Journal of Optoelectronics and Advanced Materials Vol. 7, No. 5, October 2005, p. 2601 - 2606

EXCIMER LASER INDUCED PHOTO-THERMAL CHANGES OF SOL-GEL TiO_2 THIN FILMS♣

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Nanostructured sol-gel TiO_2 thin films spin coated on Na-Ca silicate glass plates are investigated. The films are irradiated by means of excimer (KrF^*) pulsed laser irradiation with different pulse number at a constant laser energy density. The surface morphology of the virgin and laser processed films are followed applying electron optical imaging and atomic force microscopy. The evolution of the surface roughness and pore formation as a result of the laser absorption is demonstrated. The changes in the morphology of laser irradiated samples are found to be accompanied by an optical absorption edge shift to the infrared wavelength range as evidenced by optical spectrophotometric measurements. Conventional X-ray diffraction analysis is applied in order to obtain information on the structure and phase composition. It is established that an intense peak position of anatase phase of the nonirradiated sol-gel films is shifted to lower 2θ range thus evidencing the occurrence of phase transition during the laser modification. The results obtained reveal a new laser stimulated processing route for designing sol-gel titania films with high surface roughness degree and extended, infrared spectral sensitivity.

(Received August 25, 2005; accepted September 22, 2005)

Keywords: Titania, sol-gel thin films, Excimer laser modification

1. Introduction

TiO_2 is an n-type compound semiconductor that is used in sensor technique, as solar cell element, antibacterial and self-cleaning coatings, functional medium in photocatalysis in both nanoparticle and thin film form [1-6]. High chemical inertness, high mechanical stability, low cost and nontoxicity make TiO_2 in the last two decades a desirable photocatalytical material for air and water decontamination [7-12]. Spray pyrolysis, sol-gel method and solvothermal method are usually applied for preparation of nanostructured titania materials [13,14,15]. Sol-gel method appears to be very precise, cost efficient and thus industrially very effective technique [16]. It is established that titania sol-gel nanoparticles with high degree of crystallinity, high specific surface area and porosity exhibit a pronounced photocatalytic activity toward various chemical processes [11,17]. However, due to serious problems with long term stability of nanometer size particles they must be very often subjected to regeneration that is known to be very expensive and complicate procedure. [18] Unlike the nanosized particles, the sol-gel solid state thin films on suitable substrates have a very good storage stability. The low specific surface area seems to be a serious disadvantage of sol-gel films deposited on flat substrates. However, the evolution of high specific surface could be achieved applying physical processing tools as for example laser absorption [19, 20]. It should be reminded that UV light is necessary for initiation of the photocatalytic activity of titania. In order to reach high

♣ paper presented at 3rd International Symposium on irradiation phenomena in chalcogenide, oxide and organic thin films, Tryavna, Bulgaria, June 15-19, 2005

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photocatalytic efficiency titania has to be spectrally sensitized to lower energies. That spectral sensitization has been achieved by selective organic dye adsorption or doping of titania with compound semiconductors as CdS, CuO etc [7, 21]. The latter are known to have a narrower band gap as compared to that of titania. Besides, it has been established that doping with Ag^{+}, Pt^{+}, Fe^{2+}, Ga^{3+} Nb^{5+}, Ta^{5+} is accompanied by an introduction of effective traps for photo generated charge carriers thus preventing the recombination process [4, 12, 22-24]. However, toxic complexes between some chemical dopants and organic pollutants could be formed during UV irradiation [25].

In the present paper pulsed laser irradiation below the ablation threshold is used for monitoring the spectral sensitivity and surface roughness design of sol-gel titania thin films for photocatalitycal purposes. There are two main reasons to apply laser source in that research field. First of all, the laser processing is a dry, fast and versatile modification technique. Besides, the fast melting and cooling processes accompanying the absorption of laser irradiation result in the evolution of catalytically most active phase [19, 20, 26].

2. Experimental

The samples studied represented sol-gel titania thin films spin coated on glass substrates. Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, Merck 97%) was chosen as precursor, isopropanol (C_3H_7OH 97%) as solvent and nitric acid as sol stabilizer. The molar concentration of the starting sol toward the precursor and stabilizer were 0.2 mol/l and 0.02 mol/l correspondingly. In order to achieve a relatively good homogenisation, the sol solution was remained for 1.5 hour under magnet stirring conditions.

