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INVESTIGATION OF THE SURFACE MORPHOLOGY OF POLYANILINE THIN FILMS

Abstract. The surface and optical properties of polyaniline thin films on a conducting FTO/glass substrate are determined. The thin films were prepared by anodic oxidative polymerization of aniline in the galvanostatic regime from hydrochloric acid solutions containing aniline and poly-2-acrylamido-2-methyl-1-propanesulfonic acid. The thickness of the thin films was 20 and 60 nm. Thin films were characterized by the methods of XRD, SEM, ACM. An insignificant change in the structure of the glass substrate during the application of the polyaniline has been established. Thin films consist of particles with different diameters are distinguished, the maximum of which is 250 nm. The some of the particles has a diameter of 50-70 nm. Thin films with 60 nm thickness have a dense and uniform surface. Its roughness and position of individual grains, as well as the surface profile, are determined by atomic force microscopy. Optical properties of coatings are determined by UV spectroscopy. On the basis of the studies performed, it was concluded that the absorbing capacity of glass coated with polyaniline increases more in the red wavelength region. Surface roughness increases with increasing thin films thickness. However, as follows from the SEM micrographs, the density and uniformity of the thin films increase when the thickness of the electrodeposited layer is 60 nm. The width of the band gap of the polyaniline/FTO/glass system is 3.85 eV.

Key words: Polyaniline, electrodeposition, thin film, surface morphology, transmission spectrum.

Introduction

Polyaniline (PANI) is one of the representatives of the class of electrically conductive polymers. The study of polyaniline, as well as other polymer compounds, such as polythiophene, polyacetylene, polyparaphenylenevinylene, polypyrrole, showed that they possess semiconductor properties [1-3]. PANI has good electronic conductivity, thermal and ecological stability, low cost [4]. The structural formula of polyaniline is shown in Fig. 1. PANI can be synthesized both by chemical and electrochemical methods [4,5]. Due to its physical and chemical properties, PANI is an attractive conductive polymer and is used in a wide range of applications, such as batteries [5], diodes and photovoltaic cells [6].

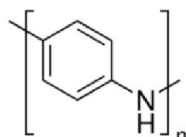


Figure 1 - The structural formula of polyaniline

Polyaniline was one of the earliest polymers used as a hole buffer layer in a photovoltaic device of organic/silicon [7,8].

Buffer layers are considered essential elements of organic photovoltaic devices with a bulk heterojunction. These additional layers, called buffer layers or interphase layers or interlayers, in solar cells can perform the function of collecting and extracting charges. For this purpose, the structure of the

organic solar cell can include both an anode buffer layer for collecting holes and a cathode buffer layer for collecting electrons. In this context, PANI is a very good hole collector and has good conductivity, which makes it an interesting material for research in the field of photovoltaics [9].

In this paper, we propose a method for the electrochemical polymerization of aniline in order to obtain film coatings of PANI that can serve as a buffer layer for transporting holes in solar cells

Experimental part

Polyaniline (PANI) films were obtained by anodic oxidative polymerization of aniline in the galvanostatic regime (0.05 mA/cm²). Precipitation was carried out on purified glass electrodes coated with a transparent conductive SnO₂:F (FTO/glass) layer with a surface resistance of 7 ohms/cm² and a working surface area of 3 cm². The counter electrode was platinum foil, and the reference electrode was a saturated silver chloride electrode (SCE). In the case of electropolymerization, the concentration of aniline was 0.05 M, HCl 0.5 M and poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPSK) 0.001 M.

Electrochemical polymerization of aniline was carried out in a special three-electrode cell using a potentiostat/galvanostat HA-501G (Hokuto Denko Ltd.). Electrodeposition of PANI on FTO/glass substrates was conducted until a charge of 15 mC/cm² was reached, where the layer thickness was about 60 nm and until a charge of 7mC/cm² was reached, where the layer thickness was about 20 nm. At the end of the electropolymerization, the obtained samples were washed with distilled water and dried in air.

