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Titanium dioxide nanoparticles and thin films deposited by an atomization method

G. Machalska [a], M. Noworolnik [b], M. Szindler [b,*], W. Sitek [b], R. Babilas [b]
[a] Graduate of the Silesian University of Technology, ul. Konarskiego 18a, Gliwice, Poland
[b] Department of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, Gliwice, Poland
* Corresponding e-mail address: marek.szindler@polsl.pl

ABSTRACT

Purpose: The article presents the results of research on titanium dioxide synthesized by a sol-gel method that is an easy process enabling the control of the shape and size of particles The purpose of this article is to examine titanium dioxide nanoparticles and thin films deposited by an atomization method.

Design/methodology/approach: Titanium dioxide sol was synthesized by using titanium isopropoxide as a precursor. Optical properties were measured by a UV-Vis spectrometer. Structural studies were performed by Raman spectroscopy. Qualitative analysis was performed by the EDS. Surface morphology of nanoparticles and thin films was performed by the SEM technique.

Findings: The sol-gel method allows the formation of uniform nanoparticles and thin films of titanium dioxide. The atomization method is a successful method for the deposition of sol to the surface of substrates.

Research limitations/implications: The next step in the research will be to investigate the obtained thin films in dye-sensitized solar cells as a semiconductive layer.

Practical implications: Unique properties of produced titanium dioxide nanostructural materials have caused the interest in them in such fields as optoelectronics, photovoltaics, medicine and decorative coatings.

Originality/value: Titanium dioxide thin films and nanoparticles were synthesized using the sol-gel method and then deposited by the atomization method.

Keywords: Sol-gel, Nanoparticles, Thin films, Titanium dioxide, Atomization

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Surface engineering is a relatively young and rapidly developing branch of science. It is applied to achieve new and improve existing properties of engineering materials. Continuous development of this discipline will follow by inventing new synthesis methods and deposition techniques. Theoretical concepts of surface engineering should also be applied to different mechanical systems and electronical devices in following years. Progress in surface engineering will cause incremental improvement of life quality. Titanium dioxide has extensive possibilities of application in environmental engineering and energetics [1]. Titanium dioxide is also commonly known as a biomaterial thanks to its high biocompatibility and osteo-conductivity [2]. It has an optimal bandgap around 3.2 eV which leads to the application as a semiconductor layer in dye-sensitized solar cells (DSSCs) [3], perovskite solar cells (PSCs) [4] and quantum dot sensitized solar cells (QDSSCs) [5]. A popular technique to synthesise nanocrystalline titanium dioxide is a sol gel method, whose final product is white paste. In solar cells this paste is deposited on a transparent substrate which has a transparent conductive layer (TCL) [6]. Most widely used methods for the deposition of titanium dioxide are doctor blade [7], dip coating [8] and spin-coating [9]. A new method which is becoming popular in the deposition of thin films is atomization (Fig. 1).

