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INFLUENCE OF STRUCTURAL FEATURES OF ZNO FILMS ON OPTICAL AND PHOTOELECTRIC CHARACTERISTICS OF INVERTED POLYMER SOLAR ELEMENTS

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In this work we investigated the effect of preliminary annealing of zinc acetate solution films on the morphology, structure, optical properties of the formed ZnO films and also on the photovoltaic properties of polymer solar cells based on the obtained ZnO films. It was found that the pre-annealing temperature significantly affects the morphology and structure of the obtained ZnO films. At pre-annealing temperatures below 200 ^oC the films have a strongly relief morphology (wrinkled morphology), while at pre-annealing temperatures above 200^oC the surface morphology of the films is smooth. The relief of ZnO films affects the photocurrent density of solar cells. Cells based on ZnO films with wrinkled morphology showed a higher photocurrent compared to smooth morphology, which is due to strong light scattering and, as a result, the optical path of light in the photoactive layer is increased due to multiple reflection of light in the wrinkled structure of ZnO. In addition, with increasing pre-annealing temperature, the photovoltage of solar cells and the rate of recombination of charge carriers increases, but the diffusion coefficient of charge carriers decreases, which indicates an increase in the density of defects in the crystal lattice of ZnO. Thus, it has been shown that smooth or highly relief thin ZnO films with controlled properties can be obtained from a zinc acetate solution.

Keywords: zinc oxide, thin films, annealing, surface morphology, absorption spectra, inverted polymer solar cells.

Introduction

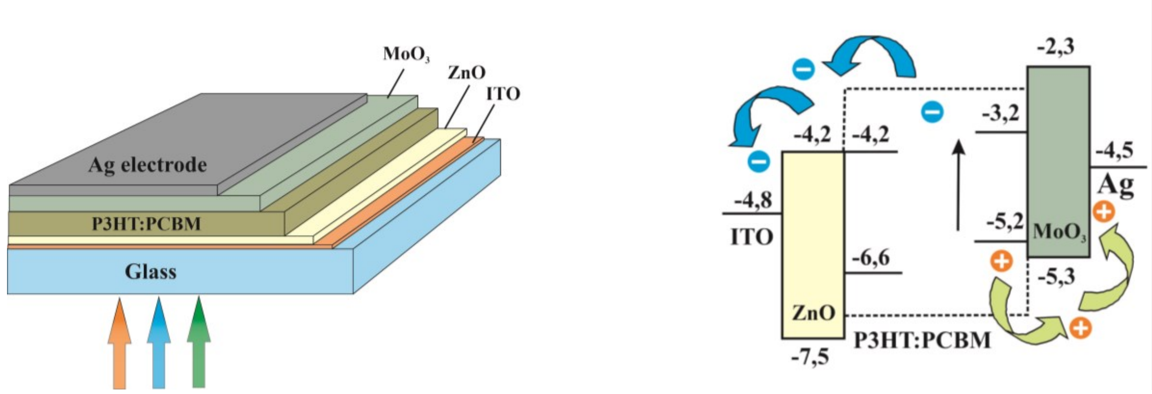
In recent years, much attention has been paid to the development of organic solar cells (OSC) due to their rapid increase in energy conversion efficiency, economy, ease of processing and flexibility. Research has experienced a renaissance with the introduction of high-performance, low-bandgap polymer donors and non-fullerene acceptors. Today, the energy conversion efficiency of polymer solar cells reaches 17-18% [1, 2]. In addition to innovations in the molecular aspects of OSC, it has also been found that processing methods and buffer layers also play a key role in obtaining better performance parameters. Various oxides of n-type metals with a wide band gap, such as TiO_2, ZnO, Cs_2CO_3 and some polyelectrolytes with a large dipole moment, have been successfully used as interfacial electron transport layers in inverted devices [3]. In addition, various forms of film nanostructuring, surface treatment, and processing aids have been studied to improve the efficiency of charge collection, transport, and selectivity [4].Therefore, the current research is focused on the study of the electron transport layer, in our case, zinc oxide (ZnO), in inverted polymer solar cells (IPSC).