XRD spectra were obtained using an X-ray diffractometer SmartLab (Rigaku) at a constant voltage of 9 kW using a rotating Cu anode for investigating the structure obtained PANI thin films.

Surface and cross-sectional micrographs were obtained using a Helios NanoLab 650 (FEI) scanning electron microscope with Schottkytype field emission electron source, focused gallium ion source (FIB). To obtain a cross-sectional image, a platinum (Pt) layer is first applied to the selected area and then a section is performed next to the platinum. The length, width and height of the platinum layer can be up to 20x2x1 μm, respectively. And the depth of section can reach 4 μm.

The morphology of the surface of PANI thin films was examined using an atomic force microscope JSPM 5200 (JEOL Ltd.). Scanning to AFM was carried out at atmospheric pressure and room temperature in a semi-contact method using an NSC 35 AIBS cantilever with a radius of curvature of 10 nm.

The optical properties of the obtained samples were studied with the SF-256 UVI spectrometer, with the possibility of recording the transmission coefficient in the wavelength range from 190 nm to 1100 nm.

Results and discussion

The PANI polymer has an amorphous structure. To determine the possible change in the structure of the coating on the FTO/glass substrate, the X-ray diffraction patterns of the conducting substrate -with and -without PANI were compared (Fig. 2). Figure 1 shows the X-ray diffraction pattern of a sample with a PANI thin film, which shows that new noticeable reflexes appear in the angular region $2\theta = 24 \div 26^\circ$, which are in good agreement with the data obtained in [10, 11].

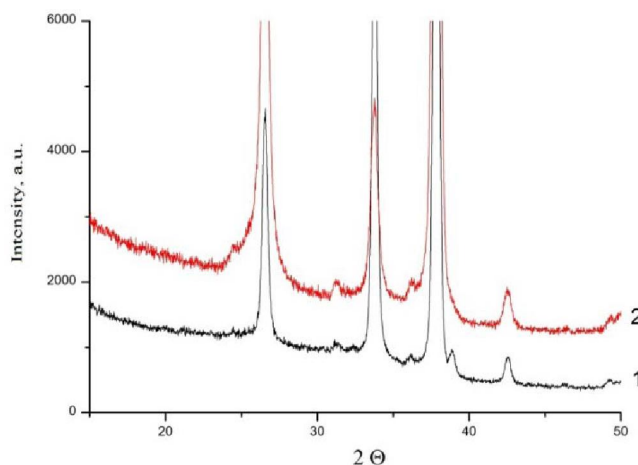
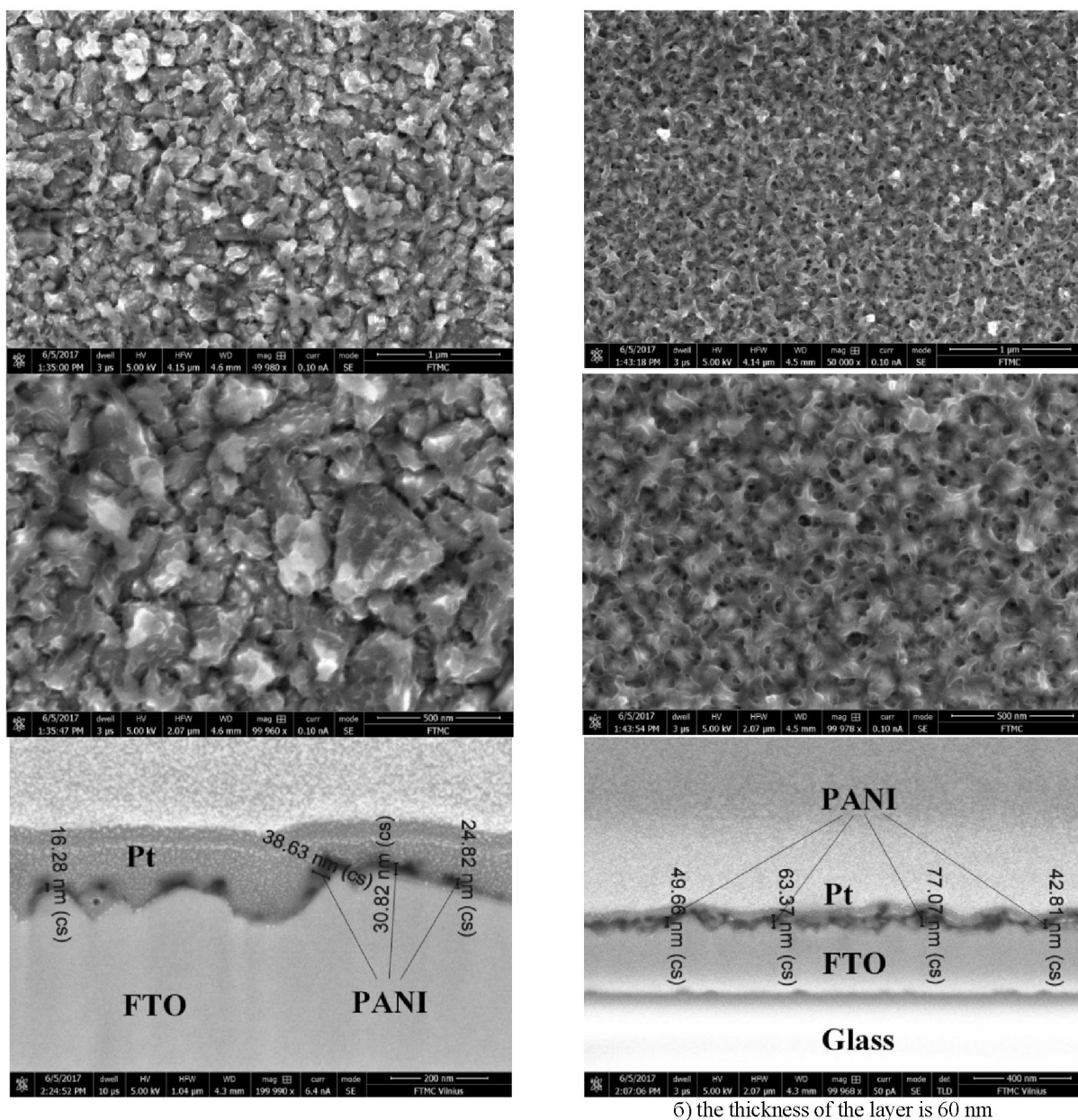


