DOI 10.31489/2022PH2/86-91

UDC: 535.215; 539.23; 535.3; 535.3; 538.9

A.K. Aimukhanov, T.E. Seisembekova*, A.K. Zeinidenov, D.S. Kambar

Karagandy University of the name of academician E.A. Buketov,
Scientific Center for Nanotechnology and Functional Nanomaterials, Kazakhstan
(E-mail: tosh_0809@mail.ru)

The impact of SnO_2 photoelectrode's thickness on photovoltaic properties of the solar cell FTO:SnO_2:PTB7-TH:ITIC/Mo/Ag

The paper reports the results of a study of the morphological, optical and electrophysical parameters of SnO_2 films. SnO_2 films are applied by spin-coating at different revolutions of the centrifuge. The topography of the surface and the thickness of the SnO_2 films are studied using an atomic force microscope. The current-voltage characteristics of solar cells are measured. The optical properties with different thicknesses of SnO_2 films are also investigated. It is shown that an increase in the rotation speed of the substrate leads to a decrease in the surface roughness of the SnO_2 films. It is found that changes in the morphology of SnO_2 films contribute to the rapid transport of injected holes to the external electrode and reduce the probability of reverse recombination. Cells with an electron transport layer of SnO_2 at 2000 revolutions showed a low efficiency of 0.17%. With a decrease in the thickness of the SnO_2 films to a value of 62 nm, there is an increase in the value of the short-circuit current by 2.3 times and a change in the no-load voltage by 1.12 times.

Keywords: Tin(II) oxide (SnO_2) surface morphology, optical and impedance spectroscopy.

Introduction

Tin oxides deserve special attention from materials scientists due to their numerous applications. Recently, tin oxide films have attracted the great attention of scientists and technologists in connection with their possible applications in solid-state gas sensors, electrodes for electroluminescent displays, protective coatings, solar cells, and the transparent field-effect transistors [1]. Currently studying two main tin oxides are SnO and SnO_2.

Due to it is efficiency, ease of processing rapid growth of the energy conversion coefficient and flexibility increasing attention has been paid to the development of ESE. After the introduction of highly effective polymer donors with a low bandgap and non-fullerene acceptors research has experienced a renaissance. Now a day, the energy conversion efficiency of polymer solar cells attains 17–18% [2]. It was also established that processing methods and buffer layers also play a crucial role in obtaining better performance parameters except for innovation in the molecular aspects of OSE.

Various n-type metal oxides with a wide bandgap and some polyelectrolytes with a large dipole moment have been successfully used as interfacial electron transport layers in inverted devices [3, 4]. In addition, various forms of nanostructuring of films, surface treatment, and technological additives have been studied to increase the efficiency of charge collection, transportation, and selectivity.

SnO_2 is one of the most promising materials for electron transfer in the ESE due to its good environmental resistance as well as high electron mobility and high transparency in the visible and near-infrared regions. SnO_2 films are produced in various ways, including the sol-gel method. The sol-gel method is a technologically simple process that allows for getting better coatings. It should be noted that the important crystalline properties of thin films depend very much on the growth conditions, growing technique, and substrate [5].

This paper presents the results of the influence of the thickness of SnO_2 films on their structural, optical, and photoelectric properties.