Zinc oxide is one of the most promising materials for electron transfer in IPSC due to its good environmental resistance, high transparency in the visible and near infrared regions, and high electron mobility. ZnO films are obtained by various methods, including the sol-gel method. The sol-gel method is a technologically simple process that allows you to obtain better quality coatings. It should be noted that the important crystal properties of thin ZnO films strongly depend on the growth conditions, the growth technique, and the substrate [5]. ZnO-based materials can be used in various optoelectronic devices, sensors, transistors, and solar cells [6]. Also, good operational stability of IPSC with ZnO was noted, due to the fact that ZnO blocks ultraviolet light, which leads to negligible photodegradation of organic materials [7]. Previous studies have presented similar effective structures of zinc oxide for IPSC. Various names have been given to these structures, such as nano-comb, ripple, wavy or wrinkled structure. For example, in article [4], nano-combs were obtained, formed by a simple process of linear annealing. In work [8], the influence of the flat and nano-ribbed morphology and thickness of the ZnO layer on the parameters of the device was studied, thereby emphasizing the sensitivity of these devices to the active film thickness. At the same time, it was mentioned that there was no significant difference in performance between the structures. In a study [9], the wrinkled structure of the surface was optimized by adding ZnO nanoparticles to a zinc acetate solution. As a result, it was found that the productivity of a device based on wrinkled ZnO with nanoparticles was two times higher than that of smooth thin films. Kim and others [10] found that the properties of wrinkled structures can be tuned by changing the concentration of zinc in the precursor solution. In addition to the uniformity and ordering of wrinkles and cavities in such surface structures, defects on them also play an important role in the operation of the device. Therefore, there is a need for a detailed study of the properties of thin ZnO films with a wrinkled structure.

In this regard, this work presents a method for obtaining thin ZnO films with different morphologies and investigates the effect of preliminary annealing on their morphological, optical, and electrophysical properties. For a complete description of morphology in detail various statistical parameters are calculated based on the AFM images. The measurement results allow to define features of the surface topography of ZnO films by pre-annealing.

1. Methods and materials

To carry out photoelectric measurements, OSCs were prepared, shown in figure 1a. The energy diagram of the functional layers of a solar cell is shown in figure 1b. The device was fabricated on pre-cleaned ITO coated glass substrates. The substrates were sonicated for 15 minutes each in acetone, deionized water, and ethanol. After ultrasonic cleaning, the substrates were dried with a stream of nitrogen (N_2) and then subjected to ultraviolet (UV) treatment for 30 minutes.



a) b)

Fig.1. Structure of the organic solar cell (a) and the energy diagram of the cells (b).

A solution of ZnO was obtained by a sol-gel method in an aqueous solution using zinc acetate dihydrate [Zn $(CH_3COO)_2$* $2H_2O$], isopropyl alcohol (C_3H_8O), and monoethanolamine (C_2H_7NO) (MEA) [11]. The concentration of zinc acetate and monoethanolamine in the solution was 0.5 M. The resulting colloidal solution was stirred for 1 hour on a magnetic stirrer at a temperature of 60 ° C until a homogeneous and transparent solution appeared. The film-forming ZnO solution was kept for 24 hours with constant stirring, after which the solution was filtered through a filter with a porosity of 0.45 μm. The resulting colloidal solution was applied onto pre-cleaned glass substrates by spin-coating. The ZnO films were applied at a centrifuge speed of 3000 rpm, and the centrifuge rotation time was 90 seconds. The obtained ZnO films were preliminarily annealed at t = 100-300°C for 20 minutes. Then, to obtain a polycrystalline ZnO film, the final annealing was carried out at t = 450°C for 30 minutes.

To obtain organic solar cells, a photoactive P3HT: PCBM layer (Sigma Aldrich,> 99.9%) at a concentration of 1:0.8 was applied to the surface of the electron transport ZnO layer by spin-coating. After that, the samples were annealed in air at a temperature of 140 ° C for 10 min, then then sprayed onto the surface of p-type layer MoO_3, then the silver electrode (Figure 2). The surface topography of the samples was studied using a JSPM-5400 high-resolution 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. Surface morphology, roughness, grain size of thin ZnO films were analyzed from AFM images. The images of the ZnO films surface were obtained in the semicontact scanning mode.

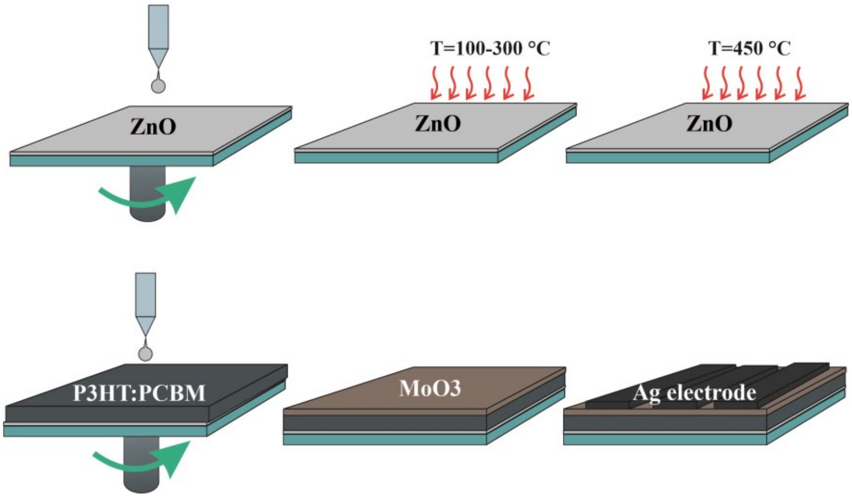


Fig.2. Scheme of obtaining organic solar cells.

