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Chemical and structural modifications of laser treated WTi surfaces at different ambient conditions

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Abstract In this work we have studied the influence of laser modification on the composition and structure of tungsten titanium (WTi) thin films, deposited on *n*-type (100) silicon wafers. After deposition, the samples were multi-pulse laser irradiated in a nitrogen, oxygen, and helium ambient. The composition of the WTi/Si sample was determined by Elastic Recoil Detection Analysis (ERDA). Surface morphology was monitored by Atomic Force Microscopy (AFM). In the experiment, typical laser output parameters were: wavelength 1064 nm, pulse duration 150 ps, and laser pulse energy 30 mJ. Surface concentrations of W and Ti, as well as the concentration of gas components nitrogen and oxygen were determinated before and after the action of laser radiation in different ambient conditions. The contents of W and Ti decreased after irradiation due to adsorbed gases from the surrounding atmosphere. After surface irradiation in the inert ambient (He), the concentrations of the components were not significantly changed. In other cases, oxygen was the dominant component at the surface, probably due to the high affinity of thin film components. Also, the morphological changes occurred at the surface of WTi, as an increase in the surface roughness and formation of the granular structures are a result of laser-induced surface oxidation and recrystallization.

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1 Introduction

Nano-structured materials compared with materials composed of a coarse granular structure have significantly improved properties. These properties are determined by the constituent domains at the surface and by their interaction at the grain boundary [1, 2]. Synthesis and modification of nano-structured materials can be carried out with laser processing. Laser processing of the materials are changed composition, chemical state, and structure of the irradiated surface. Use of a laser has many advantages in processing of materials with respect to conventional procedures, primarily due to confining the process on a small area, short processing time, and formation of new types of compounds [3]. Laser irradiation of metals and alloys leads to surface oxidation in air or in a controlled oxygen rich atmosphere [4–6].

The tungsten–titanium alloy as a refractory material has very good physicochemical properties such as thermochemical stability, high melting temperature, and low friction coefficient [7]. On the other hand, mixture of nano-structured tungsten–titanium oxide is an opto-electronic material and can be used for solar cell windows, in electrochromic devices, for information displays, and for color memory devices [8–10]. Photo-catalyst WO_x–TiO_2 can carry out selective catalytic reduction of air pollution and degradation of some organic compounds [11]. Conventional processing of the WTi alloy is extremely difficult because of its hardness and brittleness, and the use of a laser is a potential solution to achieve the desired physicochemical properties on the surface.

To our knowledge, the interaction of tungsten–titanium thin film deposited on silicon substrate (WTi/Si system) with pulsed laser systems is insufficiently studied in literature. Particularly, the studies of the picosecond laser-WTi/Si system interaction in different ambient conditions are not conducted. The purpose of this paper is to explore the impact of laser irradiation on the surface composition and morphological effects of the WTi/Si system. Modifications of WTi thin films were induced by picosecond Nd:YAG laser pulses with a relatively high pulse energy in a nitrogen, oxygen, and helium ambient.

2 Experimental

Thin film of WTi was deposited by dc sputtering (in Balzers Sputtron II system) of W:Ti = 90:10 wt% target. The used substrate was a (100)n-Si wafer, cleaned in an HF solution and in dedeionized water before mounting in the chamber. Before deposition, the sputtering chamber was evacuated by a turbomolecular pump, down to a final pressure 1×10^{-3} Pa. The substrate surface was cleaned by bias sputtering. The cleaning procedure included Ar^+ bombardment of the substrate during 2 minutes at $I = 50$ mA and $V = 1$ kV. The sputtering deposition was performed at room temperature and the partial pressure of argon 1×10^{-1} Pa. Under such conditions, the deposition rate was approximately 0.14 nm/s. The thickness of deposited WTi thin films was 190 nm, measured by Talystep.

In the experiment, the samples were irradiated by a defocused Nd:YAG laser beam with energy of 30 mJ per pulse (fluence is estimated about of 2 J/cm^2). The Nd:YAG laser (model EKSPLA SL212P) was operated in the fundamental transverse mode (TEM_{00} mode). The irradiations of the WTi/Si system were performed in a flow atmosphere enriched with nitrogen, oxygen, or helium. The incidence of the laser beam was at an angle of approximately 45° to the sample surface. The laser beam output characteristics were: wavelength 1064 nm, pulse duration about 150 ps; linearly polarized. The pulse-to-pulse energy variation $\leq$5% and a typical pulse repetition rate 10 Hz. The irradiations of the same surface area were done with 100 successive laser pulses with the constant energy.