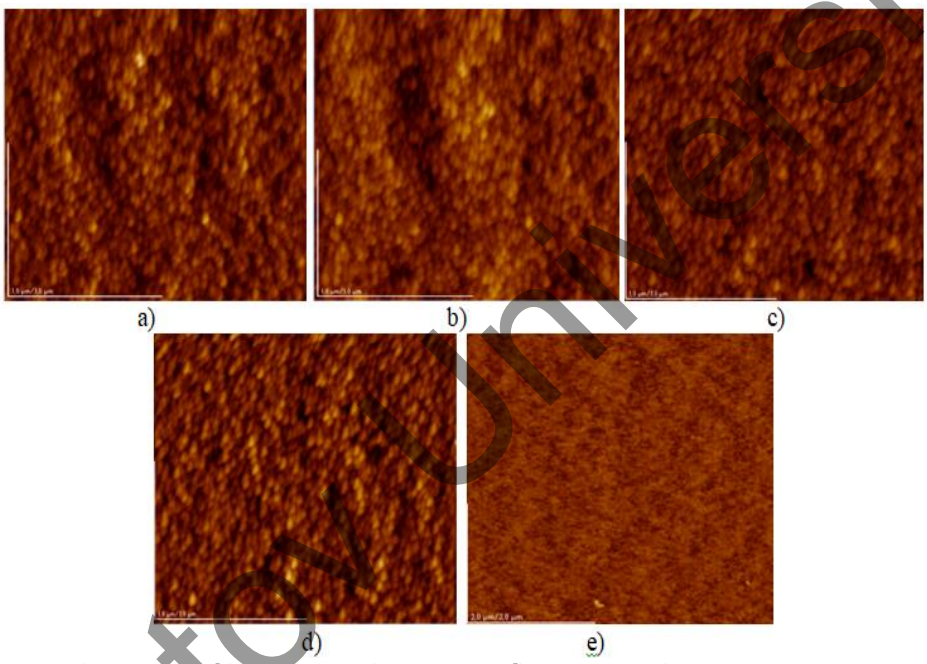
Experimental

The preparation of tin oxide films on the FTO surface was carried out as follows: solution was prepared by dissolving 183 mg of $SnCl_2$ (Brun New Material Technology Ltd, Purity: 99.99%) in 1 ml of 2-propanol (pure 99,9% Sigma Aldrich). The final solution was stirred at T = 80 ℃ temperature for 3 hours and then kept at room temperature for 24 hours. SnO_2 films were obtained by centrifugation (SPIN150i, Semiconductor Production System). The rotation rate of the substrate varied from 2000 rpm to 6000 rpm to change the

thickness of the film. Further, the film was annealed for 1 hour at a temperature of 500^0C to ensure complete films crystallization after its application. The topography of the film surface was studied using a JSPM-5400 atomic force microscope (AFM) (JEOL, Japan). A special modular program for analyzing scanning probe microscopy data (Win SPMII Data Processing Software) was used to process the images obtained with AFM. From AFM images, the morphology of the surface and the roughness of the SnO2 films were analyzed. The images of the surface of the film were obtained in the semicontact scanning mode. The absorption spectra of the samples under study were recorded on an AvaSpec-ULS2048CL-EVO spectrometer (Avantes). The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode [6]. The VAC of photosensitive cells was determined by the device Sol3A Class AAA Solar Simulators (Newport) with PVIV-1A I-V Test Station [7, 8].

Results and Discussion

Figure 1 shows images of the surface morphology of SnO_2 films obtained by using AFM. It can be seen that the solution at different revolutions of the centrifuge affects the surface morphology.



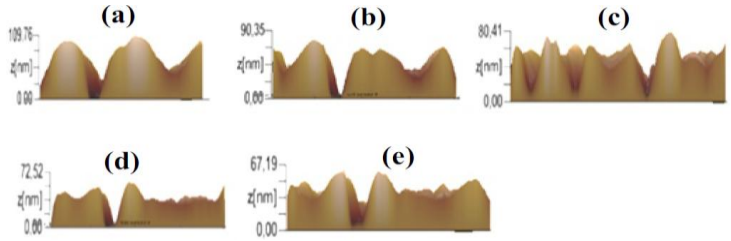
a) 2000 rpm; b) 3000 rpm; c) 4000 rpm; d) 5000 rpm; e) 6000 rpm.

Figure 1. Images of surface morphology of SnO_2 films obtained at different speeds of rotation

The roughness of film is an important factor in the characteristics of the surface film. Reducing the surface roughness of the SnO_2 improves the quality of the SnO/photoactive layer interface, which contributes to the effective injection of photoinduced electrons from the acceptor and reduces the probability of recombination of charge carriers at the interface. In the process of obtaining the film, increasing the rotation speed of the substrate leads to the smoothing of the SnO_2 surface; the roughness of the film begins to decrease. Respectively, the morphology of the SnO_2 films obtained at the rotation speed of the centrifuge 2000–4000 rpm has a surface roughness of 4.8-2.7 nm. With an increase in the rotation speed of the centrifuge to 5000–6000 rpm, the surface roughness decreases to 1.6 nm.

