Raman Spectra of TiO_2 Thin Films Deposited Electrochemically and by Spray Pyrolysis

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***Abstract* — In this paper we present our experimental results concerning the fabrication of TiO2 thin films by spray pyrolysis and electrochemical deposition method onto different substrates – Corning glass, Si and optical fibers. The surface morphology of the TiO2 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 1-3 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 TiO2 films. .**

***Index Terms* — TiO_2 thin films, spray pyrolysis, rapid photothermal processing.**

1. INTRODUCTION

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 reduction of defect concentrations and improving the crystallinity and quality of TiO_2 films deposited on glass, silicon wafers (Si, SiO_2/Si) and onto optic fiber.

2. EXPERIMENTAL

The titanium dioxide films, in our experiments, have been obtained by two methods: spray pyrolysis deposition (SPD) and electrochemical deposition.

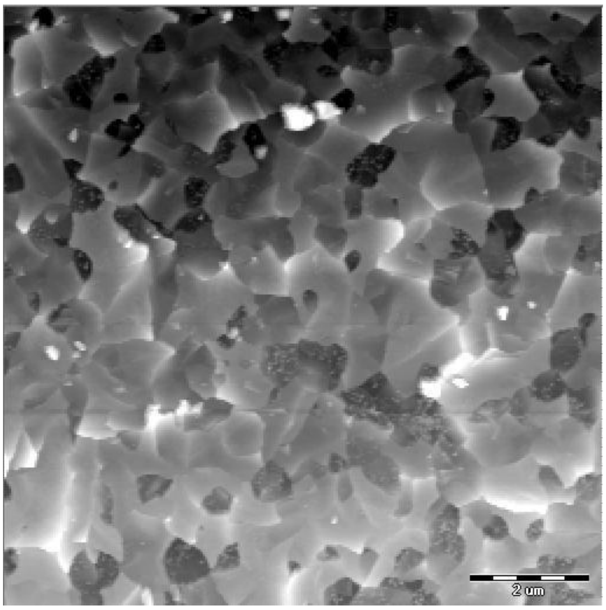
The spray pyrolysis deposition SPD of TiO_2 on the silicon wafer (TiO_2/Si) or (TiO_2/SiO_2/Si), on glass substrate (TiO_2/glass) and on optical fibers (TiO_2/f.o) have been realized at temperature of 280-320°C by optimization of distance, angle and speed of solution flux. The spray solution has been prepared by reaction of two components:

$$TiCl_4 + C_2H_5OH \rightarrow TiCl\,(OCH_2CH_3)_4 + HCl\uparrow.$$

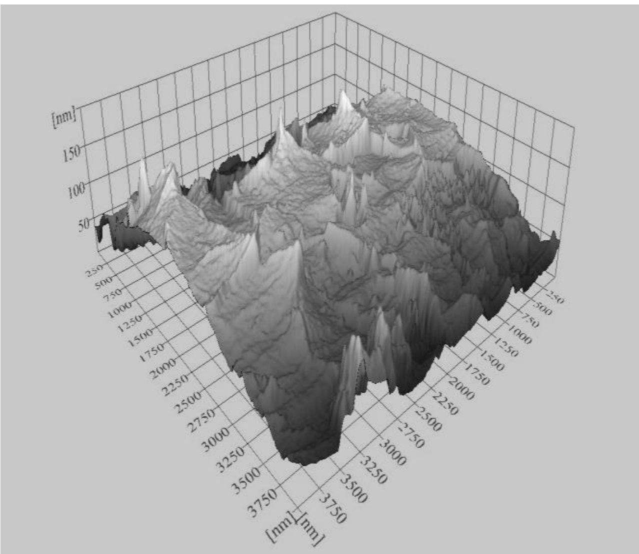
The electrochemical deposition have been done on the base of two solutions:
1) – 0.01 M $TiCl_3$ and 2) – 0.1 M KNO_3 (0.77 ml $TiCl_3$+475 mg KNO_3+50 ml H_2O). The high quality films have been obtained from precursor solution of (0.01 M $TiCl_3$) at voltage U=20 V, time 30 min and initial current intensity 100 mA. For second precursor solution ($TiCl_3$ + KNO_3 + H_2O) the TiO_2 films have been deposited at voltage U=30 V, time 3 hours and current intensity of 20 mA – 100mA.

