot10^{-3}$ is not so significant.

In the model from [9] for PVD deposition, pressure of argon is an essential parameter on the film density and crystallites size. The pressure has influence on film structure because of scattering of Ti atoms in the Ar atoms towards the substrate with the loss of energy as a result of which they lose their ability to migrate on the substrate surface due to the initial momentum and incorporate in an orderly structure and heat the substrate. The estimations of atoms free path for different pressure and gas temperature show for argon 300 K quantities of particles that reaches substrate without scattering, 8 cm for our case, are 4.6% for $2.5\cdot10^{-3}$ Torr, 0.21% for $5\cdot10^{-3}$ Torr and 0.0015% for $9\cdot10^{-3}$ Torr. So influence of particles kinetic energy on process of film formation is important for pressure $2.5\cdot10^{-3}$ Torr and neglected for more high pressure. This can explain the value of blue shift of Eg. (1) line for our films.

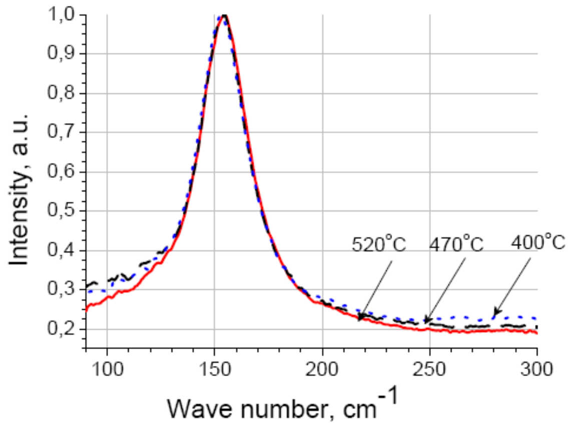


Fig. 3. Normalized Raman spectra TiO_2 films deposited for substrate temperatures 400, 470 and 520°C, pressure $2.5\cdot10^{-3}$ Torr

Other situation is for gas temperature 500 K. Note, the substrate temperature in discharge without additional heating have the same temperature. For this case, quantity of particles that reaches substrate without scattering is 15.8% for $2.5\cdot10^{-3}$ Torr, 2.5% for $5\cdot10^{-3}$ Torr и 0.13% for $9\cdot10^{-3}$ Torr. So we can expect some influence of particles kinetic energy on process of film formation up to $5\cdot10^{-3}$ Torr.

From Raman spectra of TiO_2 films, which are syntheses in range of substrate temperature 400…650°C have anatase phase and not transfer to rutile. On Fig. 3 presented normalized Raman spectra of TiO_2 films deposited for substrate temperatures 400, 470 and 520°C, pressure $2.5\cdot10^{-3}$ Torr. Increasing of substrate temperature led to decreasing the background level and blue shift in Eg. (1) peak place. The line half wide decrease too. After approximation and base line removing we see that half wide of line changing from ≈ 27 to ≈ 26 cm^{-1}, and peak shift from ≈ 154 to ≈ 153 cm^{-1}. We explain these changes as before. Decreasing of amorphous phase in film volume and increasing crystallite size. So with substrate temperature we can control phase of films and density with crystallite size too for crystal phase.

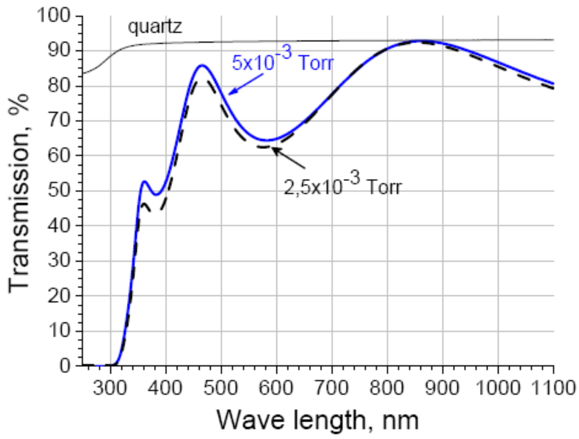


Fig. 4. Transmission spectra of film on quartz substrate and for substrate only, temperature 520°C for pressure $2.5\cdot10^{-3}$ and $5\cdot10^{-3}$ Torr