Figure 2 illustrates AFM images of the ETL thickness of the SnO_2 layer. Table 1 represents the obtained parameters of the surface morphology and thickness of SnO_2 films. The thickness of the SnO_2 film was studied by the depth of the scratch on the surface of SnO_2.

To do this, a scratch was formed with thin tweezers to the entire depth of the sample, the most suitable area was located on the optical microscope, and then this area was scanned using an atomic force microscope.



a) 2000 rpm; b) 3000 rpm; c) 4000 rpm; d) 5000 rpm; e) 6000 rpm.

Figure 2. Images of the thickness of SnO_2 films obtained at different rotational speeds

Table 1

Parameters of surface morphology and thickness of SnO_2 films

Sample	R_q, nm	Thickness, nm
SnO_2 – 2000 rpm	4,8	102
SnO_2 – 3000 rpm	3,9	88
SnO_2 – 4000 rpm	2,7	76
SnO_2 – 5000 rpm	2,1	62
SnO_2 – 6000 rpm	1,6	58

Figure 3 demonstrates the absorption spectra ETL at different thicknesses of the SnO_2 layer. The absorption spectrum is typical of the absorption spectrum of wide-band semiconductors. The measured absorption spectra of semiconductor films show that the edge of the absorption band of SnO_2 films is located at about 350 nm. At measuring the absorption spectra, it can be seen that the optical density of the films increases with increasing thickness. At the same time, the position of the maximum of the absorption spectrum does not change.

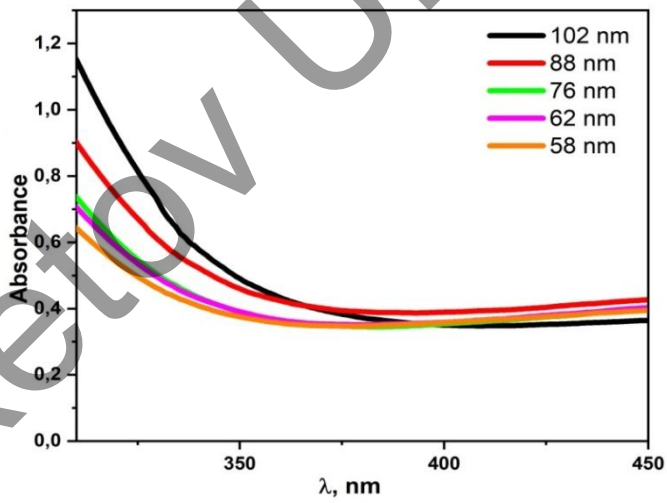
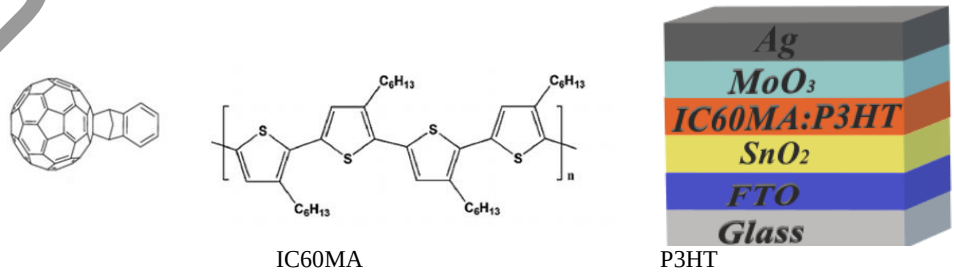


Figure 3. Absorption spectra of SnO_2 films with different thickness



IC60MA P3HT

a) b)

Figure 4. Chemical structures of BHJ compounds (a) and the architecture of the inverted PSC (b)

Further, based on the obtained SnO_2 films, solar cells were constructed and the effect of thickness on the photovoltaic parameters of the cells was studied (Figure 4).

Figure 5 shows the current-voltage characteristics of organic solar cells based on a photoactive PTB7-Th: ITIC layer with different thicknesses of SnO_2 films.