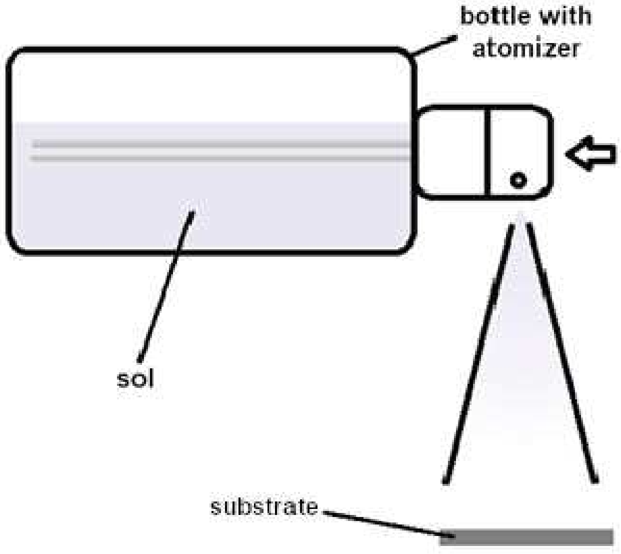

Fig. 1. Scheme of thin-films deposition by atomization method

This method is based on the deposition of sol on the surface of substrate by using a bottle with atomizer. Atomization is characterized by a low cost, simplicity and high speed of deposition. The application of this method allows the control of temperature of the substrate in a wider range than with conventional spraying deposition methods. Moreover, the deposition by atomization does not require an additional carrier gas for spraying [10]. It is reported that atomization has some additional advantages. Based on the comparison of niobium oxide thin-films deposited by conventional spraying methods and by atomization on the same substrates, it was proven that critical concentration of precursor, which affects the perturbation of properties of thin-films is higher in the atomization method. Other properties of obtained thin-films in this research were similar in both methods [11]. Various research groups have attempted to produce thin films of titanium dioxide with different spraying methods like spray pyrolysis [12], electrostatic spray assisted vapour deposition [13,14] and spray-painting [15,16]. However, up to date there have been no attempts to deposit a thin film of titanium dioxide by the atomization method. This publication describes the research on the structure and optical properties of titanium dioxide thin films deposited by the atomization method.

2. Materials and methodology

Titanium dioxide thin films were synthesized using a sol-gel method with two different recipes. The first solution was obtained by mixing 2.5 ml of the precursor in the form of high purity titanium(IV) isopropoxide (98+%), 80 ml of water, 20 ml of acetic acid and 1 ml of nitric acid as catalysts and 20 ml of ethanol as a solvent. The second solution was obtained by using titanium(IV) isopropoxide, ethanol and acetic acid. Ethanol served as a solvent and acetic acid as a catalyst. The precursor-alcohol ratio was 1:8. Two drops of acetic acid were added during mixing. The solutions were mixed with magnetic stirrers for 2 hours at an ambient temperature. Titanium dioxide thin films were deposited on chemically polished silicon substrates doped with boron from Semicon and on glass substrates from Thermo Scientific Menzel. Substrates were degreased in water with a detergent, then cleaned in an ultrasonic cleaner in ethanol for a total of 30 minutes and finally dried to evaporate the ethanol. On each of the substrates, sol was deposited by the atomization method. After each spraying, there was a 60-second interval before the solution was placed on the substrate. This stage was repeated three times. After the deposition of thin film, samples were left to dry at a room temperature. At the end, some of the samples were heated in a furnace. The furnace with the samples was heated to 300°C and 500°C with a heating ratio of 10°C/min. After reaching the planned temperatures, the samples were annealed for 30 minutes and then cooled to a room temperature. The examination of surface morphology of deposited thin films on silicon substrates was performed with a scanning electron microscope (SEM) Zeiss Supra 35. The accelerating voltage was 3-5 kV. Secondary electrons (SE) in-lens detector were used to obtain surface topography images. The images were recorded at magnifications of 2500-200 000 x. Qualitative studies of the chemical composition of obtained thin films were performed by using energy dispersive spectroscopy (EDS). Structural investigations of the deposited thin-films were carried out using an inVia Reflex device. It is an automated Raman system of modular construction equipped with: an AR ion laser of 514 nm wavelength, a single beam Raman spectrometer, a confocal microscope, a high-sensitivity video camera, a set of filters for Raman imaging, a computer with WiRETM 3.1 software. Thin-film reflectance studies were performed using a Thermo Scientific. Evolution 220 spectrophotometer. The tests were performed in a wavelength range of 250-800 nm.

3. Results and discussion

The comparison of the reflection of each sample deposited from the first solution (Fig. 2) showed the highest value for all samples at 320 nm. The surface of polished silicon behaves like a mirror and reflects approximately 100% of the light. Deposition of a layer of TiO_2 nanoparticles by atomization resulted in the reduced reflection in the following range: 350-700 nm. If the sample was not heated at 320 nm, the reflection drop was about 60% and at 350nm the reflection value was about 40%. In a wavelength range of 370-700 nm the value dropped to 20%. In the case of heated samples, the reflection was higher. With a wavelength of 350 nm the reflection value was about 80%, then at 370 nm the value of both samples it dropped to about 60% and in a range of 390-700 nm it dropped to about 40%. Comparing the reflection of the samples (Fig. 3) deposited from the second solution, it was noted that the deposition of a thin layer of TiO_2 by atomization resulted in a reduction of the reflection in a range of 350-700 nm. In the case of an unheated sample the reflection value decreased as much as 40% at 340 nm wavelength, and in a range of 420-700 nm it remained at the level of about 20%. Spectra of heated samples were similar to each other. In a wavelength range of 340-350 nm the light reflection value of both samples decreased to about 50%, then in a range of 420-700 nm it was maintained at about 40%. The results of the structural studies were compiled using WiRETM 3.1. The Raman spectrum of the produced nanoparticles of titanium dioxide was obtained (Fig. 4). Peaks for max 145, 400 and 640 cm^{-1} from anatase and overlapping peaks at 532 cm^{-1} from silicon and anatase were identified on the basis of the characteristic data sheet No. 528. Similarly, the Raman spectrum for the thin film deposited from the second solution was obtained. Peaks from anatase were identified (Fig. 5) and matched on the basis of the characteristic data sheet No. 532.

