THE IMPACT OF PHOTOTHERMAL PROCESSING ON TiO_2 THIN FILMS PROPERTIES

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Abstract. *In this paper we present our experimental results concerning the fabrication of TiO_2 thin films by spray pyrolysis deposition method onto different substrates – Corning glass, Si, SiO_2 and optical fibers. The surface morphology of the TiO_2 thin films have been investigated by Atomic Force Microscopy. Raman shift spectra measurements have been done for the optical characterization of the fabricated titania thin films. The post-growth rapid photothermal processing (RPP) at temperatures of 100-800°C for 1-2 min have been applied. Our experimental results prove that by the application of post-growth RPP is possible to essentially improve the crystallinity of the deposited TiO_2 films.*

Key words: *TiO_2 thin films, spray pyrolysis, rapid photothermal processing.*

I. Introducion

The titania (TiO_2) is one of the important materials for nonlinear optics, solar cells, photocatalyst, sensors and biomedical engineering applications. The titania exist in tree crystalline modifications [1]: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). It can be prepared as thin films, nanostructured dots, nanowires, nanotubes, and rib waveguide films [1-7]. There are used different methods of TiO_2 fabrication: sol-gel, hydrolyse, methods of chemical, electrochemical, spray pyrolysis, magnetron sputtering [1-7]. Many researchers prepared the nanostructured TiO_2 on different substrates for applications in biomedical engineering, optical sensors and optical waveguides. In this case a lot of different structural defects and phases of TiO_2 films can be formed. To minimize the concentration of defects and improve the quality of materials it is necessary to optimize the post growing thermal treatment of these structures.

Our work is designated to investigation of the impact of rapid photothermal processing on reducing defect concentrations and improving of crystallite and quality of TiO_2 films deposited on glass, silicon wafers (Si, SiO_2/Si) and onto optic fiber.

II. Experimental

The titanium dioxide films, in our experiments, have been obtained by spray pyrolysis deposition (SPD) method, schematic represented in Fig. 1.

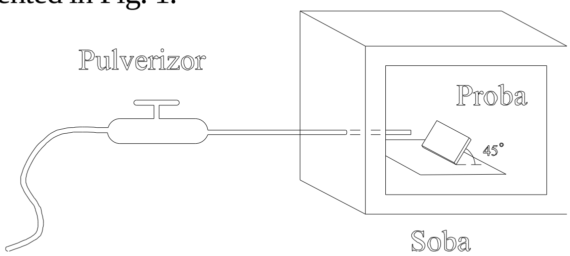


Fig.1. The scheme of the spray pyrolysis method for TiO_2/Si films deposition.

The spray pyrolysis deposition SPD of the TiO_2 on the silicon wafer (TiO_2/Si), (TiO_2/SiO_2/Si), onto Corning glass substrate (TiO_2/glass) and on optical fibers (TiO_2/f.o) have been realized at temperatures of 280-320°C by optimization of the distance, angle and speed of solution flux.

III. Results and discussion

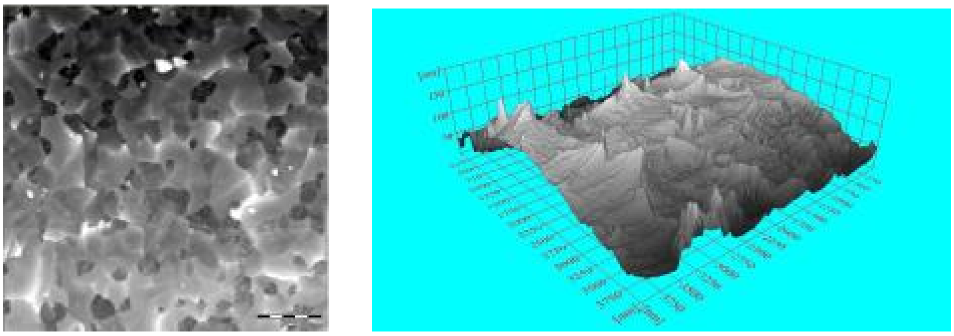
In table 1 are presented the characteristics of TiO_2 films deposited on different substrates at 300°C.

Table l. The characteristics of TiO_2 films deposited on different substrates at 300°C

Substrates	Pressure în pulverizator, (atm)	Distance pulverizator-sample, (cm)	Flux angle Degree (°)	solution mass (ml)	Homogeneity of films
Si (1)	3	14	50	6	Nonhomogen
Si (2)	2	16	45	6	Homogen
SiO_2/Si	2	16	45	6	Homogen
Optic Fibre	2	16	45	6	Nonhomogen
Glass (1)	3	11	55	7.5	Nonhomogen
Glass (2)	2	16	45	6	Homogen
Glass (3)	0.5	16	45	3	Homogen

As it is shown in Table 1, at pressure of 2 atm, distance -16cm, flux angle 45 (^{0}) and solution mass 6 ml have been obtained homogen TiO_2 thin films on different substrates – Si, SiO_2/Si, glass. But onto the optical fiber substrate it was more difficult to obtain the homogen thin films by this method.

All samples after growing have been processed by rapid photothermal treatment at temperature in interval 100-800°C for 1-2 min. By methods of AFM, Raman spectroscopy and CV-characteristics have been investigated the impact of rapid photothermal processing on properties of the samples. The high quality of TiO_2 films have been obtained by optimisation of the post growing rapid photothermal processing (RPP) at temperatures in the interval of 350- 450°C and time of 1 - 2 min. For illustration, in Fig. 2 are presented the 2D and 3D- AFM images of the TiO_2/Si film surface after RPP at 400°C for 60sec.



a) b)

Fig. 2. AFM images of TiO_2/Si after RPP at 400°C and 60sec: a) 2D, 2µm, b) 3D.