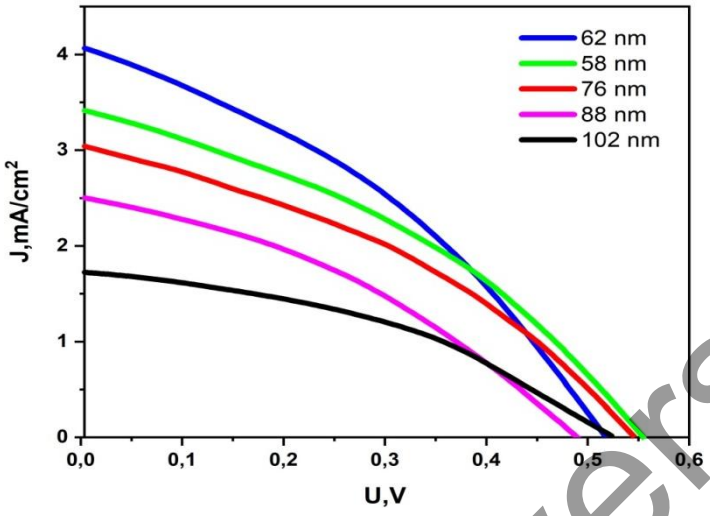


Figure 5. Current-voltage characteristic of a polymer solar cell depending on the thickness of SnO_2 films

Table 2

Photovoltaic characteristics of organic solar cells

SnO film thickness, nm	J_{sc} mA/см^2	U_{oc} V	J_{max} mA/см^2	U_{max} V	*FF* %	η %
58	3.4	0.28	2.0	0.18	0.38	0.29
62	4.0	0.25	2.4	0.16	0.38	0.38
76	3.0	0.27	1.8	0.17	0.37	0.26
88	2.5	0.24	1.7	0.15	0.43	0.23
102	1.7	0.25	1.1	0.16	0.41	0.17

When the thickness of the SnO_2 films was reduced to 62 nm, an increase in short-circuit current density by 2.3 times and a change in the no-load voltage by 1.12 times were observed (Table 2). Moreover, it can be seen that with a further decrease in the thickness of SnO_2, a decrease in the value of the short-circuit current was observed. The decrease in the current value was because the film becomes so thin that gaps appear in it, through which current leakage occurs.

With a film thickness of 62 nm, the efficiency of the cell was 0.38%. When the film thickness was reduced to 58 nm, the efficiency of the cell decreased to 0.17%.

By impedance spectroscopy, the mechanisms of transport and recombination of charge carriers in thin films of a mixture of PTB7-TH:ITIC polymers with different thicknesses SnO_2 were studied. Figure 6 shows the impedance spectra in Nyquist coordinates based on thin films. Table 3 presents the main electric transport properties. An equivalent electrical circuit was used to interpret the impedance spectra. The fitting of the impedance spectra was calculated using the software package EIS-analyzer. Using the method of impedance spectroscopy the analysis of the electric transport characteristics of solar cells was carried out. The analysis of the hodographs indicated that a change in the thickness of the SnO_2 films leads to a change in the electric transport characteristics of the polymer solar cell.

To interpret the impedance spectra, an equivalent electrical circuit of a photovoltaic cell was used, where R1 (R_w) is the equivalent resistance of a multilayer film, R2 (R_{rec}) is the resistance characterizing the recombination of localized electrons with holes (Figure 6).

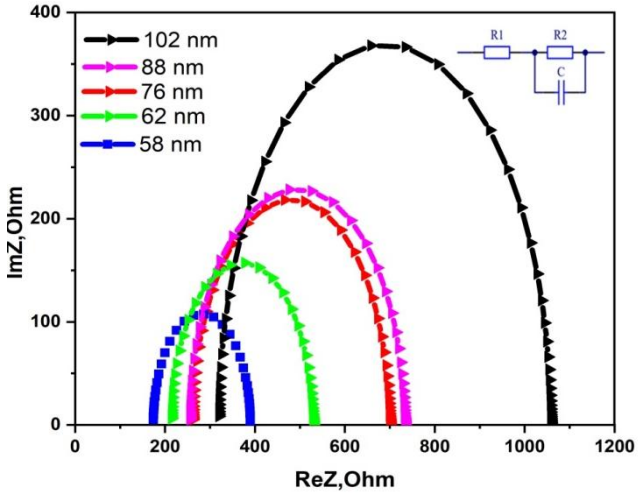


Figure 6. Impedance spectra of PSCs with different SnO_2 films thickness.

