Wetting Properties Modification of TiO_2 Layer by Femtosecond UV Pulses

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In present work we have used femtosecond laser pulses to create different surface morphologies of titanium dioxide (TiO_2). TiO_2 layers were prepared from commercially available paste 13 nm, Ti-nano-oxide on glass substrates. Third harmonics (λ = 343 nm) of femtosecond Yb:KGW laser (pulse duration τ = 300 fs) have been used to create TiO_2 surfaces (4x4 mm) of different morphology. Controllable pulse density was set to 2000 pulses per mm of length in X and Y axis. Beam diameter at $1/e^2$ was 3,2 mm. F=75 mm plano-convex focusing lens have been used. Pulse energy has been varied from 0,02 μJ to 0,17 μJ to create different surface morphology. The surfaces have been characterized using optical microscope, profiler and scanning electrons microscope (SEM). Wetting characteristics where measured directly measuring static contact angle between layers surface and surface of distilled water droplet using CMOS camera. Contact angle was measured during 60 seconds after placing droplet on TiO_2 surface, because layer is nano-porous and part of water is being absorbed. The time-dependent changes of wetting angle at specified experimental conditions were video recorded. The volume of water droplet was controlled by microliter pipette (V~0,5μL).

DOI: 10.2961/jlmn.2015.01.0005
Keywords: Femtosecond laser, surface texturing, wetting behaviour, titanium dioxide.

1. Introduction

Wetting properties of different materials, layers, preparation techniques are being actively studied because of their promising applications [1,2]. Wettability of titanium dioxide (TiO_2) is an important parameter in different applications like biomedical devices [3-7], photocatalysis [8-10.], dye – sensitized solar cells [11-14]. In present work we investigate TiO_2 wetting of different surfaces prepared by femtosecond laser irradiation with intention to apply this knowledge in further research of photoelectrical parameters of dye – sensitized solar cells deposited on different TiO_2 surface topographies. There are different ways to prepare different layers of TiO_2 like nanotubes, nanospheres [15], laser treatment [16].

2. Experimental

2.1 Sample preparation

0,7 mm thick BK-7 glass substrate has been immersed in acetone and left in an ultrasonic bath for one cycle (approximately 10 min.). Next ultrasonic bath cleaning cycle has been performed by immersing the substrate into isopropanol. TiO_2 layer have been formed by applying a commercial titanium dioxide paste (Solaronix 13 nm Ti-nanoxide) by doctor blade method [17]. Thickness of the layers was controlled by spacers with 10 μm of height. The samples have been heated in the oven at 450° C for 30 min. Thickness of prepared layers (10 μm ±1 μm) was evaluated by optical profiler.

2.2 Laser surface texturing

Yb:KGW femtosecond (τ=300 fs) laser "PHAROS" (fundamental wavelength λ=1030 nm) has been converted into 343 nm with nonlinear crystals. Laser frequency has been set to 200 kHz. Attenuator has been used to control pulse energy. Experiment has been performed with "Aerotech" linear translation stages and positioning sample regarding laser beam. "A3200, Aerotech" stage controller (with position synchronised output (PSO) function) was used to control translation stages and trigger the laser. Controllable pulse density was set to 2000 pulses per millimetre of length in X and Y axis. Beam diameter at $1/e^2$ was 3,2 mm. F=75 mm plano-convex focusing lens have been used. Pulse energy has been varied from 0,02 μJ to 0,17 μJ to create different surface morphology Software "SCA, Altechna R&D" has been used to describe laser fabrication algorithms. 5 samples were laser treated. Each sample consists of 14 fields in size of 4x4 mm. Each field has been made with different pulse energy. Experimental set-up is shown in figure 1. Laser treatment experiments have been performed in "Altechna R&D" laboratory.

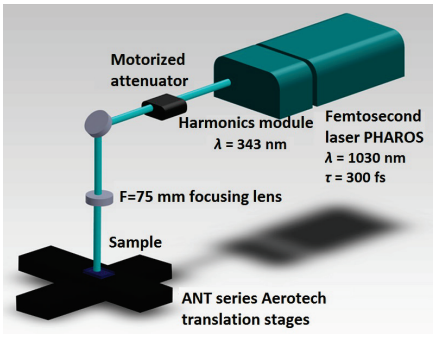

Fig. 1 Principal scheme of laser treatment set-up.