The registration of the absorption spectra of the samples under study was carried out on an AvaSpec-ULS2048CL-EVO spectrometer manufactured by Avantes, which records absorption spectra in the range of 200-1100 nm and has an optical resolution of 0.4 nm. The current-voltage characteristics (CVC) of the organic photosensitive element were measured using a P20X potentiostat-galvanostat in a linear sweep mode at an illumination intensity of 100 mW/cm^2. The values of the open circuit voltage Uoc, short circuit current Isc, and fill factor FF were determined by the method [12]. The impedance spectra were measured using a P45X potentiostat-galvanostat in the impedance mode using the setup described in detail in [13].

2. Results and discussion

Pictures of the surface morphology of ZnO films at a scale of 20x20 µm are shown in Figure 3. As can be seen from the AFM images, the temperature of preliminary annealing affects the surface morphology.

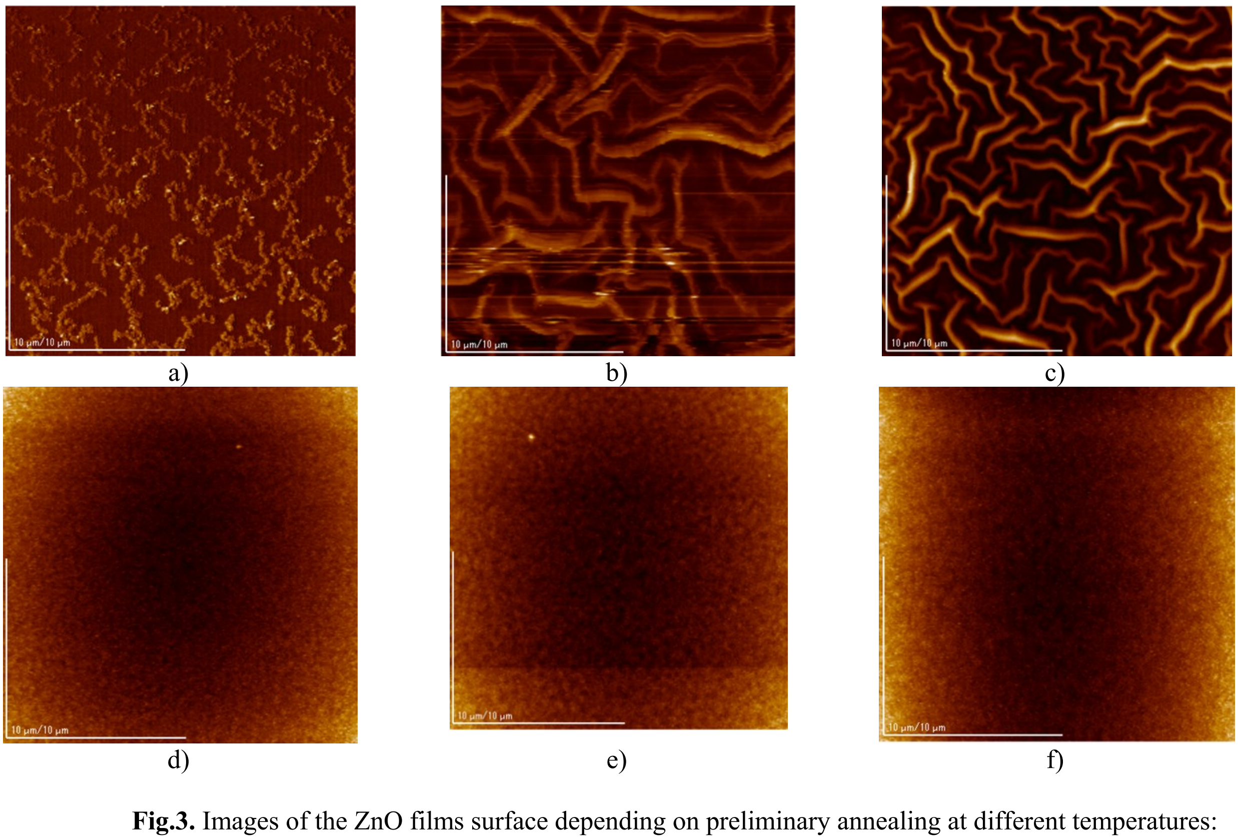


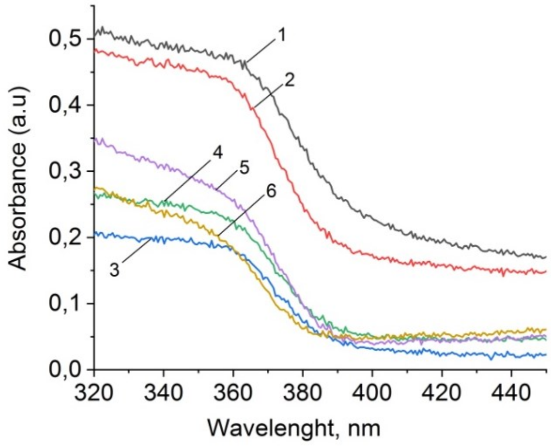
Fig.3. Images of the ZnO films surface depending on preliminary annealing at different temperatures: a - 20^{o}C, b - 100 ^{o}C, c - 150^{o}C, d - 200^{o}C, e – 300 ^{o}C, f - 450 ^{o}C