Figure 2—The XRD pattern of FTO/glass substrate with (2) and without (1) PANI

Figure 3 shows SEM images of the surface of the obtained films and shows that the film is formed by particles of various shapes and sizes. In the thin layer of the PANI (Fig. 3a) are well expressed the verges of the formed particles and their homogeneity in shape. Some reach a diameter of 200-250 nm, but the main array of particle's diameter is 50-70 nm. Increasing the thickness of the layer to 60 nm leads to uniform coating of the glass (Fig. 3b) without the formation of separate conglomerates, dendrites or globules.

Cross-sectional microphotographs show that the thickness of the PANI films varies from 16 nm to 38 nm (Fig. 3a) and from 42 nm to 77 nm (Fig. 3b).

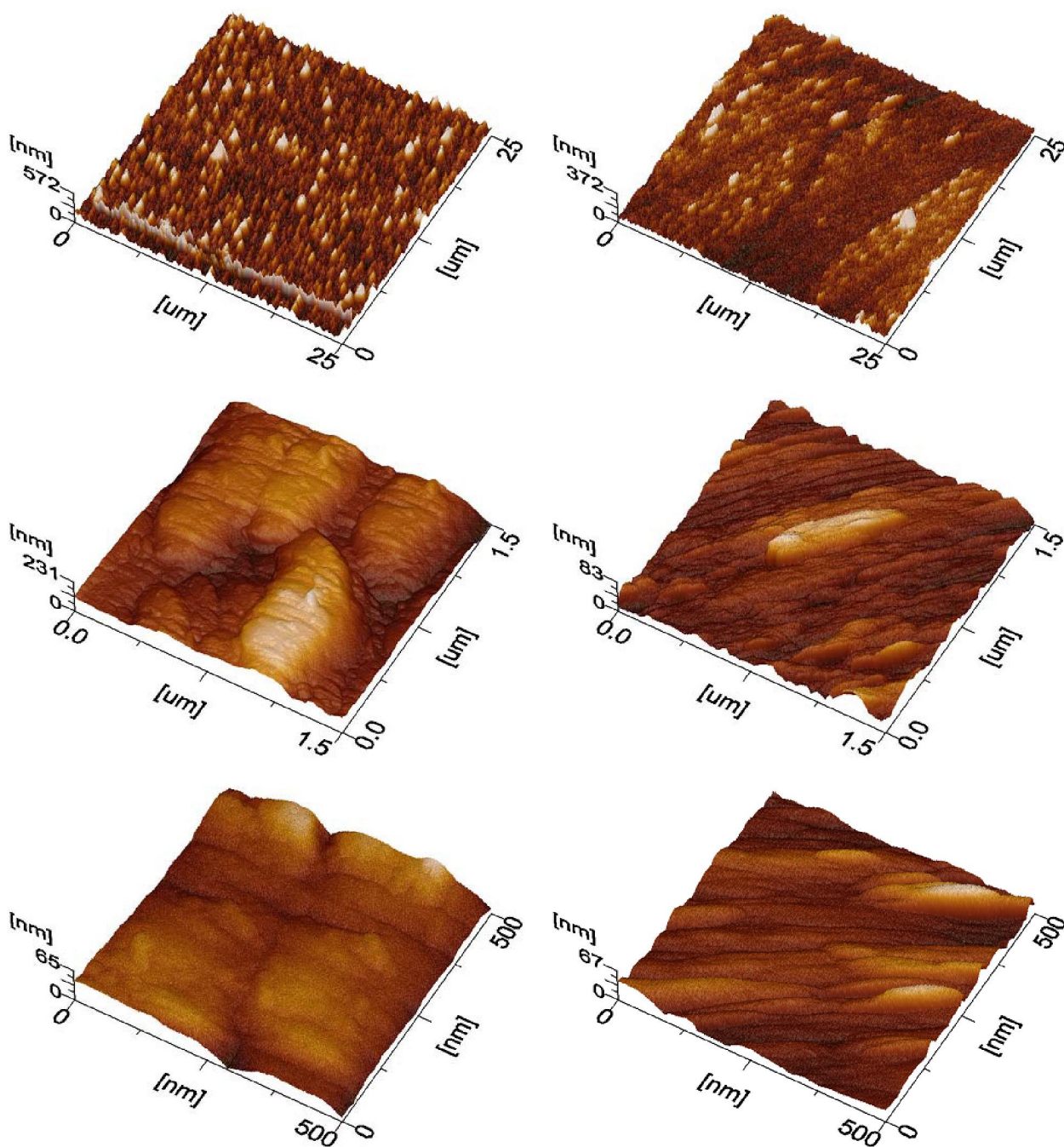


a) the thickness of the layer is 20 nm

b) the thickness of the layer is 60 nm

Figure3–SEM images of PANI thin films surface and cross-section

Figure 4a,b show surface micrographs obtained by atomic-force microscopy in various scan size. As shown in Figure 4a, PANI film with a thickness of 20 nm is formed from small and large particles of various shapes. The surface morphology of the film has a granular structure. There is heterogeneity in some areas, like pores between individual particles.



a) the thickness of the layer is 20 nm

б) the thickness of the layer is 60 nm

Figure 4— AFM images of PANI thin films at various scan size: 25x25 μm , 1,5x1,5 μm , 0,5x0,5 μm

This fact indicates that the roughness of the FTO/glass substrate affects to the microrelief of the polymer film, if the thickness of the latest is 20 nm.

The analysis of AFM images of PANI films with a thickness of 60 nm showed that the polymer layer has a granular structure with uniform surface coverage. The film is formed from more homogeneous particles, which's average length is 50-150 nm.