In all presented configurations light polarisation is linear and parallel to movement direction of translation stages. Translation stages movement trajectory is presented in figure 2.

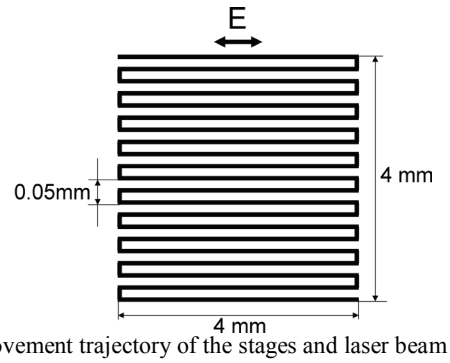

Fig. 2 Movement trajectory of the stages and laser beam polarization regarding trajectory.

2.3 Characterisation of laser treated TiO_2 layers.

After laser processing samples are investigated by SEM, equipped with energy-dispersive X-ray (EDX) detector from "Oxford instruments", optical microscope and profiler "PLμ 2300". Pictures taken with SEM have magnification from 500 to 20000 times. Pictures in the range of magnification 500-1000 are tilted ~20 degrees. Different surface morphology formed by laser irradiation where investigated using profiler to evaluate height of surface.

Wetting characteristics where measured directly measuring static contact angle between layers surface and surface of distilled water droplet using CMOS camera. Imaging setup consists of CMOS camera (744x480 pixels), *f*=200 mm plano-convex focusing lens, 5x microscope objective (NA=0,14), XY adjustable sample holder, light emitting diode λ=550 nm, *P* ~ 1 W. Sample has been illuminated from back side. Contact angle has been measured during 60 seconds after placing droplet on TiO_2 surface, because layer is nano-porous and part of water is being absorbed. Each 4x4 mm square has been measured 5 times. Average values and relative errors has been calculated and displayed in figure 11. The time-dependent changes of wetting angle at specified experimental conditions were video recorded and displayed in figure 12. The volume of water droplet was controlled by microliter pipette (V~0,5μL).

3. Results and discussion

3.1 Surface topography and morphology

SEM images of the treated surfaces and the roughness profiles taken by profiler are presented in figures 3-8. There can be seen evolution of surface profile while laser pulse energy is increasing.

When pulse energy is from ~ 0,02 μJ to ~ 0,03 μJ, periodic surface structures can be observed. Period of high spatial frequency laser-induced periodic surface structures (HSF-LIPSS) has been observed to be ~220 nm. Incident laser beam polarisation is perpendicular to observed fine normal ripples [18]. HSF-LIPSS are shown in figure 3a. Figure 3b is presented to compare ripple formation on rutile crystal TiO_2 surface [19]. In present work ripples are formed on nanoporous TiO_2 layer that gives more irregular periodic surface structures comparing to ripples formed on rutile crystal TiO_2.

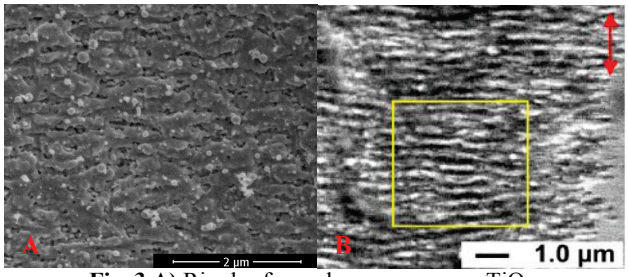

Fig. 3 A) Ripples formed on nanoporous TiO_2.
B) Ripples formed on rutile TiO_2 [19].

In range of ~ 0,03 μJ to ~ 0,04 μJ of laser pulse energy surface topography changes in micron scale appears. Surface shown on figure 4.