The WTi/Si system composition was analyzed by Elastic Recoil Detection Analysis (ERDA) which has several advantages compared to similar methods such as a non-invasive method without matrix effect and it provides absolute concentration values. Measurements were performed using a TOF-ERDA spectrometer developed at the Rudjer Boskovic Institute in Zagreb, Croatia [12, 13]. All measurements were obtained using the I^{6+} ion beam with an energy of 25 MeV before and after laser treatments. The incidence angle toward surface plane was $\theta_{\text{in}} = 20°$ and the scattering angle between the beam and the TOF-ERDA telescope was $\theta_{\text{sc}} = 37.5°$. The telescope is consisted of two timing detectors separated by 523 mm. The particle energy was detected using an ULTRA ion-implanted silicon detector with an area of 300 mm^2. The time detectors were electrostatic mirror assemblies by the Busch design. Energy and time of flight of the recoiled atoms are measured in coincidence which enables us to separate all elements by energy and mass. The accuracy percentage of the TOF-ERDA analysis is mostly limited by statistical error of the spectra and uncertainties in the stopping power values.

The changes of surface morphology induced by laser irradiation in different ambient conditions were examined by atomic force microscopy (AFM), model Solver PRO 47.

3 Results and discussion

The composition of as-deposited WTi thin film obtained by ERDA analysis (Fig. 1a) showed that the distribution of components is approximately uniform throughout the deposit. The ratio of tungsten vs. titanium in the film was

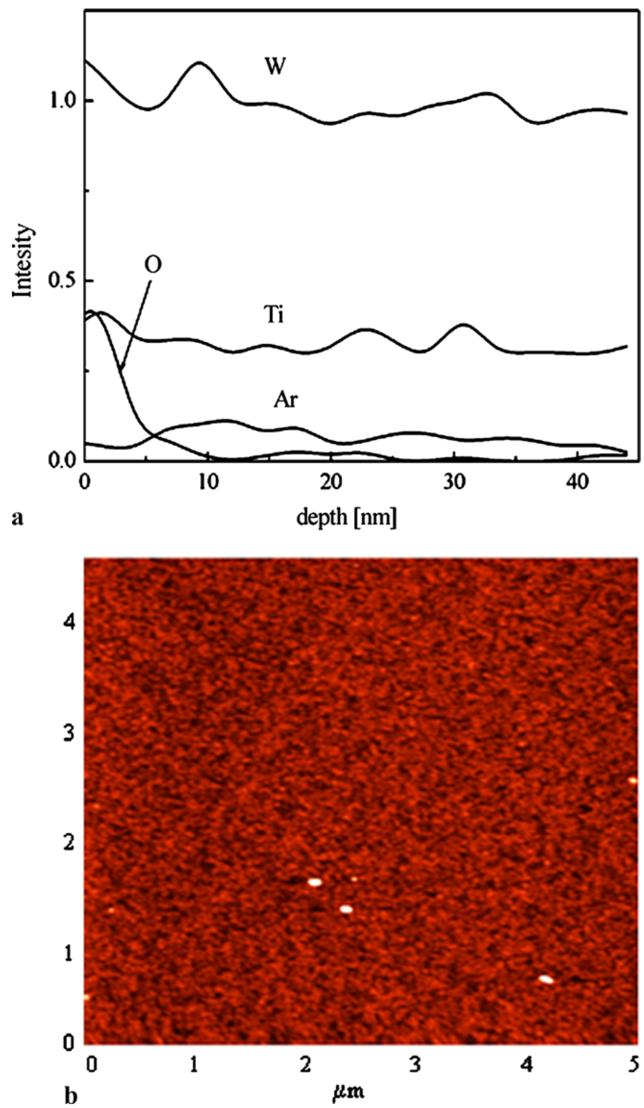

Fig. 1 Composition (**a**) and morphological (**b**) analysis of a deposited WTi thin film (thickness 190 nm) on the Si substrate: (**a**) ERDA spectra and, (**b**) AFM micrograph

nearly equal to initial composition (W:Ti = 70:30 at.%) of the target used for deposition. Minor changes in the composition with respect to the initial values were found in the subsurface region. On the surface of the WTi thin film, oxygen was detected, with relative concentrations of $N_{\mathrm{O}} = 5.6\%$. The concentrations of the main components were $N_{\mathrm{W}} \approx 68.8\%$ and $N_{\mathrm{Ti}} \approx 25.6\%$. The distribution of components in the subsurface region indicated an effect of surface contamination due to exposure of the sample to air after deposition. On other hand, WTi thin film contained a very low concentration of Ar, which was incorporated during the process of deposition. The initial non-irradiated WTi thin film deposited on Si(100) showed its polycrystalline nature with fine grain structure uniformly covering the substrate, as presented by the AFM micrograph (Fig. 1b). The mean surface roughness of the WTi thin film is very close to the value of the roughness of the Si substrate ($S_a = 0.5$ nm), indicating that the deposited film follows the substrate morphology [14].