Precleaned Ca – Na silicate glass plates were used as substrates. The spin coating of sol-gel titania films was performed at 3000 rev/min for 30 sec. After coating of every single layer the films were nonisothermaly calcinated for 20 min. at 350° C maintaining a mean heating rate of the order of 3°C/min. The thickness of the single layer thus obtained was 70 nm. In that way, 15 layered sol-gel titania films were obtained with an overall thickness of 1.0 μm.

A part of titania sol-gel samples were irradiated with KrF^{*} excimer laser (λ = 248 nm, τ = 20 ns) with single shots or in repetitive rate of 1 Hz at a constant pulse energy density of 300 mJ/cm^2.

The nonirradiated and laser modified samples were subjected to various imaging and analytical techniques. Surface morphology of the films was followed under SEM-Philips 515 scanning electron microscope while their topography was displayed under AFM-Topometrix atomic force microscope. The optical transmission and reflection spectra were recorded in the wavelength range 250 – 800 nm using Carry 5 Spectrophotometer. The structure and phase composition were studied on the basis of X-ray diffraction spectra monitored by means of Philips PW 1050 X-ray diffractometer.

3. Results and discussion

Fig. 1 shows scanning electron micrographs of the top surface of sol-gel TiO_2 thin films before (a) and after single shot (b) and five pulse laser irradiation (c). As seen from the figure the surface of the nonirradiated film (a) is nanostructured and grain like with a mean grain size less than 100 nm. After single shot laser exposures (b) the scanning electron micrographs reveal bubble formation in two distinctly different class dimensions. Most probably the larger are due to gas separation from the glass substrate [20] while the smaller ones from the multilayered titania film itself. As shown by the scanning electron micrograph on Fig. 1c pores and grooves are the morphological features of sol-gel titania samples subjected to laser irradiation with five pulses the number of remaining bubbles being substantially reduced.

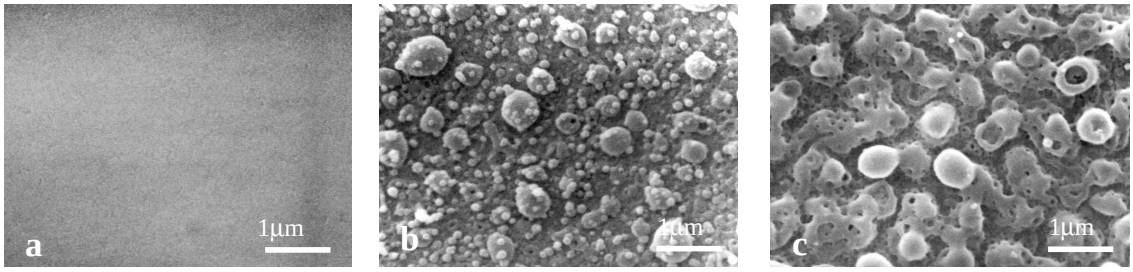

Fig. 1. Scanning electron micrographs of the top surface of 1000 nm thick sol-gel TiO_2 film on glass substrate: non irradiated (a); single shot irradiated (b); irradiated with five laser pulses (c).

Fig. 2 demonstrates the surface roughness of nonirradiated (a) and laser irradiated (b,c) sol-gel titania films as displayed under atomic force microscope. On the right hand side of all 3D – images, gray scales are present related to different surface roughness degree from very low (black) to high (white). As could be evaluated from the gray scales presented the mean surface roughness of the nonirradiated (a), single shot (b) and five-pulse (c) irradiated samples is of the order of 350 nm, 600 nm and 1000 nm respectively. On this basis it could be concluded that the surface roughness increase is a sensitive function of laser irradiation conditions.