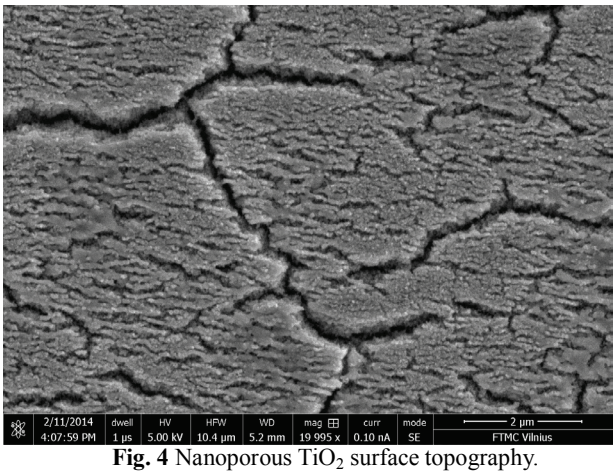

Fig. 4 Nanoporous TiO_2 surface topography.
Pulse energy *E*=0,042 μJ.

Tsukamoto Masahiro and the team reported that femtosecond laser irradiation affects photoconductive properties of TiO_2 layers [20]. Research revealed that electrical resistance of layer decreased under the illumination of visible light, because energy levels between valence and conductive bands were created and for exited electrons this helps to reach conductive band. Up to 100 mJ/cm^2 of laser energy density, resistance of TiO_2 layer decreases rapidly from 10^8 Ω to 10^4 Ω. With higher laser energy density 100 mJ/cm^2 to 150 mJ/cm^2 surface topography was changed and resistance increased by 1 kΩ. In present work surface topography is similar when pulse energy is in range of 0,02 μJ to 0,04 μJ.

When pulse energy is higher than 0,04 μJ, TiO_2 surface is melted down, while TiO_2 underneath is still nano porous. Surface density decreases comparing to volume and layer starts to delaminate. Thickness of delaminated layer is 1,5 μm – 2 μm. Delamination direction is opposite to sample movement regarding laser beam. Delamination evolution while pulse energy is being increased shown in figures 5-8. TiO_2 layer is completely delaminated when pulse energy reaches 0,082 μJ. Partially peeled of layer of TiO_2 can be removed by ultrasonic bath cleaning when laser pulse energy is higher than 0,05 μJ. After removal of peeled of layer there is 8 μm ± 1 μm of TiO_2 layer on the glass substrate left.

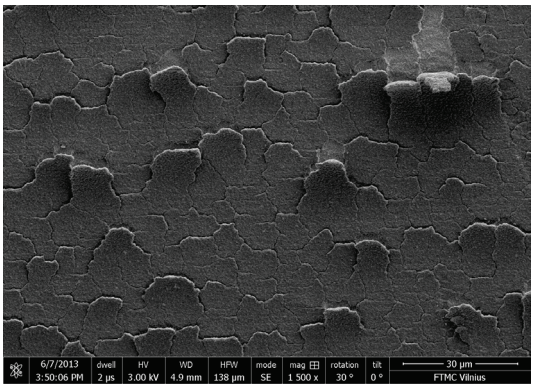

Fig. 5 TiO_2 surface topography. Pulse energy E=0,047 μJ.

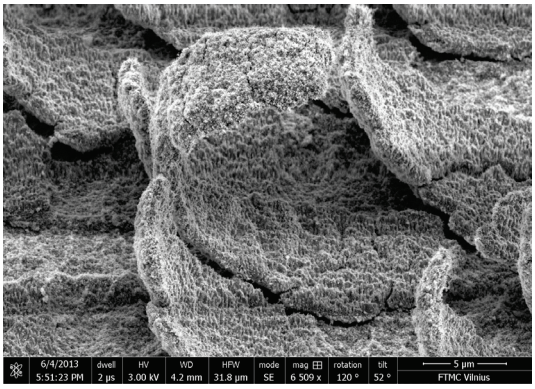

Fig. 6 TiO_2 surface topography. Pulse energy E=0,052 μJ.

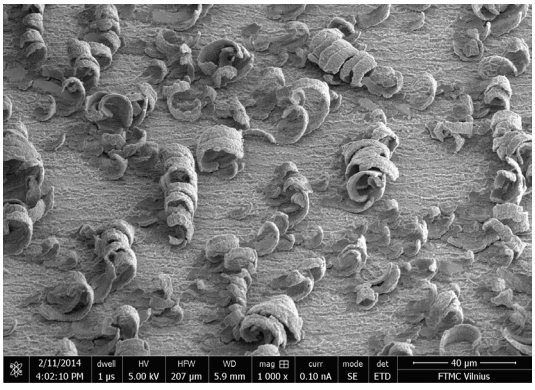

Fig. 7 TiO_2 surface topography. Pulse energy E=0,062 μJ.