3. RESULTS AND DISCUSSION

Homogeny TiO_2 thin films on different substrates – Si, SiO_2/Si, glass have been obtained by spray pyrolysis method at pressure of 2 atm., target distance 16 cm, flux angle 45(°) and solution mass 6ml. But on optical fiber substrate it was more difficult to obtain the homogenized thin films by this method.

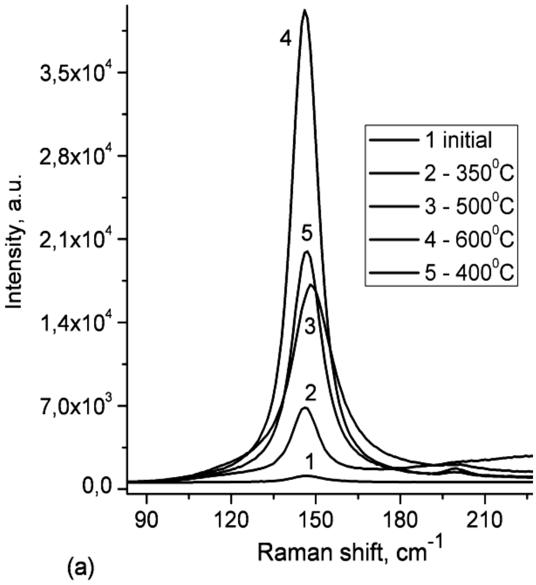


a)



b)

Fig. 1. AFM images of TiO_2/Si after RPP at 400°C and 60sec: a) 2D, (2μm scale), b) 3D.



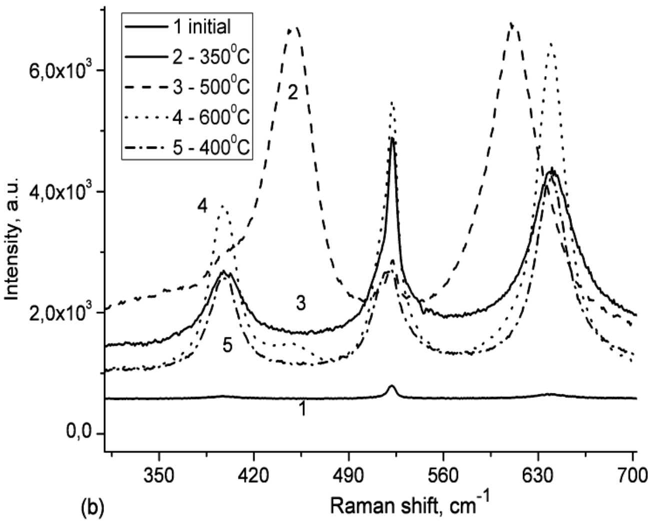


Fig. 2a,b. The Raman spectrum intensity of TiO_2/Si after RPP at different temperatures and 60 sec (obtained by spray pyrolysis method).

All samples after growing have been processed by rapid photothermal treatment at temperature in the interval of 100-800°C for 1-2 min. By AFM and Raman spectroscopy have been investigated the impact of rapid photothermal processing on properties of the TiO_2 thin films. Raman spectra were measured at room temperature with a Confocal MonoVista CRS spectrometer, excitation wavelength 532 nm.

The high quality of TiO_2 films have been obtained by optimization 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. 1 are presented the 2D and 3D-AFM images of the TiO_2/Si film surface after RPP at 400°C for 60 sec.

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 higher temperature at 600-650°C for 60 sec.

Our experimental data are comparable with data of other authors [5-7] and the obtained TiO_2 – films have the same spectra for anatase and for rutile phases.

The Raman spectra for TiO_2 were identified from different publications [3, 6, 7]. For anatase phase the values of 144 cm^{-1}, 201 cm^{-1} and 400 cm^{-1} are attributed to vibrations of O-Ti-O; values of 520 cm^{-1} and 648 cm^{-1} – to vibrations of Ti-O. For rutile phase the maximum are at 240 cm^{-1}, 448 cm^{-1}, 611 cm^{-1}.