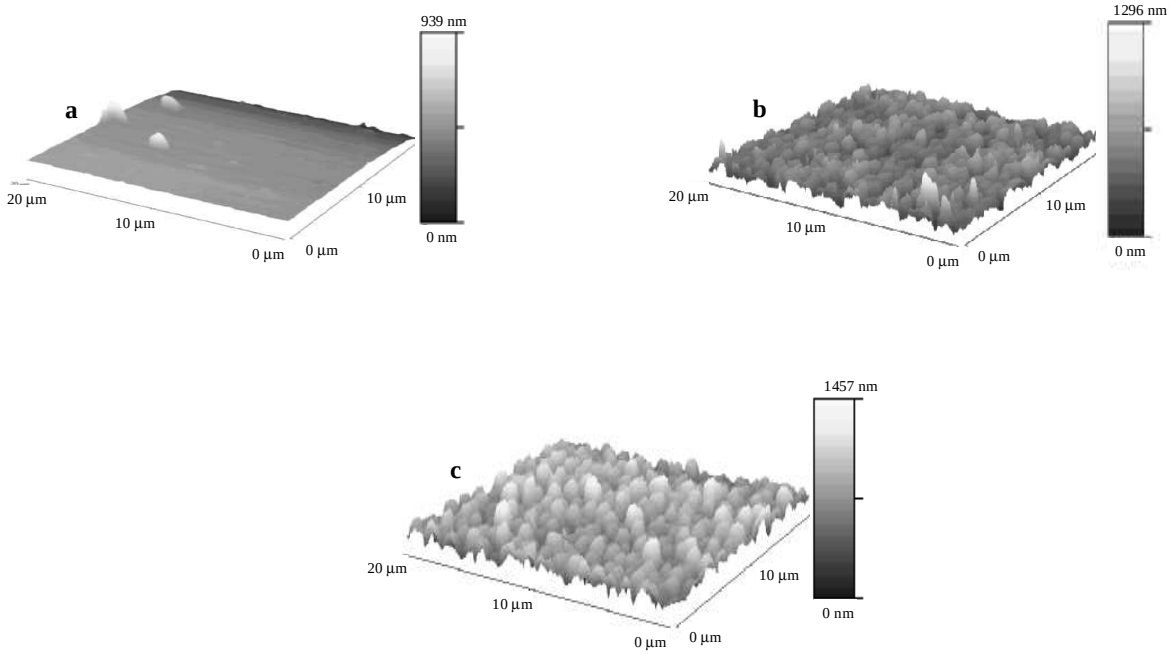

Fig. 2. Atomic force micrographs of the top surface of sol-gel TiO_2 thin film deposited on glass plates:non irradiated (a); single shot irradiated (b), irradiated with five laser pulses (c).

Fig. 3 presents recorded transmission (T) and specular reflection (R) spectra of 1000 nm thick virgin and laser-irradiated sol-gel titania films in the wavelength range 250 – 800 nm. As seen from the figure the transmission of the virgin, nonirradiated samples is of the order of 80 %. After single shots and multiple laser irradiations transmission values considerably reduce at least up to 650 nm resulting in photodarkening effect. The latter is obviously accompanied by absorption edge shift to lower energies and could be reasonably explained with the separation of nano-structured titanium phase. To remind, that photodarkening effects have been observed in excimer laser processed vacuum and sol-gel deposited alumina and zirconia thin films [19, 26].

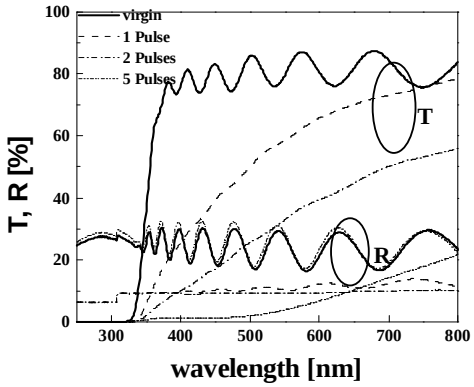

Fig. 3. Optical transmission and reflection spectra of TiO_2 thin films nonirradiated and single shot irradiated, with two and five laser pulse.

The specular reflection spectra show the same trend of decreasing after pulsed laser absorption in the whole wavelength interval studied, however, to a much lesser degree as compared to that of transmission change. On this basis it is possible to make a rough evaluation of the absorption change of sol-gel titania samples after the laser processing and the results obtained are presented on Fig.4. As seen from the figure the optical absorption of sol-gel titania films is strongly related to the laser irradiation conditions. The greater the pulse number the higher the optical absorption, at least in the wavelength range studied.