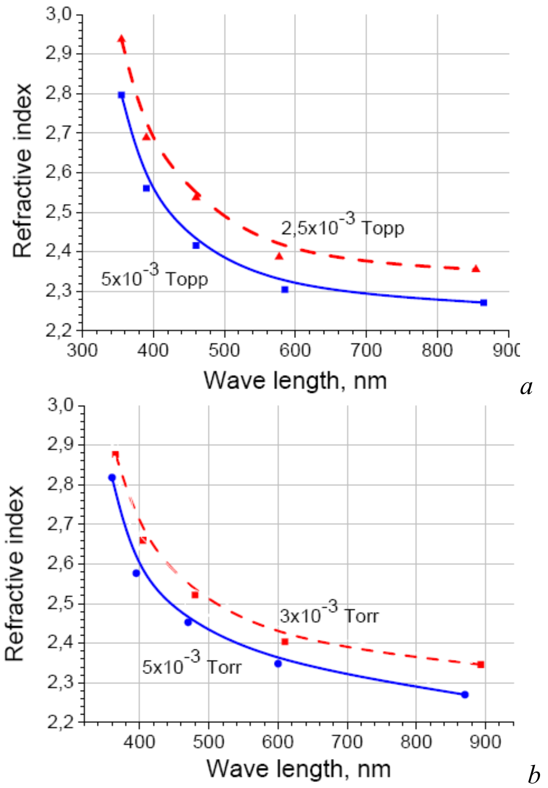


Fig. 5. Refractive index for films obtained with temperatures 400 and 520°C for two pressures 2.5·10^{-3} and 5·10^{-3} Torr for each temperature of deposition

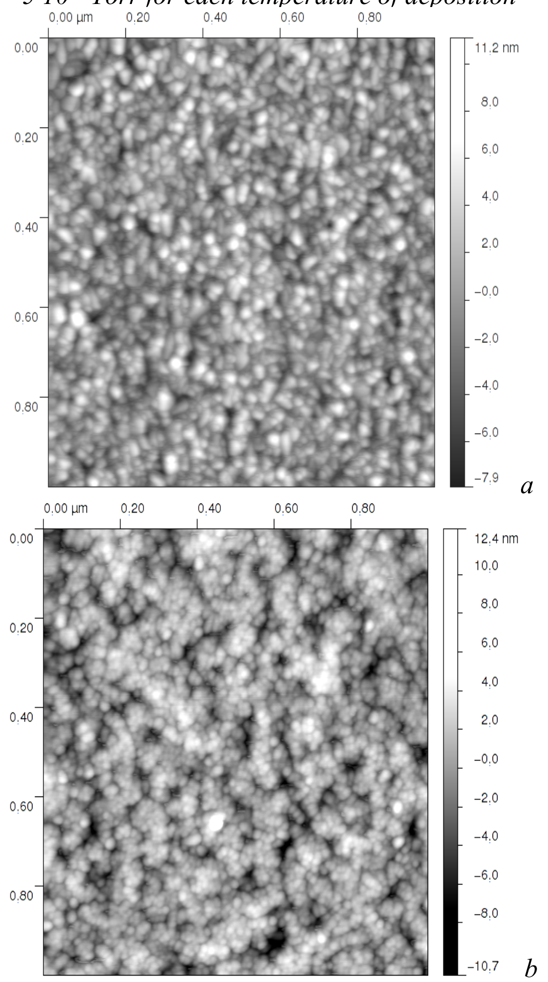


Fig. 6. The morphology of films for different pressures and temperature 400°C. a) anatase, pressure 3·10^{-3} Torr; b) anatase for 9·10^{-3}Torr

Thickness and refractive index of films was measure by method of ellipsometry (λ = 632.8 nm). A data analysis was made with method from [10, 11]. Fig. 4 demonstrates transmission spectra of film with quartz substrate and for quartz substrate only.

Fig. 5 show calculation of refractive index from transparency of film obtained for temperatures 400 and 520°C for two pressure 2.5·10^{-3} and 5·10^{-3} Torr. From Fig. 5 we can see that at lower pressures of argon films have a higher refractive index. It is known refractive index is connected with porosity of films. Thus, we can assume that at lower pressures are synthesized more dense film. This good agree with Raman data spectra.

We test morphology of our films with AFM by NanoScope IIIa Dimension 3000. The results demonstrate an influence of deposition conditions on film morphology. 2D views of film surface are presented on Fig. 6. The impacts of pressure on film structure are clear visible from this two scans 1·1 µm. For high pressure we have more porosity film with larger aggregates and pores size. This is in agreement with our assumptions above.

