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INFLUENCE OF SOLS COMPOSITION ON TOPOGRAPHY OF $TIO_2 – SIO_2$ FILMS BY AFM

SLEDOVANIE VPLYVU ZLOŽENIA SÓLOV NA TOPOGRAFIU $TIO_2 – SIO_2$ VRSTIEV POMOCOU AFM

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Abstract

Influence of composition of five initial sols on topography of prepared films on microscope slide glasses was observed and quantified in $Ti(izoC_3H_7O)_4$ - $Si(C_2H_5O)_4$ - HNO_3 -Acetylacetone - $izoC_3H_7OH$ - H_2O system for preparation of $TiO_2 – SiO_2$ films. The topography of films on microscope slide glasses was performed with AFM apparatus (NT-206) operating in the air ambient conditions. Prepared films were characterized by average height $\bar{z}$ and standard deviation σ, i.e. *rms*-roughness.

Abstrakt

V systéme $Ti(izoC_3H_7O)_4$ - $Si(C_2H_5O)_4$ - HNO_3 - Acetylacetón - $izoC_3H_7OH$ - H_2O pre prípravu $TiO_2 – SiO_2$ filmov bol sledovaný a kantifikovaný vplyv zloženia piatich sólov na topografiu filmov nanesených na mikroskopických sklíčkach. Topografia bola sledovaná pomocou atómovej silovej mikroskopie (AFM). Pripravené filmy boli charakterizované priemernou výškou $\bar{z}$ a štandardnou odchýlkou σ nazývanou drsnosť.

Key words: topography, TiO2 – SiO2 films, AFM

1. Introduction

Titania – silica ($TiO_2 – SiO_2$) based films have aroused considerable interest for optics application, including antireflective coatings and optical planar waveguides, due to their high thermal stability, high chemical durability, low thermal expansion coefficient, and flexibly adjustable refractive index [1, 2]. In addition, $TiO_2 – SiO_2$ mixed oxides can also be considered as attractive materials for catalytic applications due to their high catalytic activity and selectivity [1].

Several techniques such as sol-gel, spray pyrolysis, chemical vapor deposition can be used to prepare titanium dioxide thin films. Among these preparation techniques, the relatively simple sol-gel method is the most widely used. A great deal of experimental work has been carried out on $TiO_2 – SiO_2$ thin film. It is well known that film properties are highly dependent upon the preparation process and surface microstructure. Therefore, the characterization of the microstructure of the surface of thin films is vital to improve the properties of thin films [3, 4].

Atomic force microscopy (AFM) [5, 6] turned out to be very useful for surface projection at nanolevel up to atomic level and for determination of their characteristics. It is used not only for determination of topography of $TiO_2 – SiO_2$ films, but also for characterization using roughness, eventually complex characterization using mathematic-statistical methods. It is also used at study of relations between composition of initial sols and final surface structure and relations between surface structure and final properties [7].

Scope of presented work lies in observation and quantification of influence of composition of five initial sols for preparation of $TiO_2 - SiO_2$ films in $Ti(izoC_3H_7O)_4$ - $Si(C_2H_5O)_4$ - HNO_3 - Acetylacetone - $izoC_3H_7OH$ - H_2O system on topography of prepared films on microscope slide glasses.

2. Experiment

The sol-gel method was used for preparation of $TiO_2 - SiO_2$ films in $Ti(izoC_3H_7O)_4$ - $Si(C_2H_5O)_4$ - HNO_3 -Acetylacetone - $izoC_3H_7OH$ - H_2O system. Sols for coating have been prepared in five different mole compositions according to Table 1. The scheme of film preparation is presented in Fig. 1.