The irradiation of the WTi thin film was done with action of 100 successive pulses and the laser pulse energy was kept at a value of $E = 30$ mJ. Irradiation with picosecond pulses was accompanied by plasma appearance in all cases. During the laser treatment in an atmosphere of nitrogen and helium plasma was red, while in the atmosphere of oxygen blue plasma appeared. The plasma was created after the first several successive pulses. After laser irradiation, surface of the high reflective WTi thin film were in the form of a broad blurred area, visible with the naked eye.

The ERDA depth profile analysis of WTi thin films after laser treatments in helium, nitrogen, and oxygen atmospheres are shown (Fig. 2a–2c). Subsurface part, which included depth of about 40 nm was analysed. In these graphics can be seen that the dominant component was oxygen in all three cases, while the concentration of major constituents (W and Ti) were reduced. As could be expected, the lowest amount of oxygen was detected in the case of laser treatment in helium (Fig. 2a) and the highest concentration of oxygen was registered in an oxygen-rich atmosphere (Fig. 2c). Only after laser irradiation of the WTi/Si system in nitrogen-rich ambient, a relatively low concentration of nitrogen has been recorded mainly on the surface (Fig. 2b). The ERDA depth profile analysis indicated that probably a oxide layers were formed at the surface. Formation of the surface oxide layer could be connected with a faster diffusion of oxygen than diffusion of the thin film components and other gases, as well as high oxygen solubility in tungsten and titanium [14]. Also, the components of WTi thin film possess a high affinity to the oxygen, especially titanium, which suggests the formation of oxides.

The heat affected zone (HAZ) which was calculated [15] for WTi alloy (thermal diffusivity 0.65 cm^2/s) and laser pulse duration of 50 ps, was about 98 nm, for a single

