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Effect of the thickness and surface interface of In₂O₃ films on the transport and recombination of charges in a polymer solar cell

Indium oxide films were obtained by spin coating from a solution of indium nitrate in ethylene glycol followed by annealing at 300 °C. The influence of the thickness and surface interface of In₂O₃ films on the optical and photo-electrophysical properties of a polymer solar cell has been studied. It is shown that the surface roughness of the film gradually decreases with a decrease in the thickness of the film to 60 nm, and a further decrease in the thickness of the films leads to its increase. The absorption spectra of the films were measured. The values of the optical band gap width are determined. It was found that with a decrease in the thickness of the films, the width of the forbidden zone (E_g) also decreases. It was found that the parameters of the current-voltage characteristics (VAC) and electrophysical measurements also depend on the thickness and interface of the surface of the In₂O₃ films. It was found that with an In₂O₃ film thickness equal to 60 nm, a maximum efficiency value of 3.42 % is observed, at the same time, electrons in the photoactive layer have a maximum charge carrier lifetime and a low recombination rate.

Keywords: In₂O₃ films, polymer solar cell, current-voltage characteristics, impedance spectra.

Introduction

The conversion of solar energy into electrical energy is one of the ways that in the near future can provide a rapidly growing demand for clean energy. Among the currently existing various photovoltaic converters, organic solar cells are of great interest among various international scientific groups [1-3]. In an organic solar cell, to minimize charge recombination at both interfaces and increase the efficiency of charge extraction, a photoactive layer is placed between the electron transfer layer (ETL) and the hole transfer layer (HTL). The ETL layer in OSC plays an important role in performance. The ETL layer can not only affect the efficiency of electron extraction and charge recombination, but also has an effect on the morphology of the photoactive layer. The ETL layer based on metal oxides has attracted huge attention due to its high transparency in the visible spectral region [4, 5].

Among the known metal oxides, indium oxide (In₂O₃) is the most commonly used for organic solar cells. Indium oxide (In₂O₃) is a transparent semiconductor that has a wide band gap of ~ 3.7 eV, high transparency for visible light and chemical stability [6, 7]. In₂O₃ films are produced by various physical and chemical methods. The most common method is sol gel technology, which is characterized by versatility, cheapness and simplicity. However, there are almost no studies on the effect of the technology of obtaining on the effectiveness of OSC.

This paper presents the results of a study of the technology for obtaining an ETL layer based on In₂O₃ on the effectiveness of an OSC with an inverted structure.

Experimental

To obtain indium oxide films on the FTO surface (the FTO substrates were successively washed with ultrasound in detergent, deionized water and ethanol, then dried in air), a solution was prepared in accordance with the procedure described in our other work [8]. To obtain In₂O₃ films, the resulting solution was applied to the FTO surface by spin-coating (SPIN150i model, Semiconductor Production System) at rotational speeds of 1500 — 5000 rpm. After that, the films were annealed in an air atmosphere at a temperature of 300 °C for an hour and gradually cooled to room temperature.

To obtain organic solar cells, a photoactive layer was applied to the surface of the In₂O₃ film by the method shown in article [9], then an HTL layer of PEDOT: PSS (d~30 nm) was applied to the surface by

spin-coating (3000 rpm) and by thermal deposition at the CY-1700x-spc-2 installation (Zhengzhou CY Scientific Instruments Co., Ltd) sprayed a current-removing electrode (Ag, $d \sim 120$ nm).

Morphological and topological studies of the surface were carried out using the atomic force microscope (AFM) JSPM-5400 (JEOL, Japan). A special modular scanning probe microscopy data analysis program (Win SPMII Data-Processing Software) was used to process the images obtained on the AFM. Optical absorption spectra are recorded in the range of 200-800 nm using the AvaSpec-ULS2048CL-EVO spectrophotometer (Avantes). The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode. The VAC of photosensitive cells was determined by the Sol3A Class AAA Solar Simulators (Newport) with PVIV-1A I-V Test Station device.

Results and Discussion

The thickness of the In_2O_3 layer was determined by SEM images of the transverse cleavage of the film. Figure 1 shows SEM images of the transverse cleavage of the studied films. The average thickness of the In_2O_3 films depends on the rotation speed of the substrate on the centrifuge. With an increase in the speed of rotation of the substrate, a decrease in the thickness of the film is observed (Figure 1).