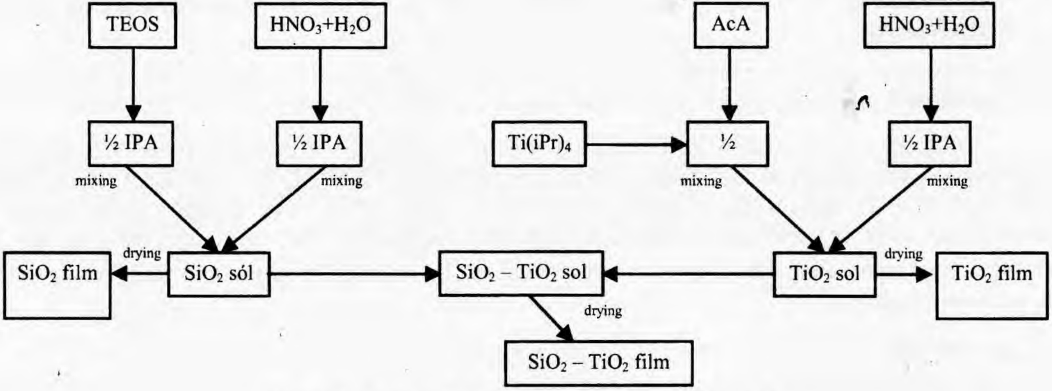

Fig. 1 Scheme of preparation SiO_2 and TiO_2 sols

Table 1 Composition of sols for films preparation

sample	*TEOS [mol]*	*$Ti(iPr)_4$ [mol]*	*IPA [mol]*	*HNO_3 [mol]*	*H_2O [mol]*	*AcAc [mol]*
S	1	0	15.31	0.11	3.92	0
S2T1	2	1	51.45	0.99	8.44	2.12
S1T1	1	1	36.13	0.89	4.52	2.12
S1T2	1	2	56.95	1.67	5.12	4.24
T	0	1	20.82	0.78	0.60	2.12

S = SiO_2, T = TiO_2, S1T1 = SiO_2:TiO_2 in mole ratio1:1, S2T1 = SiO_2:TiO_2 in mole ratio 2:1, S1T2 = SiO_2:TiO_2 in mole ratio1:2

Films have been applied to microscope slide glasses from prepared sols using "dip-coating" method at the rate of 90 mm/min. After coating the films have been dried at 80 °C for 15 minutes and further dried for 50 minutes in muffle furnace at temperatures of 500 °C with temperature increase of 10 °C/min.

Topography of layers

The measurements were performed with AFM apparatus (NT-206) operating in the air ambient conditions. Sample topography was imaged by scanning in static mode using Mikro-Masch silicon cantilevers CSC38/AlBS with spring force constant k = 0.03N/m. Images have been made with raster of 256×256 in the scale of 10×10 μm. Every film has been measured at five randomly chosen places. 2D, 3D images of studied films are in Fig. 2-6.

3. Results and discussion

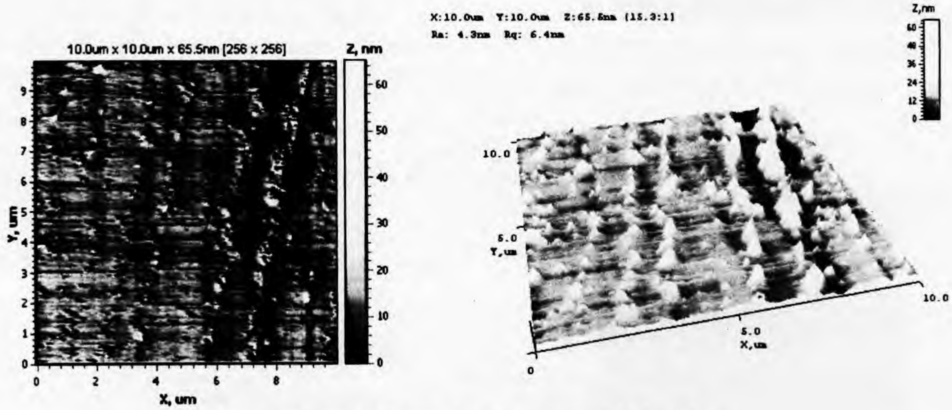

Fig. 2 2D and 3D surface displays of SiO_2 films

The arrangement of round shape in parallel band with the width up to 1 μm and the height up to 50 nm is typical f or SiO_2 film.