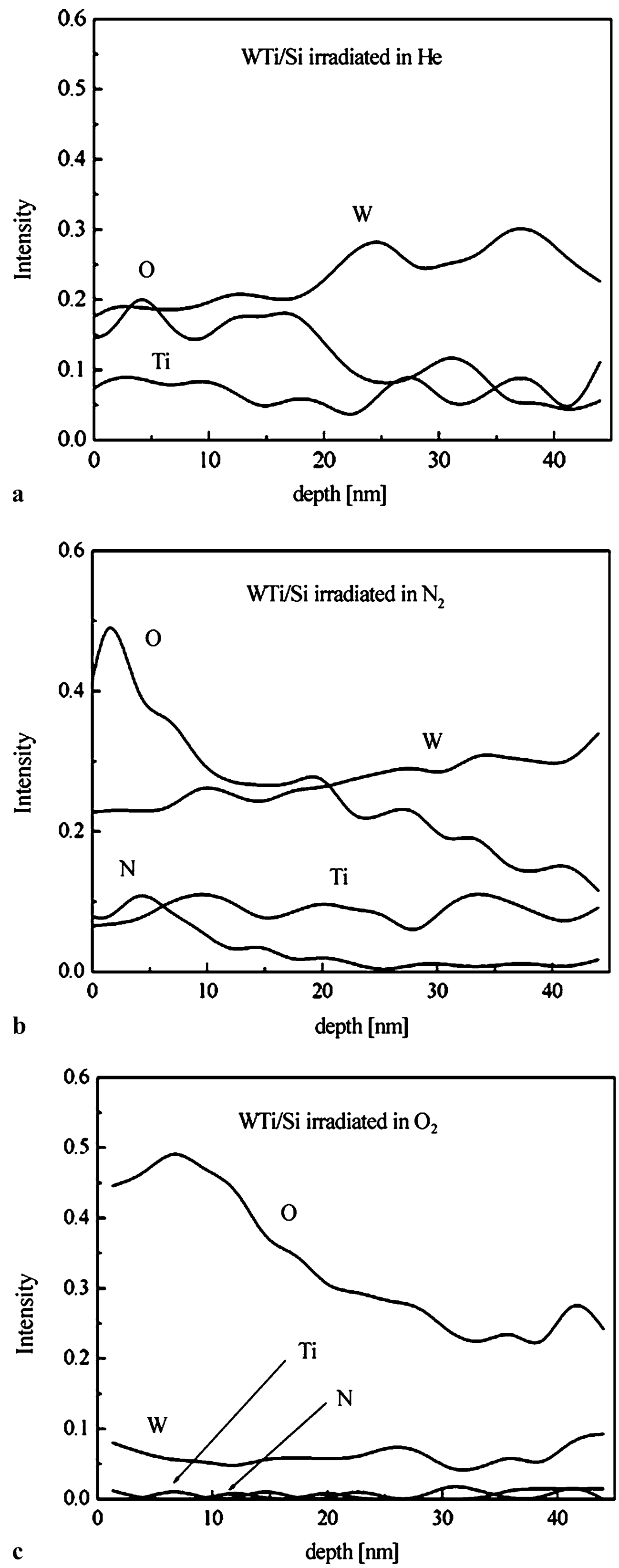

Fig. 2 ERDA spectra of the WTi/Si system after action of 100 laser pulses in: (**a**) helium, (**b**) nitrogen, and (**c**) oxygen enriched ambients

laser pulse. Multi-pulse action on the WTi surface caused reduction of high initial reflectivity (81%) and the fraction of the absorbed laser energy increased. The absorbed radiation energy involves thermalization within the electron subsystem. Due to electron thermal diffusion, energy transfers to the lattice and heat is transported into the metal or alloy. Depending on laser pulse energy, effect of laser irradiation comprises surface temperature risses, thin film melts/decomposition, resolidifaction of molten material, vaporization, ionization gases in front of target, etc. In our experiments, the WTi/silicon target was irradiated with relatively high energy per laser pulse. It could be concluded, that the absorbed energy was sufficient to cause surface melting, the formation of oxides on the surface, and plasma appearance.

Exposure of the WTi/Si samples to the laser radiation in various atmospheres produced different distribution of the components on the surface. Distributions of components on the surface and in subsurface region on depth about 25 nm are shown in histograms (Fig. 3). Concentration of oxygen is relatively high at the surface and exceeds 50% in case of laser action in an oxygen-rich ambient. The surface concentrations of tungsten and titanium were found to be reduced from the initial values (Fig. 3a) and gradually increased in the interior of WTi thin films when the oxygen concentration decreased (Fig. 3b). The ratio of surface concentration of tungsten and titanium in the as-deposited WTi thin film was $N_W/N_{Ti} \approx 2.7$. This ratio remained almost unchanged after laser action in different atmospheres. These results indicated that in all cases, there was a balanced appearance of titanium and tungsten oxides. Thermodynamically, the formation of TiO_2 ($\Delta H_{form} = -944$ kJ/mol) is energetically favored over formation of the WO_3 phase ($\Delta H_{form} = -841.3$ kJ/mol) [16]. After treatment by the laser beam, it can be assumed that the WTi/Si target was covered with an ultra-thin layer of WO_3–TiO_2 oxides.

Morphological changes of the WTi thin films induced by successive action of 100 laser pulses in various ambients were registered by AFM microscopy and presented in Fig. 4. The surface has changed differently in the case of irradiation in helium than in nitrogen and oxygen ambients. After laser irradiation in a helium-rich ambient (Fig. 4a), the most expressed effect was the appearance of micro-cracking with pores as well as vacancies which can be a consequence of vaporization or heating/cooling of the WTi/Si system. It could be assumed that the oxide layer was formed along the edge of micro-cracks during the irradiation in an inert helium ambient on the basis of surface morphology without