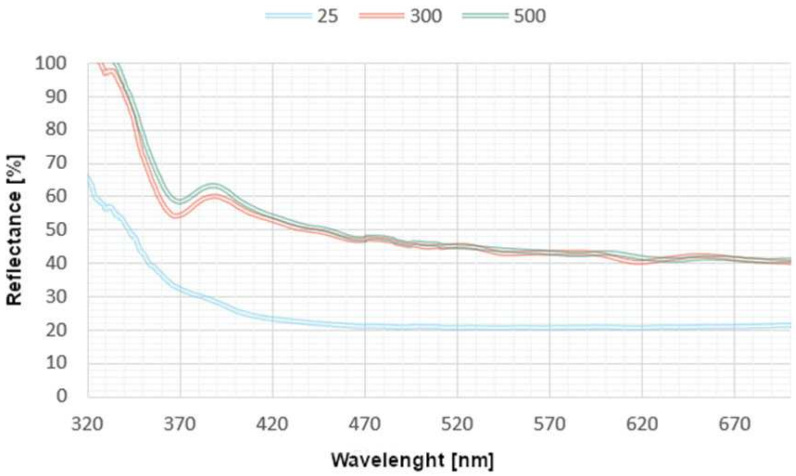

Fig. 2. Reflectance spectra of thin-films deposited from first solution

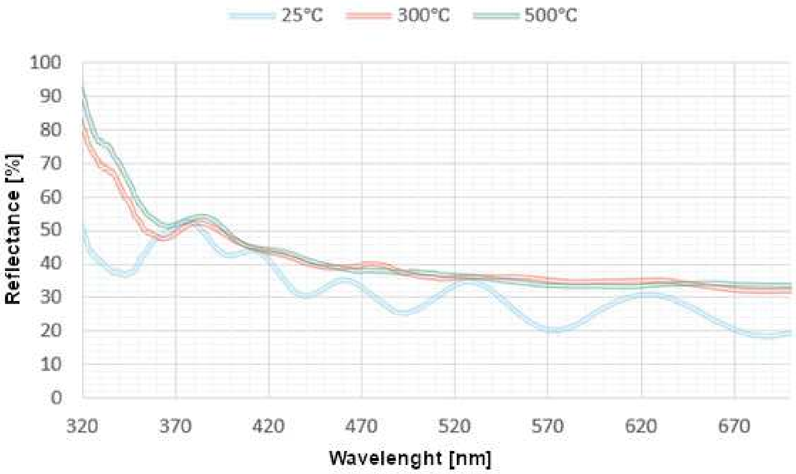

Fig. 3. Reflectance spectra of thin-films deposited from second solution

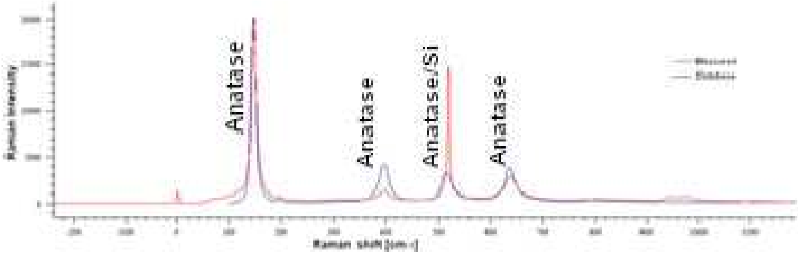

Fig. 4. Raman spectra of obtained titanium dioxide nanoparticles synthesized by sol gel method