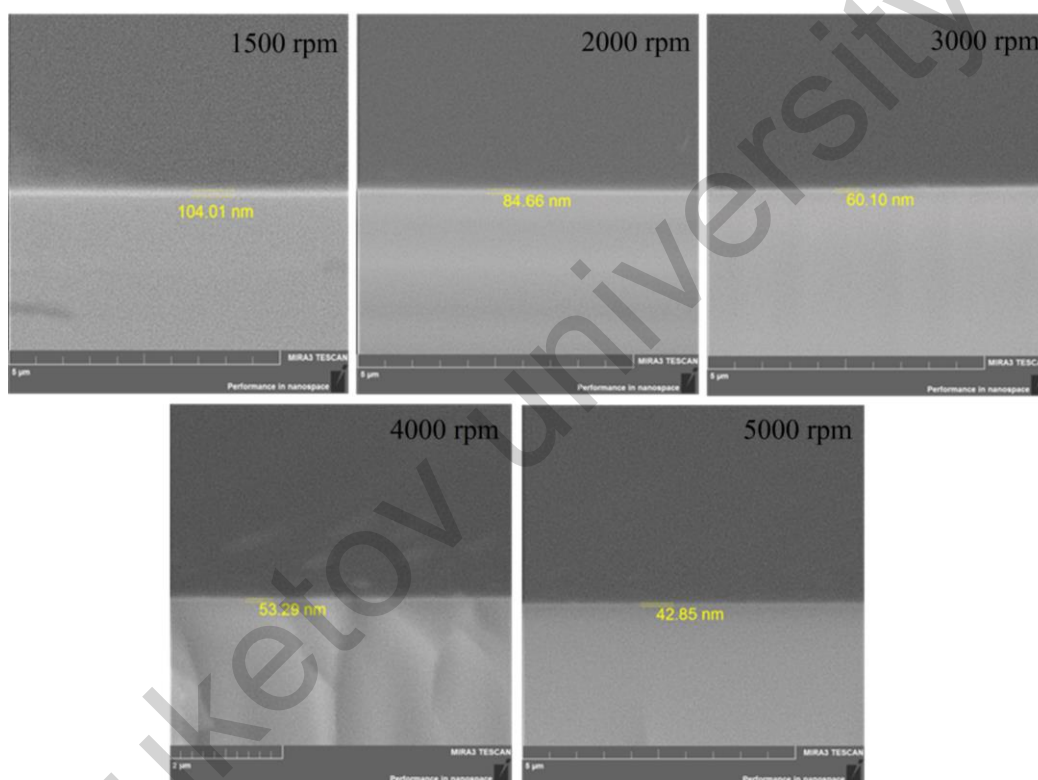
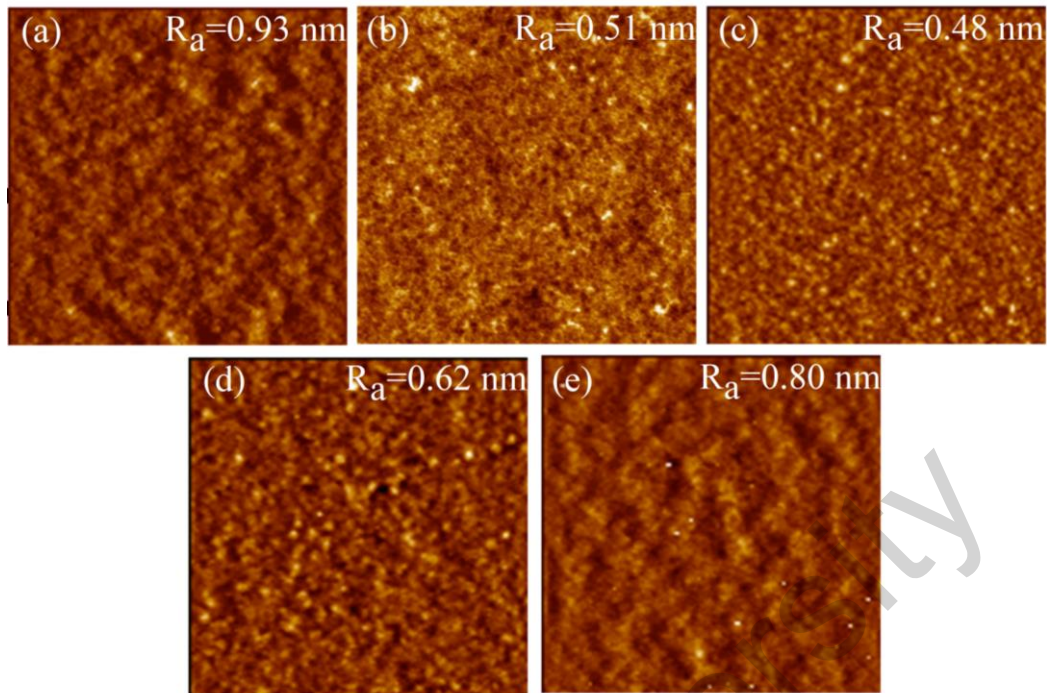