As the spin-coater rotation speed increases, the thickness of the SnO_2 films decreases; this should contribute to a decrease in the resistance (Rw) of the film. It can be seen from Table 3 that with a decrease in the thickness of the films, the resistance R_w also decreases, which in general should improve the injection of electrons into the FTO. However, a decrease in the thickness of the photoactive layer also leads to a decrease in the resistance of R_{rec}, which ensures increased recombination of electrons at the interface. On the one hand, the decrease in R_w contributes to the rapid transport of electrons, but on the other hand, there is a competing recombination process through the resistances of R_{rec}, which also decreases, which increases the recombination rate.

We assume that there is an optimal thickness of SnO_2 films, at which there is a balance between injection efficiency and recombination of charge carriers. In this case, the electrons in the photoactive layer have the maximum lifetime of charge carriers and a low probability of recombination. From the analysis of the impedance spectra, it follows that the thickness of 58 nm is optimal, at which the lifetime of the charge carriers was τ_{eff} = 0.9 ms (Table 3).

Table 3

The value of the electrophysical parameters of SnO_2 films

Film thickness, rpm	R_w, (Ohm)	R_{rec}, (Ohm)	R_{rec} /R_w	τ_{eff}, (ms)	k_{eff}, (s^{-1})
58	174	215	1.2	0.9	10704
62	214	314	1.4	0.8	12221
76	245	458	1.8	0.5	18190
88	262	437	1.6	0.4	20768
102	320	738	2.3	0.4	23711

Conclusions

As a result of the research, a method for the synthesis of SnO2 films was developed. The results demonstrated that with an increase in the rotation speed of the substrate, a decrease in the surface roughness of SnO2 films was observed. It was found that the edge of the absorption band of SnO_2 films is located at about 350 nm. When the thickness of the SnO_2 films was reduced to 62 nm, there was also an increase in the value of the short-circuit current by 2.3 times and a change in the no-load voltage by 1.12 times. With a further decrease in the thickness of SnO_2, a decrease in the value of the short-circuit current was observed. With a film thickness of 62 nm, the efficiency of the cell was 0.38%. When the film thickness was reduced to 58 nm, the efficiency of the cell decreased to 0.17%. The decrease in the current value for SnO_2 films was because the film becomes so thin that gaps appear in it, through which current leakage occurs.

Acknowledgements

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP09561879).

References

1 Roge, V., Didierjean, J., Crepelliere, J., Arl, D., Michel, M., Fechete, I., Dinia, A., & Lenoble, D. Tuneable. (2020). Functionalization of Glass Fibre Membranes with ZnO/SnO_2 Heterostructures for Photocatalytic Water Treatment: Effect of SnO_2 Coverage Rate on the Photocatalytic Degradation of Organics. *Catalysts*. 10, 1–18. DOI: 10.3390/catal10070733

2 Moniruddin, M., Ilyassov, B., Seliverstova, E., Shabdan, Ye., Bakranov, N., Ibrayev, N., & Nuraje, N. (2017). Bioinspired study of energy and electron transfer in photovoltaic system. *Journal of Experimental Nanoscience.* 12(1), 285–296. doi.org/10.1080/17458080.2017.1321794

3 Huang, Y.F., Inigo, A.R., Chang, C.C., Li, K.C., Liang, C.F., Chang, C.W., Lim, T.S., Chen, S.H., White, J.D., Jeng, U.S., Su, A.C., Huang, Y.S., Peng, K.Y., Chen, S.A., Pai, W.W., Lin, C.H., Tameev, A.R., Novikov, S.V., Vannikov, A.V., & Fann, W. (2007). Nanostructure-dependent Vertical Charge Transport in MEH-PPV Films. *Advanced Functional Materials.* 17(15), 2902–2910. DOI:10.1002/adfm.200600825

4 Ibrayev, N.K., Ilyassov, B.R., & Afanasyev, D.A. (2017). Influence of the morphology of ZnO nanostructures on luminescent and photovoltaic properties. *Optics and Spectroscopy.* 122(3), 462–468. doi:10.1134/s0030400x17030092