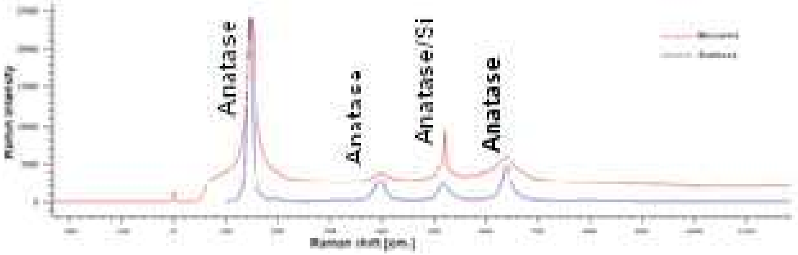

Fig. 5. Raman spectra of obtained titanium dioxide thin films synthesized by sol gel method

The results of qualitative analysis using the EDS, both for samples deposited from first solution (Fig. 6) and second solution (Fig. 7), showed characteristic peaks for titanium and oxygen. No peaks from other elements were recorded, which proves the purity of the samples.

Surface morphology studies were performed using a scanning electron microscope. The results are presented in Figures 8-13. Agglomerates of nanoparticles with a diameter of 10-200 nm were obtained in the examined samples prepared from the first solution (Figs. 8-10). Nanoparticles are parallel to each other (Fig. 8), and heat treatment at 300°C and 500°C did not cause the nanoparticles to grow into microparticles (Figs. 9 and 10).

In Figures 11-13, the topography of the surface of thin films of TiO_2 was recorded as a result of the deposition of the second solution. Depending on the heat treatment temperature, the surface topography of the samples varies considerably. The unheated sample surface is characterized by a low degree of development, uniformity and no precipitation (Fig. 11). In the case of heated samples, numerous cracks have been formed on the surface (Figs. 12-13).