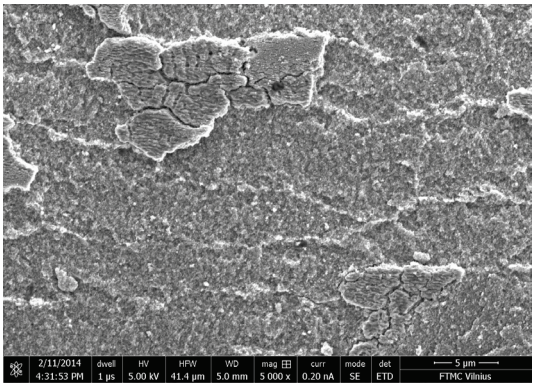

Fig. 8 TiO_2 surface topography. Pulse energy E=0,082 μJ.

When pulse energy is in the range of 0,04 μJ, - 0.08 μJ porous TiO_2 surface is covered with "hook" shaped structures. "Hook" shape structures wall thickness is ~2 μm and height is from 5 μm to 10 μm. Width of this structures is ~ 20 μm and correlates to distance between beam pass path (figure 2). Profile of the surface is shown in figure 9. As discussed later this surface structure influences lower wetting angle.

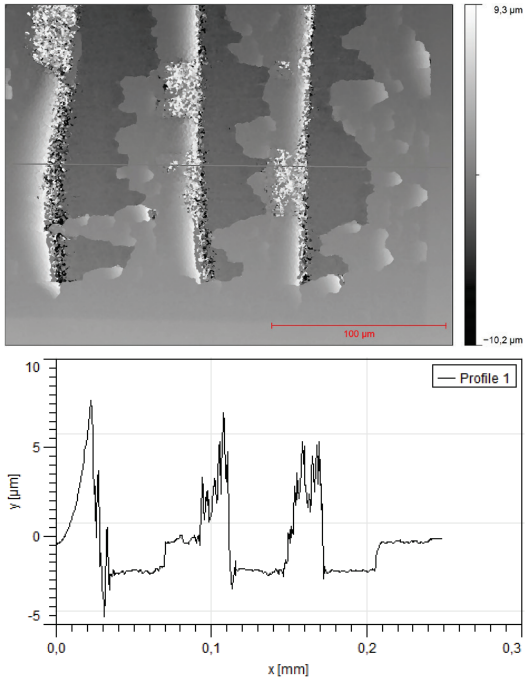

Fig. 9 TiO_2 surface profile. Pulse energy E=0,06 μJ.

Femtosecond laser texturing changes not only surface parameters but also composition of TiO_2. Higher pulse energy causes decrease of O_2 by ~5% and increase of Ti (figure 10). Potassium (K) and silicon (Si) elements comes from glass substrate under the TiO_2 layer. Investigated by EDX spectroscopy method.

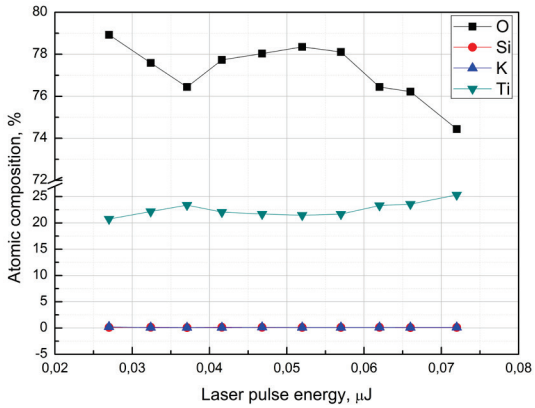

Fig. 10 TiO_2 layer atomic (%) composition dependence on laser pulse energy.