AFM images show, that there are the differences between films of different thickness (Fig.4a,b). The surface of the PANI film 60 nm thick has a more uniform and fine-grained structure than a film with a thickness of 20 nm.

Roughness parameters of electrodeposited PANI films with 60 nm thickness are shown in Figure 5 as an image surface and information about the parameters of the particles on a selected area.

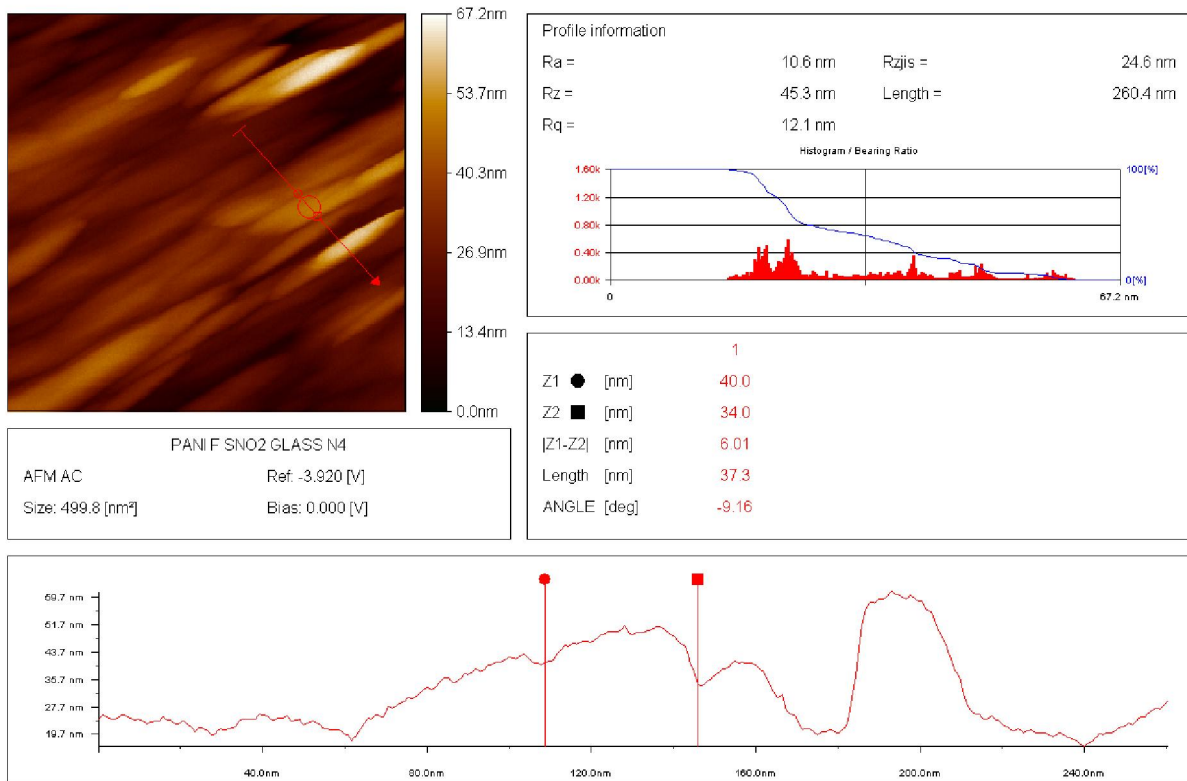


Figure 5 –AFM image and graph of PANI’s particles size distribution for the selected surface area (500x500 nm)

Figure 6 shows the histograms of the particle distribution on the selected area 500x500 nm and the isolated square 250x250 nm.