Figure 1. SEM images of transverse cleavage of In_2O_3 films.

Figure 2 shows AFM images of the surface of the studied In_2O_3 films obtained by centrifugation. It can be seen from the AFM data that the thickness of the film affects the morphology of the surface of the In_2O_3 films. The surface roughness of the films is determined by the formula:

$$R_q = \sqrt{\frac{1}{N} \sum_{j=1}^N r_j^2}$$

Where, R_q represents the root-mean-square roughness, i.e. the average value of the measured height deviations taken within the length of the estimate and the measurement from the median line. According to the AFM data, it can be seen that the surface roughness of the studied In_2O_3 films has a non-unambiguous dependence on the thickness.



a) 1500 rpm; b) 2000 rpm; c) 3000 rpm; d) 4000 rpm; e) 5000 rpm.
Figure 2. Images of the morphology of the surface of In_2O_3 films

Thus, the roughness of the films decreases to 0.48 nm with a decrease in the film thickness to 60 ± 5 nm. However, a further decrease in the thickness of the films leads to an increase in the roughness of the In_2O_3 films. The dependence of the roughness of In_2O_3 films on the thickness is shown in Figure 3.

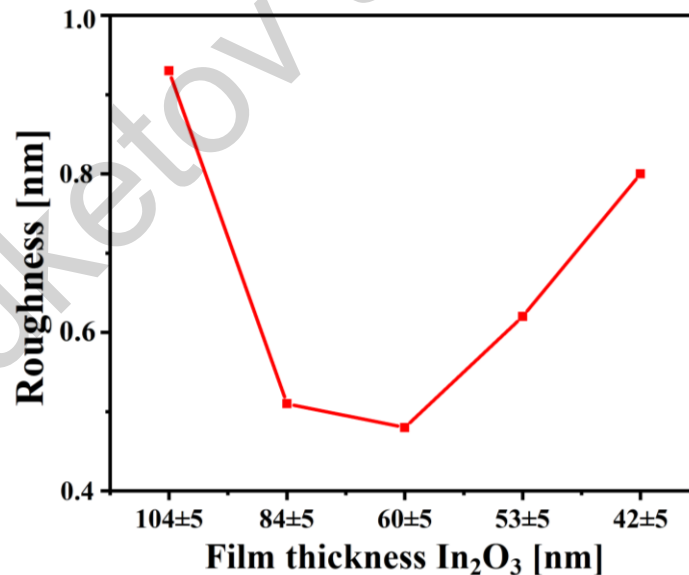


Figure 3. Dependence of the roughness of In_2O_3 films on the thickness

It is known that the morphology of the surface of thin films during growth is determined by two parameters: energy and kinetic. The energy factor is determined by the excess surface energy of the growing film, and the kinetic factor is determined by the diffusion mobility of the atoms of the deposited substance, which depends on temperature. The ratio of these parameters determines the roughness of the deposited film [10]. The observed ambiguous dependence of roughness on the thickness of the In_2O_3 film is related to the dependence of the boiling point and viscosity of the rasterizer used for the preparation of films.

Absorption spectra were measured to determine the effect of film thickness on optical characteristics (Fig. 4). The parameters of the absorption spectra of In_2O_3 films at different thicknesses are given in Table 1. The absorption spectrum is typical of the absorption spectrum of wide-band semiconductors such as TiO_2 , ZnO , SnO_2 , etc. The edge of the fundamental absorption band falls at 212 nm, which corresponds to the optical transition of the In_2O_3 band gap. Measurement of absorption spectra showed that the absorption of films decreases with a simultaneous decrease in thickness (Fig. 4). At the same time, the thickness of the films does not affect the shape of the absorption spectrum [11].