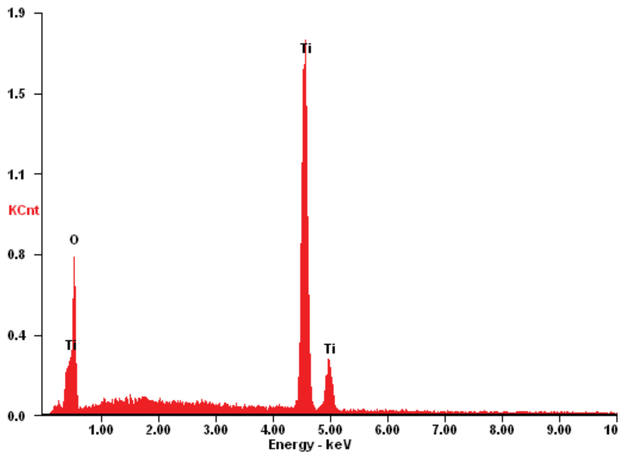

Fig. 6. EDS spectrum of titanium dioxide nanoparticles

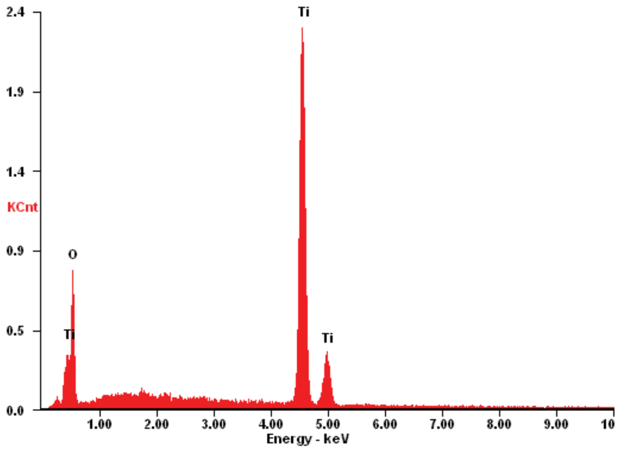

Fig. 7. EDS spectrum of titanium dioxide thin films

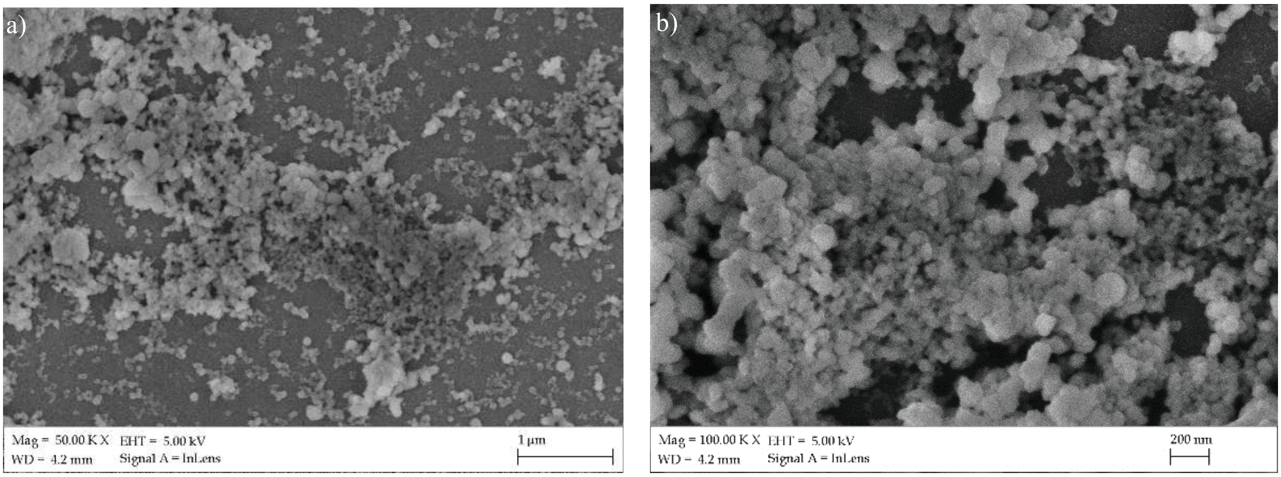

Fig. 8. SEM image of obtained nanoparticles at 50 000 x (a) and 100 000 x (b) magnification

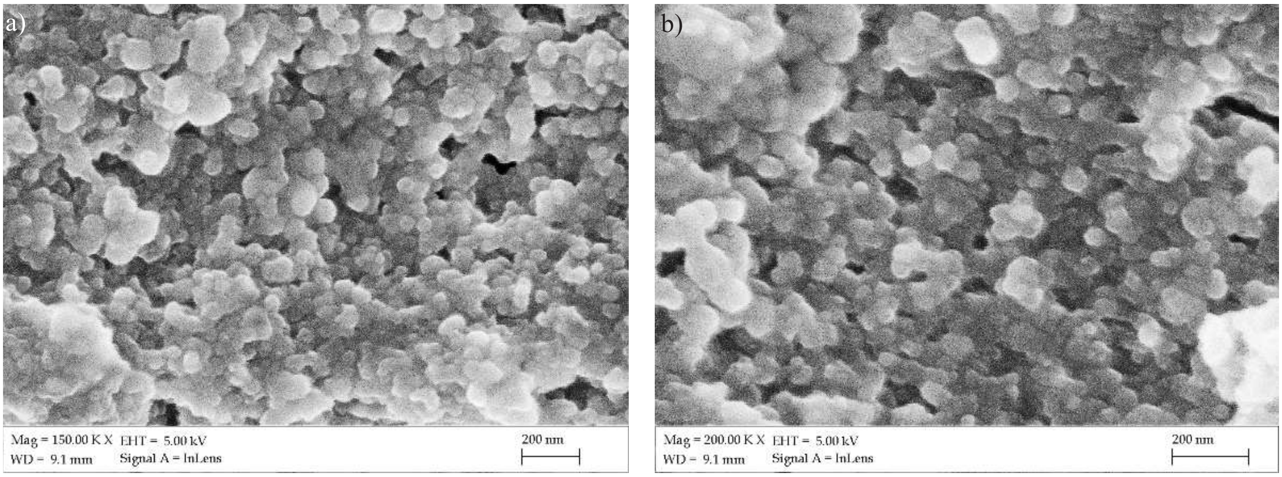

Fig. 9. SEM image of obtained nanoparticles at 150 000 x (a) and 200 000 x (b) magnification after heat treatment at 300°C