5 Liao, H.H., Chen, L.M., Xu, Z., Li, G., & Yang, Y. (2008). Highly efficient inverted polymer solar cell by low temperature annealing of Cs_2CO_3 interlayer. *Applied Physics Letters*. 92. 173303. DOI: 10.1063/1.2918983

6 Huang, J., Li, G., & Yang, Y. (2008). A Semi-transparent Plastic Solar Cell Fabricated by a Lamination Process. *Advanced Materials.* 20. 415–419. DOI: 10.1002/adma.200701101

7 Yuan, X. (2010). EIS Equivalent Circuits In Electrochemical Impedance Spectroscopy in PEM Fuel Cells. *Springer*. DOI:10.1007/978-1-84882-846-9

8 Banik, A., Ansari, M.S., & Qureshi, M. (2018). Efficient Energy Harvesting in SnO2-Based Dye-Sensitized Solar Cells Utilizing Nano-Amassed Mesoporous Zinc Oxide Hollow Microspheres as Synergy Boosters. *ACS Omega*, 3, 14482−14493. DOI:10.1021/acsomega.8b02520

А.К. Аймуханов, Т.Е. Сейсембекова, А.К. Зейниденов, Д.С. Камбар

SnO фотоэлектроды қалыңдығының FTO:SnO:PTB7-TH:ITIC/Mo/Ag күн ұяшығының фотоэлектрлік параметрлеріне әсері

Мақалада SnO_2 пленкаларының морфологиялық, оптикалық және электрофизикалық параметрлерінің зерттеу нәтижелері берілген. SnO_2 пленкаларын центрифуганың әр түрлі айналу жылдамдығында айналдыру *spin-coating* әдісі арқылы жасалды. Эксперименттік зерттеулер оптикалық спектроскопия, вольтамперометрия және импедансты өлшеу әдістерімен жүргізілді. Атомдық күш микроскопының көмегімен SnO_2 бетінің топографиясы мен пленкаларының қалыңдығы зерттелді. Қалыңдығы әр түрлі SnO_2 пленкаларының оптикалық қасиеттері анықталды. Айналу жылдамдығының артуы SnO_2 пленкаларының бетінің кедір-бұдырының төмендеуіне әкелетіні көрсетілді. SnO_2 пленкаларының морфологиясының өзгеруі инжекциялық тесіктердің сыртқы электродқа тез тасымалдануына және кері рекомбинация ықтималдығын азайтуға ықпал ететіні анықталды. Электронды тасымалдау қабаты бар SnO_2 ұяшығы 2000 айналымда 0,17% төмен тиімділікті көрсетті. SnO_2 пленкаларының қалыңдығының 62 нм мәніне дейін төмендеуімен қысқа тұйықталу тогының мәні 2,3 есе және бос жүріс кернеуі 1,12 есе артады.

Кілт сөздер: калайы (II) тотығының (SnO_2) беттік морфологиясы, оптикалық және импеданс спектроскопиясы.

А.К. Аймуханов, Т.Е. Сейсембекова, А.К. Зейниденов, Д.С. Камбар

Влияние толщины фотоэлектрода SnO на фотоэлектрические параметры солнечной ячейки FTO:SnO:PTB7-TH:ITIC/Mo/Ag

В статье представлены результаты исследования морфологических, оптических и электрофизических параметров пленок SnO_2. Пленки SnO_2 наносились методом *spin-coating* при различных оборотах вращения центрифуги. Экспериментальные исследования проводились методами оптической спектроскопии, вольтамперометрии и измерения импеданса. С помощью атомно-силового микроскопа исследовались топография поверхности и толщина пленок SnO_2. Исследованы оптические свойства пленок SnO_2 с различной толщиной. Показано что увеличение скорости вращения подложки приводит к уменьшению шероховатости поверхности пленок SnO_2. Установлено, что изменение морфологии пленок SnO_2 способствует быстрому транспорту инжектированных дырок к внешнему электроду и уменьшению вероятности обратной рекомбинации. Ячейки с электрон-транспортным слоем SnO_2 в 2000 оборотах показали низкую эффективность (0,17 %). С уменьшением толщины пленок SnO_2 до значения 62 нм наблюдается возрастание значения тока короткого замыкания в 2,3 раза и изменения напряжения холостого хода в 1,12 раз.