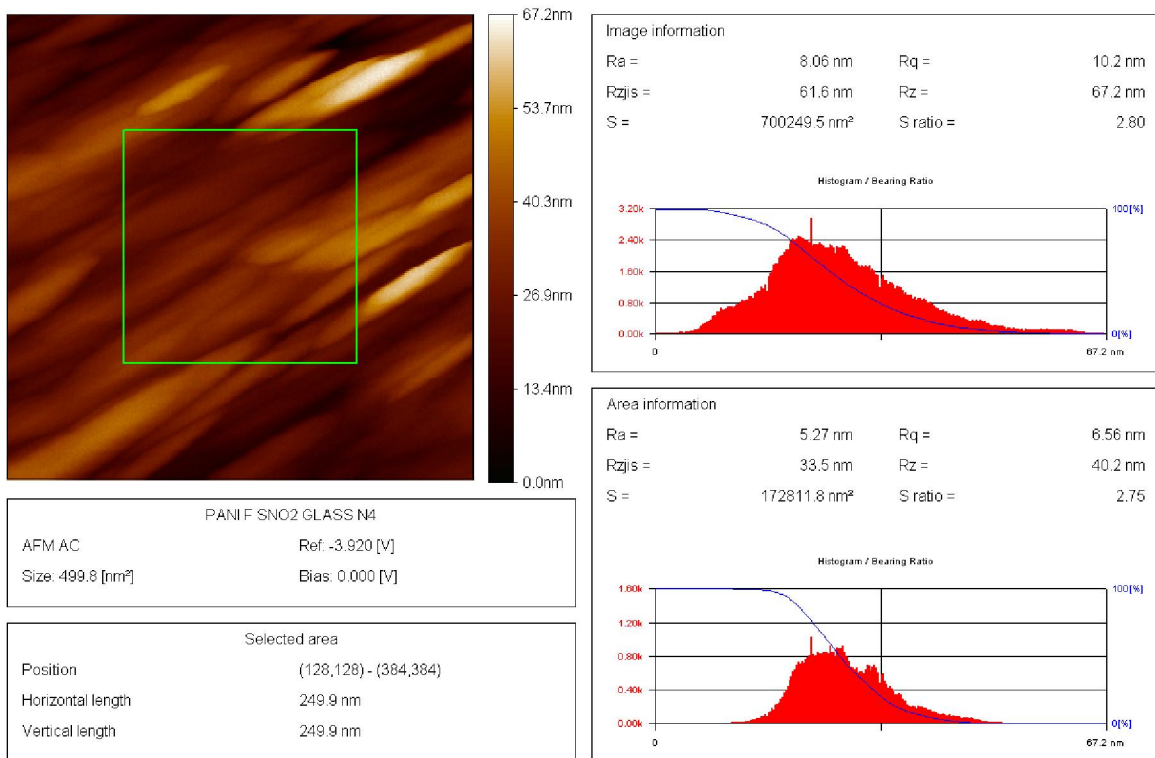


Figure 6 –AFM image of PANI thin film and histograms of the particle distribution on the selected area (500x500 nm) and the isolated square (250x250 nm)

The roughness parameters of the surface of PANI film at the selected area (500x500 nm) are shown in Table 1.

Table 1 – Parameters of the surface structure of PANI thin films on FTO/glass substrate

R_a , nm average roughness	$R_{z_{iis}}$, nm average roughness of 10 points	R_q , nm square root of square roughness	R_z , nm the difference between the maximum and minimum height of the analyzed image	
10,6	24,6	12,1	45,3	Fig.5
8,06	61,6	10,2	67,2	Fig.6

The obtained results attest to the high quality of PANI films obtained by electrodeposition on a conducting glass.

An important optical parameter for the characteristics of a semiconductor compound is the size of the band gap. This value for electrodeposited PANI films was determined on the basis of the transmission spectra obtained with the spectrometer CF-256-UVI.

Figure 7 shows the transmission spectra for the FTO/glass substrate and the PANI coated substrates. As shown in Fig. 7, the edge of the absorption band corresponds to a wavelength of 460 nm. In the visible region of 400-700 nm, the transmittance is maximal, and when shifted to the red and infrared regions, PANI coated glass absorbs more radiation and the transmittance decreases to almost 50%.