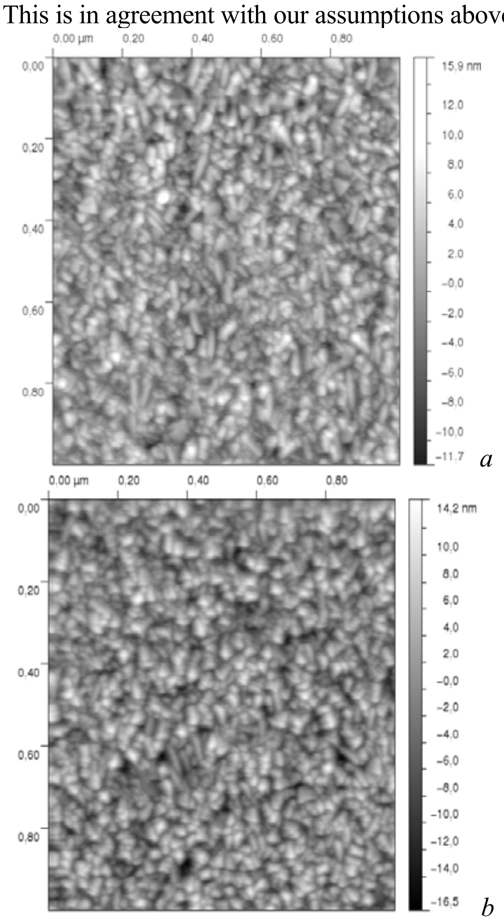
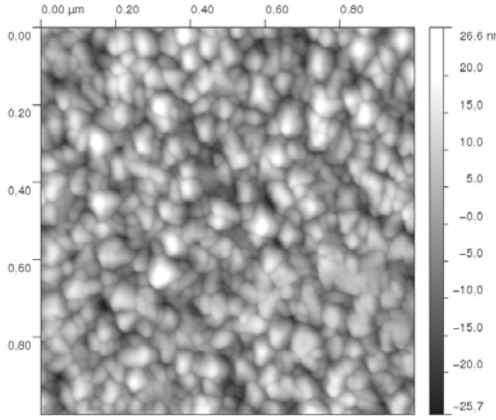


Fig. 7. AFM scans 1·1 µm of anatase films for different pressure, temperature 520°C. a) surface for pressure 2,5·10^{-3} Torr; b) surface for pressure 5·10^{-3} Torr

Fig. 7 present 2D views of film surface for substrate temperature 520°C for two pressure, 2.5·10^{-3} Torr and 5·10^{-3} Torr. We also can see here the influence of pressure on film morphology. The influence is not too impressive because more high substrate temperature. The coming particles can obtain energy for surface migration from substrate. For heated substrate we can see some preferred direction for crystallite growth. This tendency is clearer for lower pressure due to higher kinetic energy of particles in this case. Fig. 8 shows the surface morphology for substrate temperature 640°C. It can see that with increasing of substrate temperature we have increasing of size of conglomerates and a highly developed surface relief.



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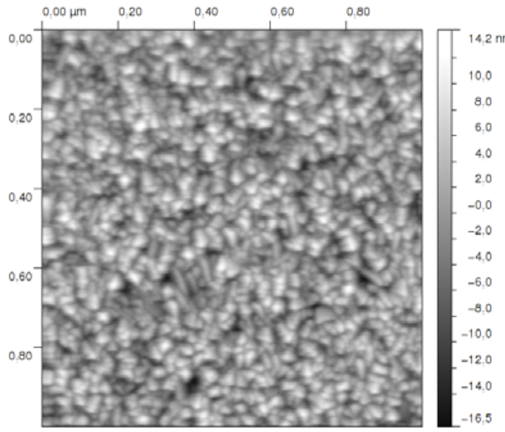

b

Fig. 8. AFM scans 1·1 μm of anatase films for different temperature. a) anatase for substrate temperature 640ºC; б) anatase for pressure $5\cdot10^{-3}$ Torr and substrate temperature 520ºC

CONCLUSIONS

Thus, the obtained experimental results clear show the influence of main parameters of deposition magnetron sputtering process on structure and morphology of TiO_2 anatase structured nano films.

The variation of plasma forming gas pressure and substrate temperature allows to change crystallite size, porosity and morphology of film surface.

For fixed substrate temperature, increasing of pressure lead to arising of the film porosity and, in part, to decreasing crystallites size.

At the same time, the growing of substrate temperature stimulates decreasing porosity and increasing crystallites size and size of crystallites conglomerates. In the substrate temperature range of 400...650°C for titanium dioxide films we observe anatase and no rutile.

Pressure lower $5\cdot10^{-3}$ Torr allow obtaining dense films with low percent of amorphous phase, higher refractive index and higher crystallites size. The increasing of pressure up to 10^{-2} Torr form porous films with developed surface relief and large conglomerates.

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ОСАЖДЕНИЕ СТРУКТУРИРОВАННЫХ НАНОПЛЕНОК TiO_2 В ГАЗОВОМ МАГНЕТРОНЕ

А.Н. Добровольский, А.А. Гончаров, Е.Г. Костин, Е.К. Фролова

Представлены данные об особенностях получения нанопленок диоксида титана в цилиндрическом газовом магнетроне. Показано влияние основных параметров разряда, таких как давление плазмообразующего газа и температура подложки на структуру, морфологию и оптические свойства получаемых покрытий на примере стехиометрического TiO_2.

ОСАДЖЕННЯ СТРУКТУРОВАНИХ НАНОПЛІВОК TiO_2 У ГАЗОВОМУ МАГНЕТРОНІ

А.М. Добровольський, О.А. Гончаров, Є.Г. Костін, О.К. Фролова

Представлено дані про особливості одержання наноплівок двоокису титану в циліндричному газовому магнетроні. Показано вплив основних параметрів розряду, таких як тиск плазмоутворюючого газу та температура підкладки на структуру, морфологію та оптичні властивості одержуваних покриттів на прикладі стехіометричних плівок TiO_2.