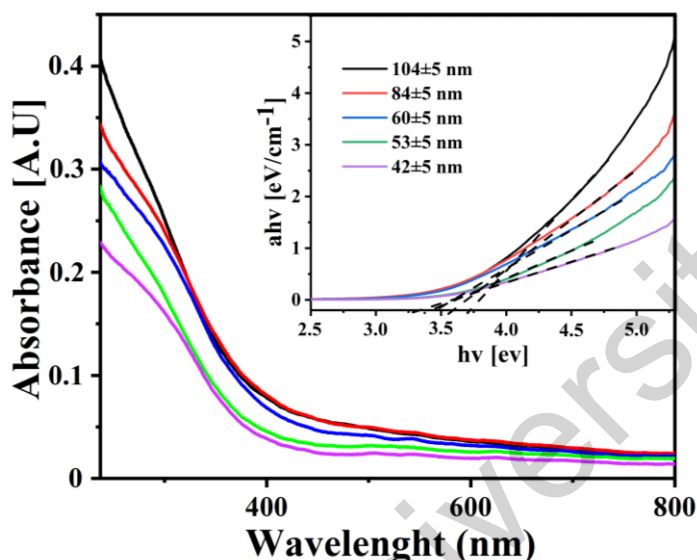


Figure 4. Optical characteristics of In_2O_3 films

The optical band gap width of In_2O_3 films was estimated by the Tauc ratio [12]. The change in the width of the E_g band gap depending on the thickness of the In_2O_3 films is shown in Figure 4. The 104 nm thick film has the highest band gap of 3.71 eV, with a decrease in the thickness of the films, the width of the E_g band gap also decreases to 3.34 eV (Table 1). The observed decrease in the optical width of the band gap with a decrease in thickness is due to the presence of surface defects in the film, the concentration of which increases with a decrease in thickness.

Table 1

Parameters of optical absorption spectra of In_2O_3 films

№	Film thickness In_2O_3 , nm	D, A.U.	Bandgap, eV
1	104±5	0.40	3.71
2	84±5	0.33	3.59
3	60±5	0.30	3.44
4	53±5	0.27	3.40
5	42±5	0.22	3.34

To determine the effect of the thickness of In_2O_3 films on the transport and recombination of charges in a polymer solar cell, an $\text{In}_2\text{O}_3/\text{P3HT}:\text{ICMA}/\text{PEDOT}:\text{PSS}/\text{Ag}$ cell was assembled. Upon photoexcitation of the photoactive OSC layer, an electron-hole pair is formed, which then decays into free electrons and holes at the interface $\text{In}_2\text{O}_3/\text{P3HT}:\text{ICMA}$ and $\text{P3HT}:\text{ICMA}/\text{PEDOT}:\text{PSS}$. The electrons are injected into the ETL layer In_2O_3 , and the hole into the HTL layer $\text{PEDOT}:\text{PSS}$.

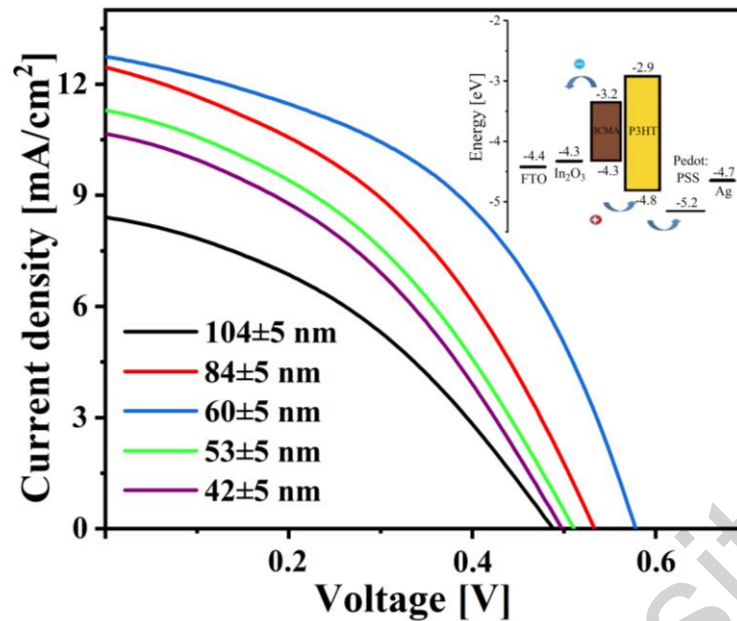


Figure 5. Current-voltage characteristic of a polymer solar cells In₂O₃/P3HT: ICMA/ PEDOT: PSS/Ag