3.2 Wetting behaviour.

Contact angle dependence on laser pulse energy that surface is treaded is shown in figure 11. For comparison contact angle measurement result of laser not affected area (~20°) is presented. The mean of contact angle measurement of laser affected area is smaller in all tested laser pulse energy range. With pulse energy range from ~ 0,02 μJ to ~ 0,03 μJ, contact angle decreases from ~16° to 10°.

This pulse energy range represents surface shown in figures 3 and 4. Micro – scale structures induced by laser reduces contact angle to ~ 10°. Two times lower comparing to laser not affected area. While pulse energy range from ~ 0,03 μJ to ~ 0,07 μJ contact angle is difficult to observe because water droplet spreads very fast and camera set with 5 frames per second cannot exactly detect the moment when water droplet reaches the surface of the sample. XY sample holder is used to move to the edge of the spread droplet to detect the angle. When pulse energy is higher than 0,7 μJ wetting angle increases because pealed parts detaches from substrate.

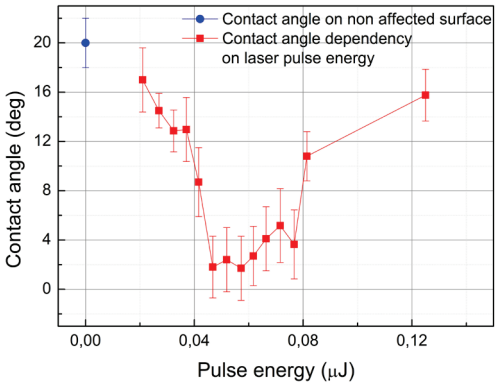

Fig. 11 Dependence of measured contact angle between surfaces of TiO_2 layer and water droplet on energy of treating laser pulse.

Nano porous TiO_2 absorbs water and this makes measurement of contact angle a difficult task. Contact angle evolution of surfaces treated with different laser pulse energy is presented in figure 12. Pulse energy range from 0,02 μJ to 0,042 μJ influences faster dynamics of water droplet. Micro scale cracks absorbs water into the bulk of the layer 4 times faster comparing to surface with no laser treatment. When pulse energy is higher than 0,042 μJ water spreads on the surface and is absorbed instantly. Because of nano porous TiO_2 high surface area in 4x4 mm square water evaporates from the surface in 300 seconds, while the same amount of water stays on the substrate after 800 s where surface is not modified by laser. When pulse energy is higher than 0,08 μJ evolution of water droplet on the surface becomes similar to one where is no laser modification.

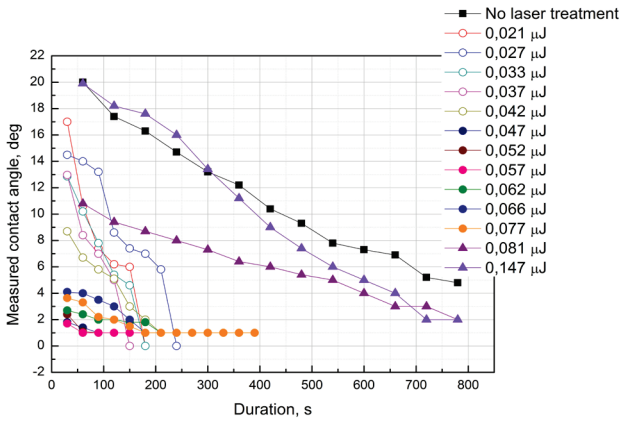

Fig. 12 Observed contact angle dynamics depending on laser treated surface.

4. Conclusions

Femtosecond UV laser treatment enables to modify TiO_2 layer surface. Modifications depending on laser energy density can be from nano ripples to structures up to 10 μm of height (figures 5-9). Laser treatment changes not only surface structure but also atomic composition. With higher laser energy density there is decrease of O_2 and increase of Ti (figure 10). Different surface structure has influence to wetting properties of TiO_2 layer (figure 11 and 12). Increase of hydrophilic properties of TiO_2 layer is a promising improvement in Grätzel type organic solar cells and light emitting diodes.

Acknowledgments

This work was supported by research grant No. VP1-3.1-SMM-10-V-02-007 (Development and utilization of a new generation industrial laser material processing using ultrashort pulse lasers for industrial applications) from the European Social Fund Agency.

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(Received:August 19, 2014, Accepted: December 1, 2014)