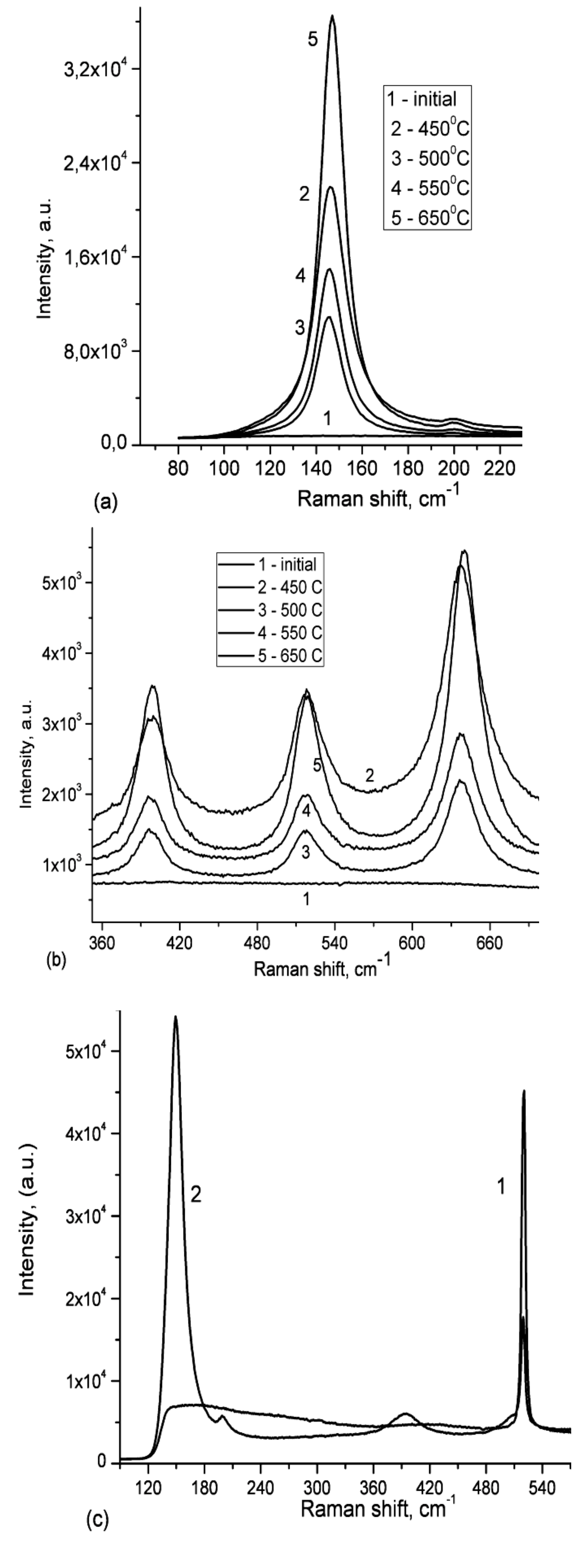


Fig. 3. The Raman spectrum intensity of TiO_2/glass (a,b) after RPP at different temperatures and time of 60 sec (obtained by spray pyrolysis); (c) –samples obtained by electrochemical deposition, 1 – initial; 2 – RPP 450°C.

In Fig. 2 are presented the Raman spectra of TiO_2 films deposited on Si (a,b) by spray pyrolysis method, after RPP at different temperatures and for 1 min: 300-600°C.

In Fig. 3a,b are presented the Raman spectra of TiO_2 films deposited on Corning glass substrate by spray pyrolysis method, and TiO_2 deposited by electrochemical method (c) after RPP at different temperatures for 1 min: 300- 650°C.

From the experimental data presented in Fig. 2 and Fig. 3 one can see that after RPP at temperatures 400-450°C the maximum intensity of the crystalline anatase TiO_2 (144cm^{-1}) increased from 5634 a.u. to 4×10^4 a.u. for TiO_2/Si and from 1860 a.u. to 3.5×10^4 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 60 sec they transformed to crystallite phase with Raman spectrum corresponding to anatase TiO_2. The results obtained for the electrochemical deposited TiO_2 films are presented in Fig. 3c.

4. CONCLUSIONS

In this paper we presented our experimental results concerning the results of RPP impact on TiO_2 thin films obtained by spray pyrolysis and electrochemical deposition methods. Measurements of Raman shift spectra and AFM shown that by application of post-growth rapid photothermal processing at different temperatures is possible to reduce the concentration of structural defects and improve the crystallinity of TiO_2 films deposited onto different substrates.

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