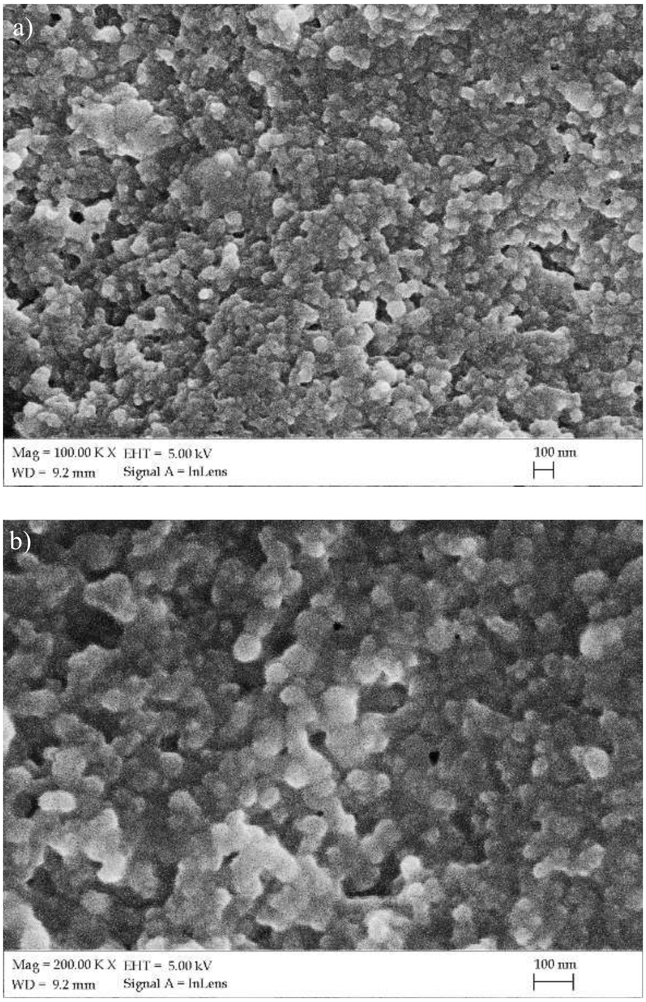

Fig. 10. SEM image of obtained nanoparticles at 100 000 x (a) and 200 000 x (b) magnification after heat treatment at 500°C

However, on a sample heat-treated at 300°C, the thin film is also uniform despite existing cracks. By recording the image at 200,000 x magnification, as shown in (Fig. 12c), the surface of the thin film is smooth and even. There are numerous cracks in the 500°C sample (more than in the 300°C sample), where the layer was delaminated, as can be seen in (Fig. 13b). Even at a higher magnification (Fig. 13c), it can be observed that the surface morphology of this sample is different from that of the others.