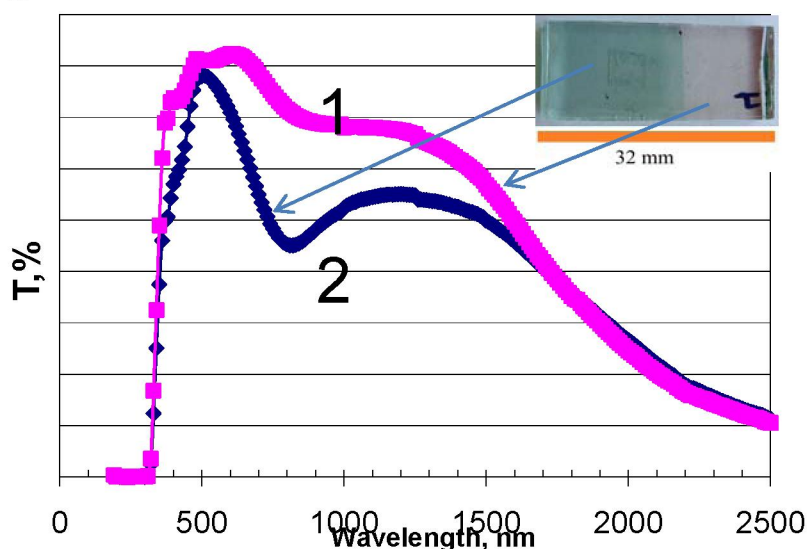


Figure 7 – Transmission specters of FTO/glass (1) and PANI/FTO/glass (2)

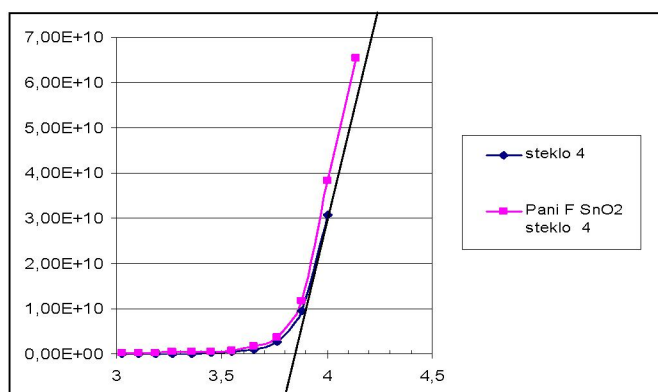


Figure 8 – Graph of the transmission coefficient versus wave energy

The dependence of the transmittance on the energy of the wave is shown in Fig. 8. According to this dependence, the width of the band gap for glass with and without coating is determined by the value on the abscissa axis cut off by the tangent and is 3.85 eV. The difference for both samples is insignificant.

Conclusion

Based on the investigations it was concluded that the absorption capacity of PANI coated glass increases more in the red region of wavelengths. Surface roughness increases with increasing coating thickness. However, as shown in SEM micrographs, the density and uniformity of the coating increase when the thickness of the electrodeposited layer is 60 nm.

Acknowledgments

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REFERENCES

- [1] Skotheim T.A., Ronald L.E., Reynolds J.R. Handbook of Conducting Polymers. 2nd edn. New York: CRC Press, 1997. 1120 pages. (in Eng.)
- [2] Bhattacharya A. and De A. Conducting composites of polypyrrole and polyaniline – A review // Prog. Solid State Chem. 1996. №24, P.141-181. (in Eng.)
- [3] Rodriguez J., Grande H.J., Otero T.F. Handbook of Organic Conductive Molecules and Polymers. New York: John Wiley & Sons, 1997. 3334 pages. (in Eng.)
- [4] Inzelt G. Conducting Polymers. 2nd edn. Berlin: Springer, 2012. 310 pages. (in Eng.)
- [5] MacDiarmid A.G., Yang L.S., Huang W.S., Humphrey B.D. Polyaniline: electrochemistry and application to rechargeable batteries // Synth. Met. 1987. №18. P.393-398. (in Eng.)
- [6] Sariciftci N.S., Braun D., Zhang C., Srdanov V.I., Heeger A.J., Stucky G., Wudl F. Semiconducting polymer-buckminsterfullerene heterojunctions – diodes, photodiodes, and photovoltaic cells // Appl. Phys. Lett. 1993. №62. P.585-587. (in Eng.)
- [7] Renkuan Y., Hong Y., Zheng Z., Youdou Z., Yongnan W., Polyaniline/silicon heterojunctions // Synth. Met. 1991. №41. P.731-734. (in Eng.)
- [8] Renkuan Y., Yuxue L., Hong Y., Yongbin W., Xiangqin Z., Jian X., Xuechu S. Study of photoelectric characteristics of p-PAN/n-Si junction // Synth. Met. 1993. №57. P. 4087-4092. (in Eng.)
- [9] Choy W. C. H. (ed.). Organic Solar Cells. London: Springer, 2013. 266 pages. (in Eng.)
- [10] Chaudhari H. K. and Kelkar D. S. X-ray diffraction study of doped polyaniline // J. Appl. Polym. Sci. 1996. №62. P.15-18. (in Eng.)
- [11] Manivel P., et al. Optical and electrochemical studies of polyaniline/SnO₂ fibrous nanocomposites // Materials Research Bulletin, 2013. V.48. №2. P.640-645. (in Eng.)