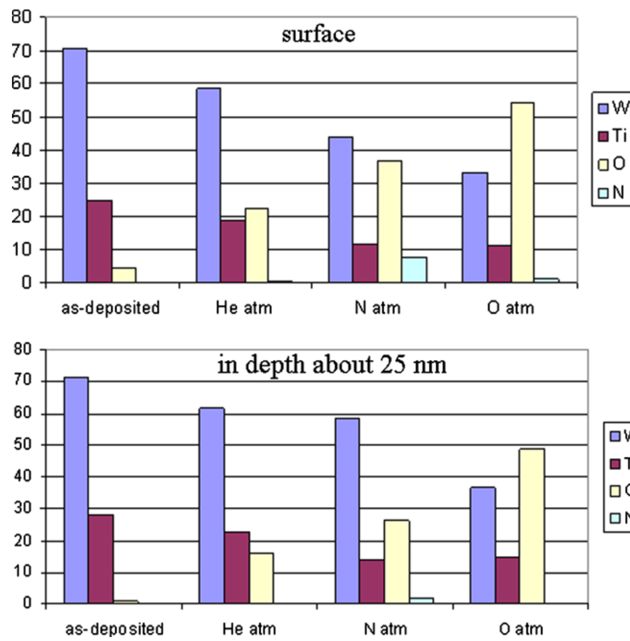

Fig. 3 Histograms of the components distribution on the surface and in depth about 25 nm of the WTi/Si system after laser action in different ambient conditions

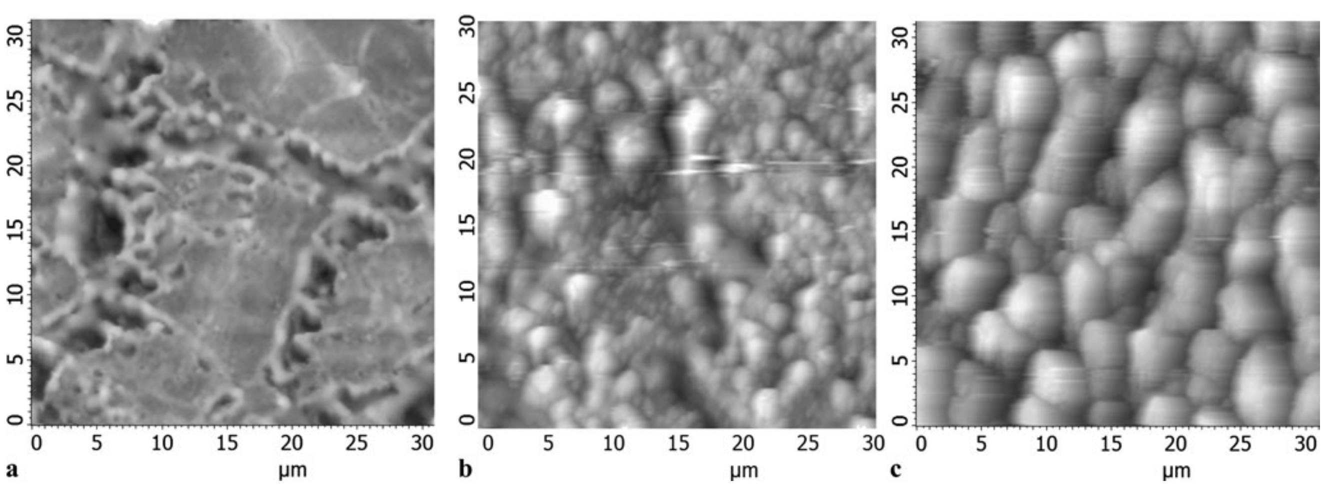

Fig. 4 AFM micrographes of WTi surface after the action of laser radiation in: (**a**) helium, (**b**) nitrogen, and (**c**) oxygen ambients

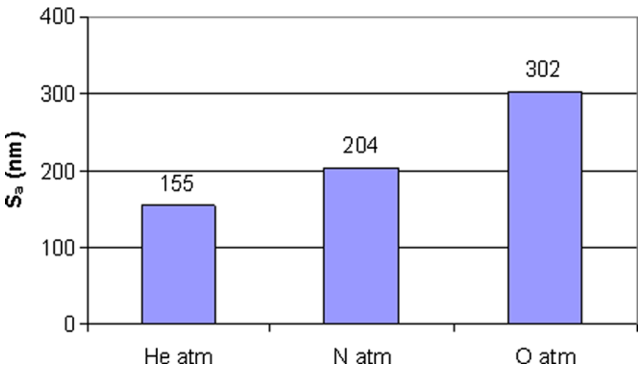

Fig. 5 Histogram of the mean surface roughness WTi thin films after irradiation in different ambient conditions

granular structure and a relatively low concentration of oxygen.