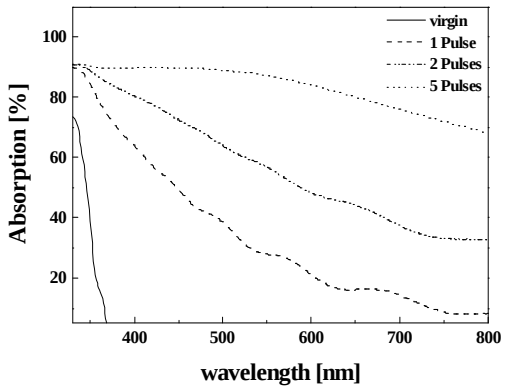

Fig. 4. Absorption of titania thin film before and after the laser irradiation.

X-ray diffraction spectra of the virgin and laser irradiated sol-gel titania films in the range of 2θ 20 °– 70° are presented on Fig. 5.

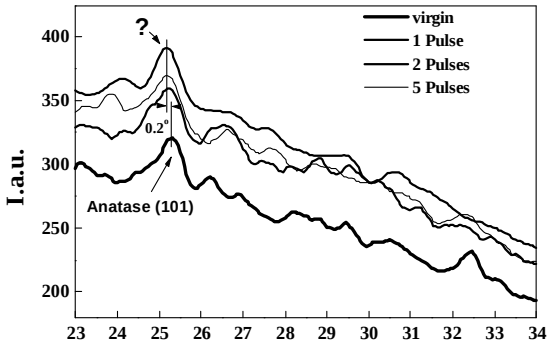

Fig. 5. XRD patterns of TiO_2 thin film virgin, single shot,two and five pulse irradiated.

It was established that the peak in X-ray spectrum at $2\theta = 25.4°$ of nonirradiated sample corresponds to (101) anatase phase that is formed during the calcination process. This peak is obviously shifted to lower 2θ values after laser irradiation. The value of the shift is of the order of 0.2° that is beyond the limit of the experimental determination of the peak position. Formation of metastable titanium oxide phase during the laser induced shock melting and resolidification could be supposed having in mind the evolution of c-ZrO2 and γ–Al2O3 phases in laser modified zirconia and alumina thin films [19, 26]. The results of the evaluation of X-ray peaks at $2\theta = 26.55°$, $2\theta = 29.45°$ $2\theta = 32.41°$ performed gave the reason to make a first conclusion for the presence of oxygen deficient titanium oxide crystalline phases, Ti/O ratio not exceeding 0.54. Since the laser induced changes are known to occur in the near surface region, low angle X-ray diffraction (LAXRD) and selected area high energy electron diffraction (SAED) analysis are necessary in order to establish the proper phase composition of both nonirradiated and laser processed sol-gel titania films.

5. Conclusions

The results obtained in the present study unambiguously show that excimer laser processing at constant energy density varying the pulse number could be successfully used for tailoring the structure and properties of sol-gel titania films that are of great importance for their further application as photocatalyst. The established photo-thermal changes follow the same trend as those observed earlier in laser modified samples at constant pulse number on increasing the pulse energy density thus confirming the versatility of the laser modification as a processing tool. The evolution of high surface roughness that is accompanied by bubble, pore and groove formation upon pulsed UV light absorption in sol-gel titania films is demonstrated. Experimental evidence for the occurrence of light stimulated spectral sensitization resulted in infrared induced spectral sensitivity is presented. Therefore, a promising way is revealed increasing the efficiency of the photocatalytic process on irradiation with low light energies.

In summary, the present results could be regarded as tracing of a new approach for designing sol-gel titania films with high surface roughness degree and extended, infrared spectral sensitivity for the purpose of water decontamination and purification.

Acknowledgements

The authors are gratefully acknowledged to Dr. N. Starbov for the helpful discussions during the experiments and writing the manuscript and to Mr. M. Reppin for AFM analysis.

V. Yordanova is highly obliged to German Academic Exchange Service for Ph.D. Scholarship and the possibility for experimenting at Otto-von-Guericke University - Magdeburg, Germany.

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