The structural homogeneity of TiO_2 films after RPP at temperature 400°C for 60sec was better compare to initial films and structures after RPP at high temperature at 600-800°C for 60sec (not presented here).

In Table 2 are presented the Raman spectrum maximum (shift, cm^{-1}) of TiO_2 films deposited on Si (TiO_2/Si) and on the glass substrates (TiO_2/glass). The same results have been obtained and for structures TiO_2/SiO_2/Si (not presented). More complicate was Roman spectrum for optical fibres (TiO_2/fibre, not presented). For comparison in Table 2 are presented and the results of other authors [5-8].

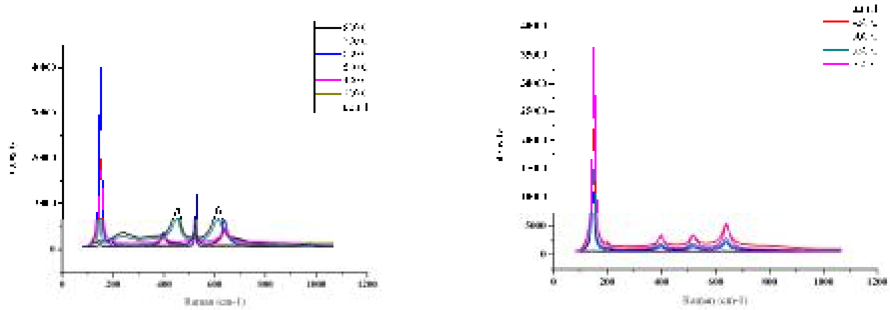
Table 2. The Raman spectral maximum (shift, cm^{-1}) of TiO_2 films deposited on Si and glass substrates

Nr. samples	Raman shift, cm^{-1}											
	Own data											
	Anatase							Rutil				
TiO_2/ Si	144	201	400	514	520	648	-	144	240	449	611	-
TiO_2/ Si	144	198	396	-	519	638	949	144	240	446	612	-
TiO_2/ glass	145	-	398	-	519	639	-	-	-	-	-	-
TiO_2/ glass	145	-	393	-	517	638	-	-	-	-	-	-
	Data from publications [5-8]											
[1]	144	197	399	513	519	639	3208	143	-	447	612	826
[2]	144	197	399	-	-	-	3208	-	446	-	-	-
[3]	144	197	400	516	-	-	-	-	-	-	-	-
[4]	-	197	399	-	-	-	-	-	-	-	-	-

These experimental data demonstrate that our results are comparable with other publications [5-8] and the obtained TiO_2 – films have the same spectra for anatase and for rutile phases. The Raman spectrum for TiO_2 was identified in different publications [3,6,7]. For anatase phase the values of 142 cm^{-1}(our date 144), 196 cm^{-1}(201) and 400 cm^{-1} are attributed to vibrations of O-Ti-O; values of 517 cm^{-1}(520) and 641 cm^{-1}(648) – to vibrations of Ti-O.

For rutile phase 230 cm^{-1}(240), 445 cm^{-1}(448), 610 cm^{-1} (611). The value of 826cm^{-1} is attributed to Si-O-Si bond [26]. Other values of 949 cm^{-1} and 3208 cm^{-1} are not identified.

In Fig. 3 are presented the Raman spectra of TiO_2 films deposited on Si (a) and Corning glass substrate (b).



a) b)

Fig. 3. The Raman spectrum intensity of TiO_2/Si (a) and TiO_2/glass (b) after RPP at different temperatures and time of 60 sec.

Experimentally obtained data are presented in Table 3a,b including all observed intensity maximum for anatase and rutile phases.

From Fig. 3 and Table 3a we can see that after RPP at temperatures 400-450°C the maximum intensity of crystalline anatase TiO_2 (144cm^{-1}) increased from 5634 a.u to 17172 a.u. for TiO_2/Si and from 1860 a.u. to 21951 a.u. for TiO_2/glass. At temperatures higher than 500°C the TiO_2 films transformed from anatase phase to rutile phase and the intensity of each maximum behaves differently.

We observed that the TiO_2 films before RPP are in the amorphous phase, but after RPP at 400°C for 30 sec they transformed to crystallite phase with Raman spectrum corresponding to atanase TiO_2.

Table 3. The Raman spectrum intensity of TiO_2/Si (a) and TiO_2/glass (b) after RPP at different temperatures and duration of 60 sec.

Temperature, a) TiO_2/Si	Raman shift spectra intensity, u.a.										
	Anatase							Rutil			
	1	2	3	4	5	6	7	8	9	10	11
Initial	5636	-	4567	-	5011	5458	-	-	-	-	-
400°C	17172	-	2695	-	4887	4397	-	-	-	-	-
500°C	-	-	-	-	-	-	-	6845	2910	6750	6797
600°C	40234	-	3758	-	5502	6434	-	-	-	-	-
800°C	-	-	-	-	-	-	-	2006	3756	8948	9271

b) TiO_2/glass	Anatase					
	1	2	3	4	5	6
Inițiala	1860	-	1053	-	1024	1145
450°C	21951	-	1374	-	3490	5345
500°C	10882	1045	1508	-	1491	2203
550°C	14984	-	1919	-	1993	2863
600°C	5377	-	1093	-	1134	1551
650°C	36511	-	3541	-	3392	5459

IV. Conclusions

In this paper we presented our experimental results concerning the fabrication of TiO_2 thin films by spray pyrolysis deposition method. Measurements of Raman shift spectra have been done for the optical characterization of the of the titania thin films. We shown that by application of post-growth rapid photothermal processing at different temperatures is possible to improve the crystallinity of TiO_2 films deposited onto different substrates – glass, Si, SiO_2 and optical fibers.

V. Referenses

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