The current-voltage characteristics of solar cells at different values of In₂O₃ thickness are shown in Figure 5. Table 2 shows the photovoltaic parameters of the OSCs. As can be seen from Figure 5 and Table 2, the VAC parameters depend on the thickness of the In₂O₃ films. Thus, when the thickness of the In₂O₃ film decreases to 60 nm, the efficiency of OSCs increases to 3.42 %. However, further reduction of the film thickness to 42 nm leads to a decrease in the values of current, FF, voltage and efficiency of OSCs.

Table 2

Parameters of the VAC solar cells

Film thickness In ₂ O ₃ , nm	V _{oc} (V)	J _{sc} (mA/cm ²)	V _{max} (V)	J _{max} (mA/cm ²)	FF	PCE %
104±5	0.49	8.38	0.3	5.25	0.38	1.58
84±5	0.53	12.41	0.34	7.91	0.41	2.69
60±5	0.58	12.74	0.39	8.78	0.46	3.42
53±5	0.51	11.25	0.32	7.04	0.39	2.25
42±5	0.5	10.67	0.31	6.68	0.39	2.07

The observed changes in the VAC are due to the effect of the surface interface of indium oxide films with a decrease in thickness on the transfer of charge carriers to OSCs. For a detailed study of the detailed study of this issue, the impedance spectra of OSCs were measured. The impedance spectra of solar cells In₂O₃/P3HT: ICMA/PEDOT: PSS/Ag are shown in Figure 6. The equivalent electrical circuit is characterized by impedance spectra, shown in the inset of Figure 6, where R_w is the resistance of the film In₂O₃, R_{rec} C describes the boundary of the photoactive layer/ In₂O₃. A decrease in the thickness of In₂O₃ contributes to the rapid transfer of electrons to the cathode (FTO), but it also contributes to an increase in the recombination of injected electrons at the boundary with the photoactive layer, which affects the photoelectric characteristics of OSCs.

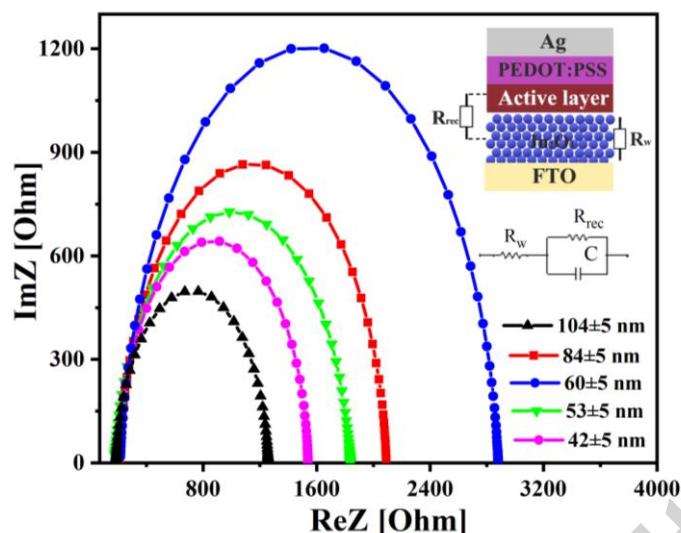


Figure 6. Equivalent electrical circuit and impedance spectra of cells

Table 3 shows the values of the film parameters, where k_{eff} and τ_{eff} are the recombination index characterizing the recombination rate and the effective lifetime of charge carriers in In_2O_3 .

Table 3

The value of electrophysical parameters of films

Film thickness In_2O_3 , nm	R_w , (Ω)	R_{rec} , (Ω)	C , (Φ) $\cdot 10^{-8}$	τ_{eff} , (μ s)	k_{eff} , (c^{-1})
104±5	174.39	1093	3.3751	0.6	1666
84±5	133.3	1982.7	6.8205	1.3	769
60±5	117.81	2681.7	2.3751	1.7	588
53±5	145.88	1694.3	4.047	1.1	909
42±5	159.22	1362.8	1.2928	0.9	1111

It can be seen from the table that with a decrease in the thickness of the films, the resistance R_w also decreases, this improves the transport of injected electrons to the FTO. At the same time, a decrease in the thickness of In_2O_3 leads to an increase in the recombination resistance, which leads to a decrease in the recombination of injected electrons. The lifetime of the charge carriers τ_{eff} increases and the recombination efficiency k_{eff} decreases. However, a further decrease in the film thickness $d \leq 60$ nm leads to an increase in the resistance R_w , and to a decrease in the resistance R_{rec} , which indicates an increase in recombination processes. The observed changes in the electrophysical characteristics of the OSCs are associated with a decrease in the thickness of the In_2O_3 films are associated with a change in the interference. Thus, the results of impedance spectroscopy correlate with AFM microscopy data and VAC data.