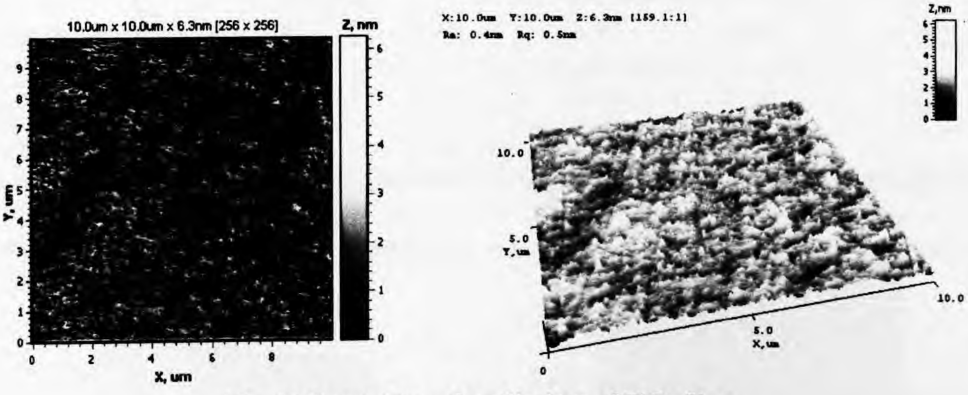

Fig. 3 2D and 3D surface displays of TiO_2 films

TiO_2 film on glass creates „hillocks" with the average height up to 10 nm and the width up to 200 nm and „slots" with the average depth up to 3 nm and the width up to 100 nm.

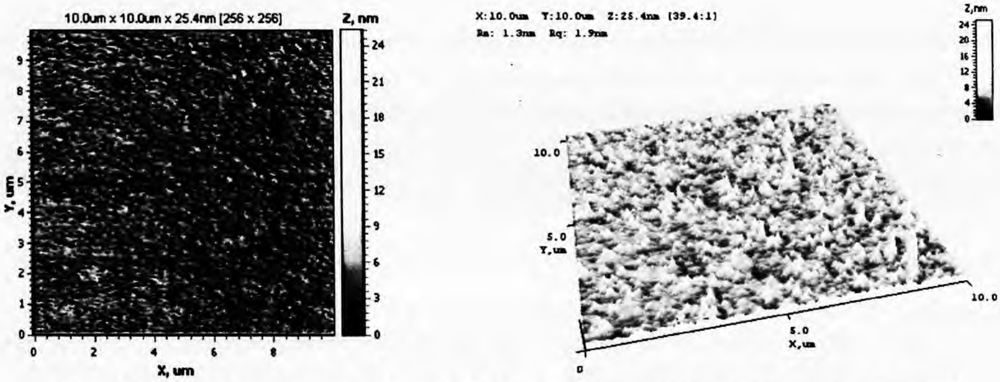

Fig. 4 2D and 3D surface displays of $TiO_2 - SiO_2$ films (SiO_2:TiO_2 in mole ratio 2:1)

The „hillocks“ with the average height up to 10 nm and the average width up to 400 nm are visible on S2T1 film (SiO_2:TiO_2 in mole ratio 2:1).

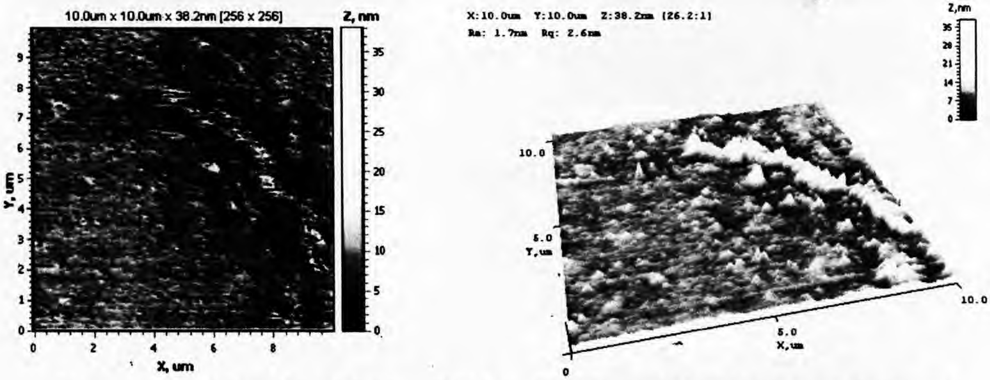

Fig. 5 2D and 3D surface displays of $TiO_2 - SiO_2$ films (SiO_2:TiO_2 in mole ratio 1:1)

The „hillocks“ with the average height up to 10 nm and the average width up to 100 nm are created on glass with S1T1 film (SiO_2:TiO_2 in mole ratio 1:1).