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ПОЛИАНАЛИН ҚАБЫҚШАЛАРЫНЫҢ БЕТКІ МОРФОЛОГИЯСЫН ЗЕРТТЕУ

Аннотация. Жұмыста электрохимиялық жолмен қалыңдығы 20 және 60 нм болатын ПАНИ жұқа қабықтары өткізгіш FTO/шыны төсеніштерінде алынғаны көрсетілді. Алынған ПАНИ қабықшаларының құрылымы мен беткі морфологиясы РФА, СЭМ, АСМ әдістерінің көмегімен зерттелді. Шыны төсеніштерді полианилинмен қаптаған кезде, олардың құрылымы кішкене өзгертін анықталды. Жұқа қабықшалардың бөлшектері әртүрлі өлшемді екені және олардың ең үлкені 250 нм болатыны анықталды. Қалыңдығы 60 нм қабықшалардың беті тығыз біртекті болып келеді. Оның кедір-бұдыры және кейбір бөлшектердің орны, сонымен қатар беткі профилі атомды күш микроскопия әдісімен анықталды. Оптикалық қасиеттері УФ-спектроскопия әдісімен анықталды. Орындалған зерттеулердің негізінде полианилинмен қапталған шынының сіңіру қабілеті толқын ұзындығының қызыл аймағында жоғарлайтыны туралы қорытынды жасалды. Дайындалған ПАНИ/FTO/шыны жүйесінің рұқсат етілмеген аумағының өлшемі 3,85 эВ болатыны анықталды.

Түйін сөздер: Полианилин, электротұндыру, жұқа қабық, беткі морфология, өткізгіштік спектрі.

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ИССЛЕДОВАНИЕ МОРФОЛОГИИ ПОВЕРХНОСТИ ПЛЕНОК ПОЛИАНАЛИНА

Аннотация. В работе показан электрохимический способ получения тонких пленок полианилина (ПАНИ) с толщиной 20 и 60 нм на FTO/стекло подложках. Структура и морфология поверхности полученных пленок ПАНИ исследовали с помощью методов РФА, СЭМ, АСМ. Установлено незначительное изменение структуры стеклянной подложки при нанесении полианилина. На тонких покрытиях выделены частицы с различными диаметрами, максимальный из которых составляет 250 нм. Покрытия толщиной 60 нм представляют собой плотную однородную поверхность. Ее шероховатость и положение отдельных зерен, а также профиль поверхности определены методом атомной силовой микроскопии. Оптические свойства покрытий определены методом УФ-спектроскопии. На основании выполненных исследований сделан вывод, что поглощающая способность стекла, покрытого полианилином увеличивается больше в красной области длин волн. Ширина запрещенной зоны системы ПАНИ/FTO/стекло составляет 3,85 эВ.

Ключевые слова: Полианилин, электроосаждение, тонкая пленка, морфология поверхности, спектр пропускания.