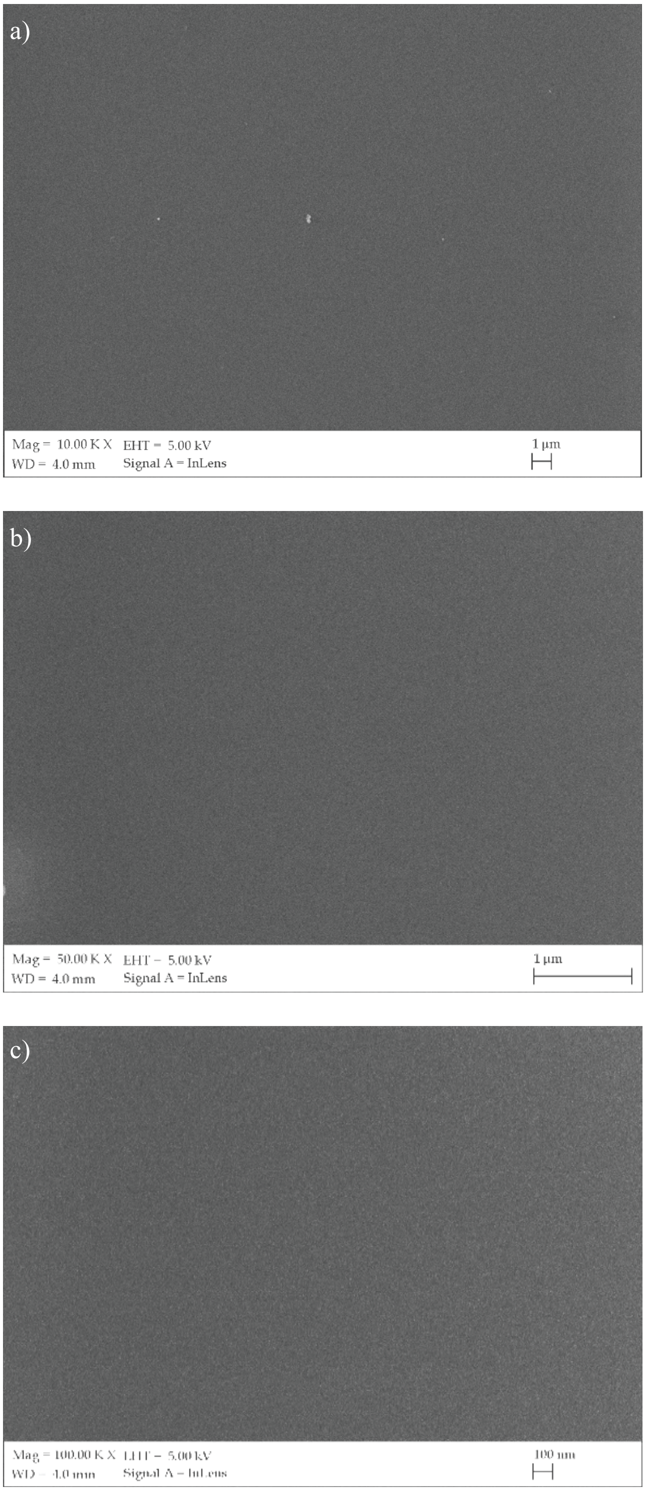

Fig. 11. SEM image of obtained thin film at 10 000 x, 50 000 x and 100 000 x magnification

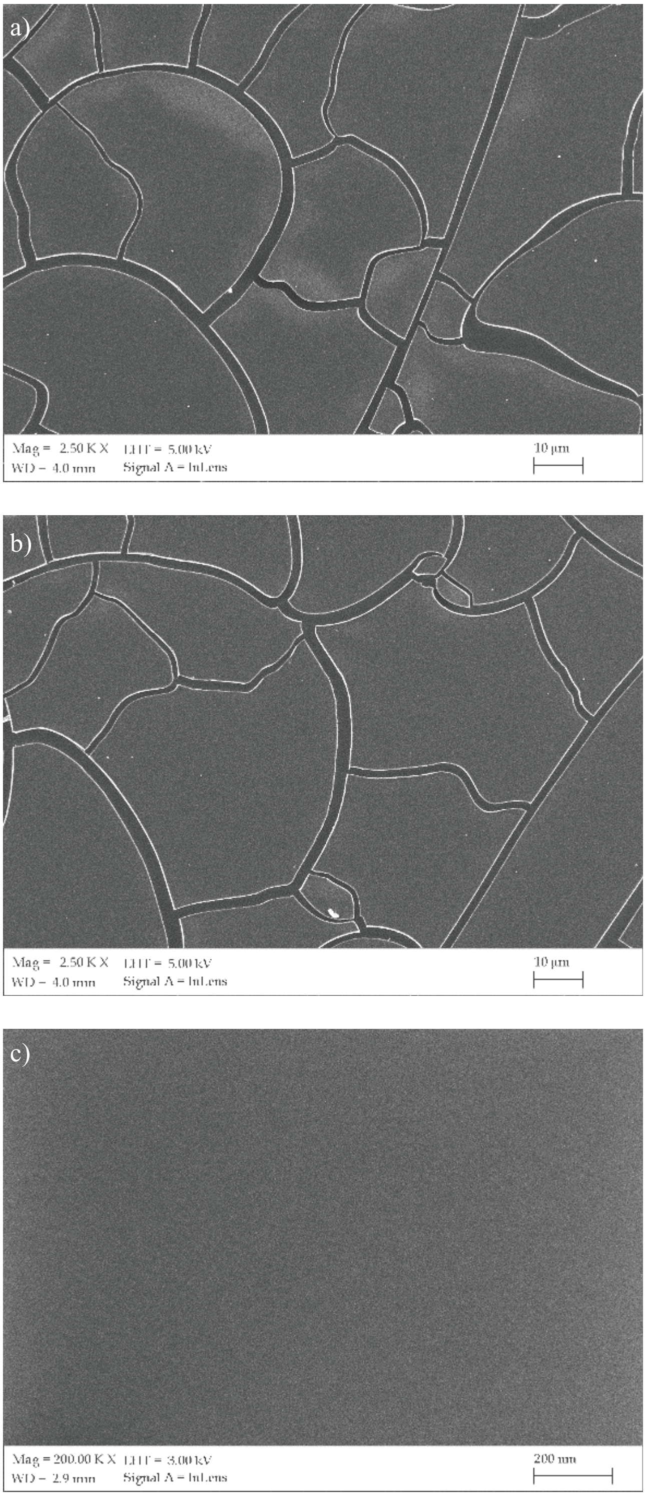

Fig. 12. SEM image of obtained thin film at 2500 x (a, b) 200 000 x (c) magnification after heat treatment at 300°C