Conclusion

This paper presents the results of the influence of the thickness and surface interface of In_2O_3 films on the optical and photo-electrophysical properties of a polymer solar cell. It was found that with a decrease in the film thickness to 60 ± 5 nm, the roughness of the films decreases to 0.48 nm, and a further decrease in the thickness of the films leads to an increase in the roughness of the In_2O_3 films. It is shown that the optical width of the band gap also decreases to 3.34 eV with a decrease in the thickness of the films. The decrease in the optical width of the band gap is explained by the presence of surface defects in the film, the concentration of which increases with decreasing thickness. It is shown that the parameters of the VAC depend on the thickness of the In_2O_3 films. It is established that with the thickness of In_2O_3 films equal to 60 nm, the highest parameters of the VAC and efficiency of the polymer solar cell are observed. The nonlin-

ear dependence of electric transport characteristics on the thickness and surface interface of In_2O_3 films is established.

References

- 1 Che X. High fabrication yield organic tandem photovoltaics combining vacuum- and solution-processed subcells with 15 % efficiency / X. Che, Y. Li, Y. Qu, S.R. Forrest // *Nature Energy*. — 2018. — Vol. 3. — P. 422–427. <https://doi.org/10.1038/s41560-018-0134-z1>.
- 2 Zhang S. Over 14 % Efficiency in Polymer Solar Cells Enabled by a Chlorinated Polymer Donor / S. Zhang, Y. Qin, J. Zhu, J. Hou // *Advanced Materials*. — 2018. — Vol. 30. — P. 1800868. <https://doi.org/10.1002/adma.201800868>.
- 3 Li S. Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2 % Efficiency in Polymer Solar Cells / S. Li, L. Ye, W. Zhao, H. Yan, B. Yang, D. Liu, W. Li, H. Ade, J.A. Hou // *Journal of the American Chemical Society*. — 2018. — Vol. 140 — Issue 23. — P. 7159–7167. <https://doi.org/10.1021/jacs.8b02695>.
- 4 Yang G. Recent progress in electron transport layers for efficient perovskite solar cells / G. Yang, H. Tao, P. Qin, W. Ke, G. Fang // *Journal of Materials Chemistry A*. — 2016 — Vol. 4. — P. 3970–3990. <https://doi.org/10.1039/C5TA09011C>.
- 5 Aimukhanov A.K. The impact of SnO_2 photoelectrode's thickness on photovoltaic properties of the solar cell FTO: SnO_2 :PTB7-Ti: ITIC/Mo/Ag / A.K. Aimukhanov, T.E. Seisembekova, A.K. Zeinidenov, D.S. Kambar // *Bulletin of the University of Karaganda-Physics*. — 2022. — No. 2 — Issue 106. — P. 86–91. <https://doi.org/10.31489/2022PH2/86-91>.
- 6 Kraini M. Properties of In_2O_3 films obtained by thermal oxidation of, sprayed In_2S_3 / M. Kraini, N. Bouguila, I. Halidou, A. Timoumi, S. Alaya // *Mat SciSemiconProc*. — 2013. — Vol. 16. — P. 1388–1396. <https://doi.org/10.1016/j.mssp.2013.04.021>.
- 7 Savarimuthu E. Synthesis and materials properties of transparent conducting In_2O_3 films prepared by sol-gel-spin coating technique / E. Savarimuthu, K.C. Lalithambika, A. Moses Ezhil Raj, L.C. Nehru, S. Ramamurthy // *J PhysChem Solids*. — 2007. — Vol. 68. — P. 1380–1389. <https://doi.org/10.1016/j.jpcs.2007.02.038>.
- 8 Omarbekova G.I. The role of surface defects in the charge transport in organic solar cells based on oxidized indium thin films / G.I. Omarbekova, A.K. Aimukhanov, B.R. Ilyassov, D.T. Valiev, A.K. Zeinidenov, V.V. Kudryashov // *Surfaces and Interfaces*. — 2022. — Vol. 31. — P. 102026. <https://doi.org/10.1016/j.surfin.2022.102026>.
- 9 Seisembekova T.E. Competitive charge transport processes in inverted polymer solar cells based on ZnO thin films / T.E. Seisembekova, A.K. Aimukhanov, A.K. Zeinidenov, B.R. Ilyassov // *Applied Physics A*. — 2022. — Vol. 128. — P. 407. <https://doi.org/10.1007/s00339-022-05560-7>.
- 10 Панин А.В. О природе шероховатости поверхности тонких диэлектрических пленок / А.В. Панин, А.Р. Шугуров, Л.Н. Пучкарева // *Физическая мезомеханика*. — 2000. — № 3. — С. 53–60.
- 11 Ismail R.A. Preparation of colloidal In_2O_3 nanoparticles using nanosecond laser ablation in water / R.A. Ismail // *Micro & Nano Letters*. — 2011. — Vol. 6. — P. 951–954. <https://doi.org/10.1049/mnl.2011.0459>.
- 12 Ma Q. Atomic-Layer-Deposition of Indium Oxide Nano-films for Thin-Film Transistors / Q. Ma, H.-M. Zheng // *Nanoscale Research Letters*. — 2018. — Vol. 13. — P. 1. <https://doi.org/10.1186/s11671-017-2414-0>.