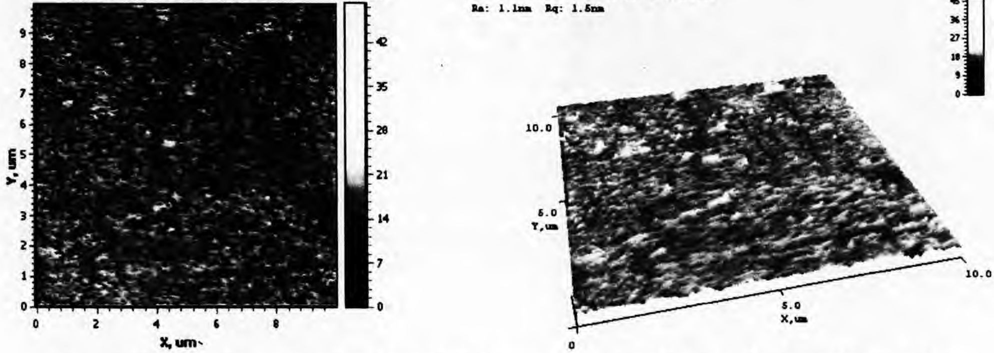

Fig. 6 2D and 3D surface displays of $TiO_2 - SiO_2$ films (SiO_2:TiO_2 in mole ratio 1:2)

S1T2 film (SiO_2:TiO_2 in mole ratio 1:2) on glass creates the „hillocks“ with the average height up to 20 nm and the average width up to 300 nm.

The values of unevenness height at particular points on surface were determined during measuring of surface topography using AFM. As the output of measuring we get the set of unevenness height values that has to be processed in an appropriate manner. We have used following process. Acquired height values were adapted so that in the direction of quick scanning they have been associated to straight line going through two lowest values for particular scan. The same adaptation has been made subsequently in the direction of slow scanning. These adaptations allow acquiring image of the surface that for randomly chosen rough surfaces corresponds with reality the most. These values have been then associated to the lowest point of the image placed at zero position. Set of height values (z_{ij}) acquired in such a way had served for calculation of values describing layer properties for particular images and these are [8]:

1). Mean $\overline{z}$ of measured height values z_{ij}: $\overline{z} = \frac{1}{n.m}\sum_{i=1}^{n}\sum_{j=1}^{m} z_{ij}$ (1)

Mean value $\overline{z}$ characterizes heights z_{ij} associated to the lowest point of the processed AFM image.

Standard deviation σ of measured values z_{ij} around $\overline{z}$: $\sigma = \sqrt{\frac{1}{n.m}\sum_{i=1}^{n}\sum_{j=1}^{m}(z_{ij} - \overline{z}^2)}$ (2)

Values of standard deviation σ of measured heights z_{ij} characterize roughness of particular surface. In the literature it is usually labelled as rms – roughness. Statistical characteristics of TiO_2 – SiO_2 films are in Tab.2.

Table 2 Statistical characteristics of TiO_2 – SiO_2 films

	T	S	S2T1	S1T1	S1T2
Average height / nm	5.358	14.796	6.93	9.612	15.282
Roughness / nm (standard deviation)	0.658	4.668	2.066	2.426	3.21

From Tab. 2 we can see that the films of S2T1 and S1T1 have a smaller average height and smaller roughness than film S (pure SiO_2), while the S1T2 film has larger average height and smaller roughness. The S1T1, S1T2 and S2T1 films have a larger average height and larger roughness than film T (pure TiO_2).

4. Conclusion

TiO_2 – SiO_2 thin films have been prepared by sol-gel process and their topography were performed. The SiO_2 film assigns markedly height values of the average height and roughness than TiO_2 film. The average height and roughness of the mixed films increase when the content of TiO_2 increases. The explanation of obtain results is the object our next study.

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