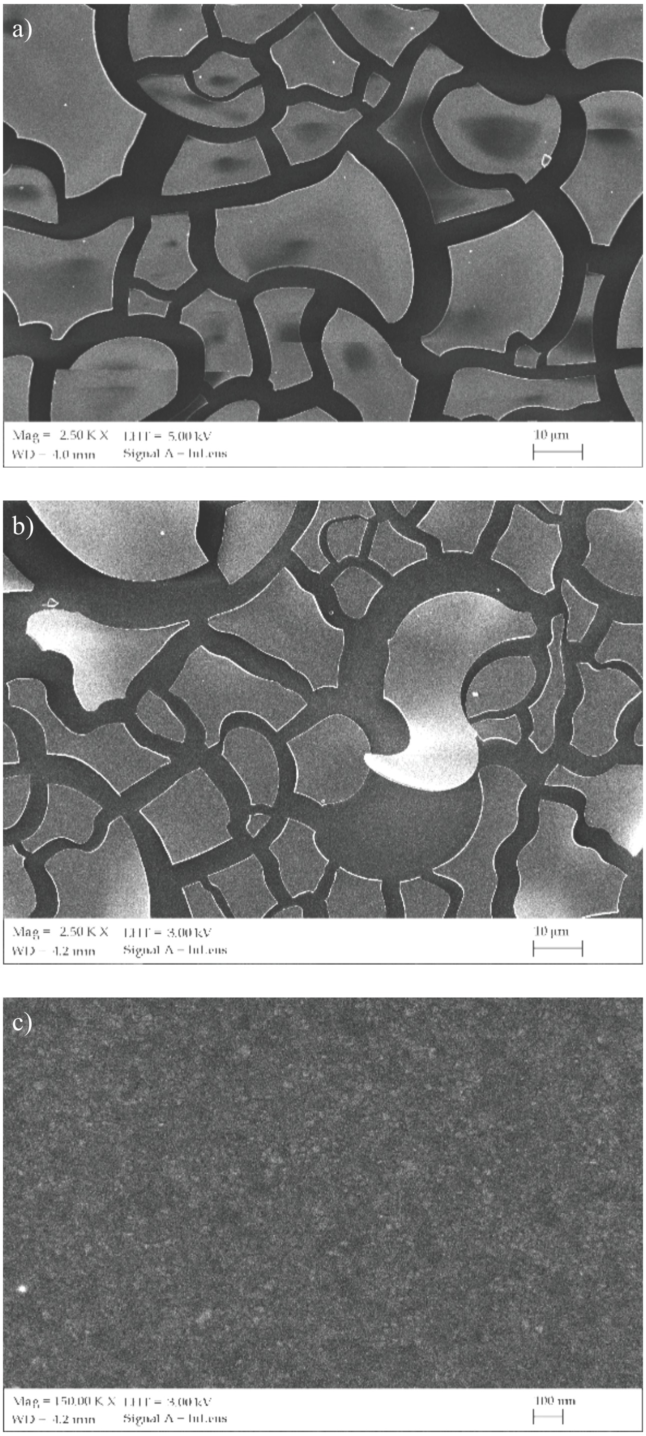

Fig. 13. SEM image of obtained thin film at 2500 x (a, b) 200 000 x (c) magnification after heat treatment at 500°C

4. Conclusions

On the basis of the obtained results, it can be concluded that the atomization method is a promising alternative for other deposition methods for sol gel prepared solutions. Using the same precursor in different recipes of solutions, it is possible to obtain different nanostructures like nanoparticles and thin-films. Heat treatment of obtained thin-films leads to the changes in their surface morphology and optical properties. Further research on the atomization deposition method should be performed to improve the quality and scalability of this method.

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