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Полимерлі күн элементіндегі зарядтардың тасымалдануы мен рекомбинациясына In_2O_3 қабыршақтарының қалыңдығы және беттік интерфейсінің әсері

Индий оксидінің қабыршақтары этиленгликольдегі индий нитратының ерітіндісінен *spin coating* әдісімен, содан кейін оны $300\text{ }^\circ\text{C}$ күйдіру арқылы алынды. Полимерлі күн элементінің оптикалық және фото электрофизикалық қасиеттеріне In_2O_3 қабыршақтарының қалыңдығы мен беткі интерфейсінің әсері туралы зерттеулер жүргізілді. Қабыршақ бетінің кедір-бұдырлығы қабыршақ қалыңдығы 60 нм-ге дейін жұқарғанда біртіндеп азаятыны, ал қабыршақ қалыңдығының одан әрі жұқарғанда қайта өсе бастайтыны көрсетілді. Қабыршақтардың жұтылу спектрлеріне өлшеу жүргізілді. Тыйым салынған аймақтың оптикалық снінің мәндері анықталды. Қабыршақтардың қалыңдығы жұқарған кезде тыйым салынған аймақтың оптикалық (E_g) ені де азаятыны айқындалды. Вольтамперлік сипаттамалардың (ВАС) және электрофизикалық өлшемдердің параметрлерінің In_2O_3 қабыршақтарының қалыңдығы мен беткі интерфейсіне де тәуелді екендігі белгілі болды. In_2O_3 қабыршақтарының қалыңдығы 60 нм-ге тең болған кезде тиімділіктің максималды мәні 3,42 % болатындығы, сонымен қатар фотобелсенді қабаттағы электрондар заряд тасымалдаушылардың максималды өмір сүру ұзақтығына және рекомбинацияның төмен жылдамдығына ие болатындығы анықталды.

Кілт сөздер: In_2O_3 қабыршақтары, полимерлі күн элементі, вольтамперлік сипаттамалары, импеданс спектрлері.

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Влияние толщины и поверхностного интерфейса пленок In_2O_3 на транспорт и рекомбинацию зарядов в полимерном солнечном элементе

Пленки оксида индия были получены методом *spin coating* из раствора нитрата индия в этиленгликоле с последующим отжигом при 300 °С. Проведены исследования влияния толщины и поверхностного интерфейса пленок In_2O_3 на оптические и фотоэлектрофизические свойства полимерного солнечного элемента. Показано, что шероховатость поверхности пленки постепенно уменьшается со снижением толщины пленки до 60 нм, а дальнейшее уменьшение толщины пленок приводит к ее возрастанию. Проведены измерения спектров поглощения пленок. Определены значения оптической ширины запрещенной зоны. Установлено, что при снижении толщины пленок ширина запрещенной зоны (E_g) также уменьшается. Было установлено, что параметры вольтамперных характеристик и электрофизических измерений также зависят от толщины и интерфейса поверхности пленок In_2O_3 . Доказано, что при толщине пленки In_2O_3 , равной 60 нм, наблюдается максимальное значение КПД 3,42 %, в то же время электроны в фотоактивном слое имеют максимальное время жизни носителей заряда и низкую скорость рекомбинации.