Otherwise, the WTi thin films were fairly uniformly modified after treated by laser radiation in nitrogen and oxygen ambient conditions (Figs. 4b and 4c). A common feature of both cases was the formed granular structure at the surface, but with different grain sizes. The lateral dimensions of the grains at the surface after laser modification were estimated at about 1 µm in a nitrogen-rich ambient, and even up to 5 µm in an oxygen-rich environment. The mean surface roughness of the irradiated areas were significantly increased (Fig. 5) compared to the initial value of as-deposited WTi thin film. The mean surface roughness was determined from irradiated areas which the dimension was 40 µm × 40 µm, in all three cases. The mean surface roughness reached values of 204 nm and 302 nm in nitrogen and oxygen enriched ambients, respectively. Changes of the surface roughness were caused by increasing the temperature of the WTi surface after laser treatment, which generates a series of effects. It is known that these effects include surface hydrodynamic instabilities of the melt, redeposition of the material, condensation, etc. [3]. Also, the material evaporates during the laser pulse action and recondensed on the solidified surface as clusters, whereby the clusters chemically reacted with the surrounding gases [3]. In the present experiment, clusters reacted with oxygen, which was confirmed by high concentrations of oxygen on the surface and in the subsurface region after irradiation.

4 Conclusions

A study of laser-induced surface oxidation on nano-sized WTi thin film deposited on Si substrate is presented. The irradiation process was carried out with the picosecond Nd:YAG laser operated at 1064 nm in the different ambient conditions. Laser pulse energy of 30 mJ was found to be sufficient for inducing chemical and structural changes on the target system. The distribution of components on the surface and in subsurface region was indicated that an oxide layers were formed at the surface due to reduction of the W and Ti concentration and a relatively high concentration of oxygen; however, the irradiation in the inert ambient (He), the concentration of the components were not significantly changed, as well as morphological changes were not indicated to the uniformly formation of the granular structured oxide layer. In the nitrogen- and oxygen-rich ambients, the oxide layers were generated in the form of the granular structure. The lateral dimension of grains were approximately 1 µm and 5 µm in the nitrogen- and oxygen-rich ambients, respectively. The mean surface roughness increases which causes an increase of the oxygen content at the surface, wherein it is at least 155 nm in an inert He ambient and reached a value of 302 nm in the oxygen-rich ambient.

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References

1. H. Gleiter, Acta Mater. **48**, 1 (2000)
2. J. He, J.M. Schoenung, Mater. Sci. Eng. A **336**, 274 (2002)
3. D. Baurle, *Laser Processing and Chemistry* (Springer, Berlin, 2000)
4. P. Stefanov, N. Minkovski, I. Belchev, I. Avramova, N. Sabotinova, Ts. Marinova, Appl. Surf. Sci. **253**, 1046 (2006)
5. L.L. Sartinski, S. Barchikovski, N. Wagenda, B.M. Rud, I.I. Timofeeva, Appl. Surf. Sci. **253**, 4295 (2007)
6. A.K. Mondal, S. Kumar, C. Blawent, N.B. Dahotre, Surf. Coat. Technol. **202**, 3187 (2008)
7. V.G. Glebovsky, V.Yu. Yuschak, V.V. Baranov, E.L. Sackovich, Thin Solid Films **257**, 1 (1995)
8. M. Ferroni, V. Guidi, G. Martinelli, G. Sberveglieri, J. Mater. Res. **12**, 793 (1997)
9. S. Ichikawa, R. Doi, Thin Solid Films **292**, 130 (1997)
10. C. Martinet, V. Paillard, A. Gagnaire, J. Joseph, J. Non-Cryst. Solids **216**, 77 (1997)
11. X.Z. Li, F.B. Li, C.L. Zang, W.K. Ge, J. Photochem. Photobiol. A, Chem. **141**, 209 (2001)
12. I. Bogdanovic Radovic, Z. Medunic, M. Jaksic, Z. Siketic, N. Skukan, Nucl. Instrum. Methods B **231**, 123 (2005)
13. Z. Siketic, I. Bogdanovic Radovic, M. Jaksic, Nucl. Instrum. Methods B **266**, 1328 (2008)
14. S. Petrovic, N. Bundaleski, D. Perusko, M. Radovic, J. Kovac, M. Mitric, B. Gakovic, Z. Rakocevic, Appl. Surf. Sci. **253**, 5196 (2007)
15. B. Gakovic, M. Trtica, D. Batani, T. Desai, P. Panjan, D. Vasiljevic-Radovic, J. Opt. A, Pure Appl. Opt. **9**, S76 (2007)
16. L. Knunyanc, *Chemical Encyclopedia* (Sovietskaya Enciklopediya, Moskva, 1988) (in Russian)