Ключевые слова: пленки In_2O_3 , полимерный солнечный элемент, вольтамперные характеристики, спектры импеданса.

References

- 1 Che X., Li, Y., Qu, Y., & Forrest, S.R. (2018). High fabrication yield organic tandem photovoltaics combining vacuum- and solution-processed subcells with 15 % efficiency. *Nature Energy*, 3, 422–427. <https://doi.org/10.1038/s41560-018-0134-z1>.
- 2 Zhang S., Qin Y., Zhu J., & Hou, J. (2018). Over 14 % Efficiency in Polymer Solar Cells Enabled by a Chlorinated Polymer Donor. *Advanced Materials*, 30, 1800868. <https://doi.org/10.1002/adma.201800868>.
- 3 Li, S., Ye, L., Zhao, W., Yan, H., Yang, B., Liu, D., Li, W., Ade, H., & Hou, J.A. (2018). Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2 % Efficiency in Polymer Solar Cells. *Journal of the American Chemical Society*, 140(23), 7159–7167. <https://doi.org/10.1021/jacs.8b02695>.
- 4 Yang, G., Tao, H., Qin, P., Ke, W., & Fang, G. (2016). Recent progress in electron transport layers for efficient perovskite solar cells. *Journal of Materials Chemistry A*, 4, 3970–3990. <https://doi.org/10.1039/C5TA09011C>.
- 5 Aimukhanov, A.K., Seisembekova, T.E., Zeinidenov, A.K., & Kambar, D.S. (2022). The impact of SnO_2 photoelectrode's thickness on photovoltaic properties of the solar cell FTO: SnO_2 : PTB7-TH: ITIC/Mo/Ag. *Bulletin of the University of Karaganda-Physics*, 2(106), 86–91. <https://doi.org/10.31489/2022PH2/86-91>.
- 6 Krainin, M., Bouguila, N., Halidou, I., Timoumi, A., & Alaya, S. (2013). Properties of In_2O_3 films obtained by thermal oxidation of, sprayed In_2S_3 . *Mat SciSemiconProc*, 16, 1388–1396. <https://doi.org/10.1016/j.mssp.2013.04.021>.
- 7 Savarimuthu, E., Lalithambika, K.C., Moses Ezhil Raj, A., Nehru, L.C., & Ramamurthy, S. (2007). Synthesis and materials properties of transparent conducting In_2O_3 films prepared by sol-gel-spin coating technique. *J PhysChem Solids*, 68, 1380–1389. <https://doi.org/10.1016/j.jpcs.2007.02.038>.
- 8 Omarbekova, G.I., Aimukhanov, A.K., Ilyassov, B.R., Valiev, D.T., Zeinidenov, A.K., & Kudryashov, V.V. (2022). The role of surface defects in the charge transport in organic solar cells based on oxidized indium thin films. *Surfaces and Interfaces*, 31, 102026. <https://doi.org/10.1016/j.surfin.2022.102026>.
- 9 Seisembekova, T.E., Aimukhanov, A.K., Zeinidenov, A.K., & Ilyassov, B.R. (2022). Competitive charge transport processes in inverted polymer solar cells based on ZnO thin films. *Applied Physics A*, 128, P.407. <https://doi.org/10.1007/s00339-022-05560-7>.
- 10 Panin, A.V., Shugurov, A.R., & Pushkareva, L.N. (2000). О природе шероховатости поверхности тонких диэлектрических пленок [On the nature of surface roughness of thin dielectric films]. *Fizicheskaya mezhmekhanika — Physical mesomechanics*, 3, 53–60 [in Russian].
- 11 Ismail, R.A. (2011). Preparation of colloidal In_2O_3 nanoparticles using nanosecond laser ablation in water. *Micro & Nano Letters*, 6, 951–954. <https://doi.org/10.1049/mnl.2011.0459>.
- 12 Ma, Q., & Zheng, H.-M. (2018). Atomic-Layer-Deposition of Indium Oxide Nano-films for Thin-Film Transistors. *Nanoscale Research Letters*, 13, 1. <https://doi.org/10.1186/s11671-017-2414-0>.