The morphology of the ZnO film with preliminary annealing at a temperature of 100°C (fig. 3b) and 150°C (fig. 3c) has branched protrusions (wrinkles). The average distance between the protrusions during annealing at 100°C was 1213 nm, at 150°C 995 nm, the average height of the protrusions was 287 nm and 124 nm, respectively. A further increase in the preliminary annealing temperature of 200-450°C (fig. 3 d-f) leads to a smoothing of the surface ZnO films. An analysis of the surface roughness was carried out at a scale of 20 μm*20 μm and the grain size of ZnO on an enlarged scale (1 μm*1 μm). The calculated average grain diameter showed that a change in the pre-annealing temperature affects the grain size, that is, when the film surface is smoothed, the grain diameter decreases from 9.3 nm to 0.8 nm. There is also a decrease in the surface roughness of the ZnO films with increasing temperature (Table 1).

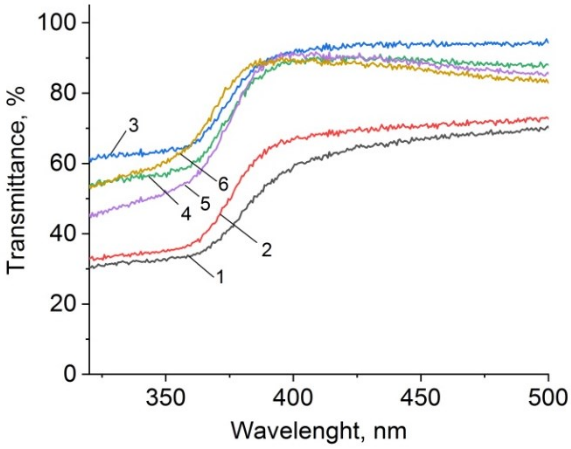
Table 1. Roughness of the film surface and the particle diameter of ZnO grains depending on the temperature of preliminary annealing.

Parameters	Pre-annealing temperature				
	100^0C	150^0C	200^0C	300^0C	450^0C
Roughness, R_a	78 nm	47 nm	7 nm	7 nm	3.5 nm
Grain diameter	9.3 nm	6.6 nm	1.3 nm	1.2 nm	0.8 nm

The absorption (a) and transmission (b) spectra of ZnO layers deposited at different annealing temperatures on glass substrates are shown in figure 4. It can be seen from the figure that the morphology and surface roughness also influenced the optical properties of the ZnO layer, such as light transmission and absorption, which are the key factors in the use of the material in the manufacture of solar cells. ZnO layers at a pre-annealing temperature of 200-450^0C showed insignificant absorption and light transmission efficiency of about 90% (fig. 4a, 4b).



a)



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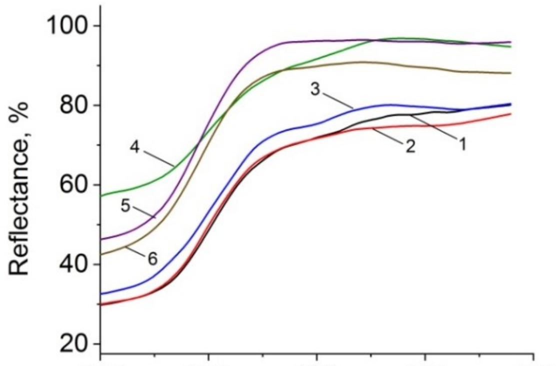

c)

Fig.4. Absorption (a), transmission (b) and reflection (c) spectra of ZnO films:
1 - 100°C, 2 - 150 °C, 3 - 175°C, 4 - 200°C, 5 – 300 °C, 6 - 450 °C

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However, at low pre-annealing temperatures (100°C-150°C), the light transmission of the ZnO layer decreased (correspondingly, the optical density increased) due to the formation of wrinkled structures, which leads to strong diffuse scattering. The reflectance spectra are shown in Fig.4c.

The influence of ZnO layers with different surface morphology on the electrophysical properties of solar cells is shown in figure 5. The main characteristics are shown in table 2. As can be seen from the CVC in figure 5 and the data in the table, the dynamics of an increase in the photovoltage and the dynamics of a decrease in the photocurrent with an increase in the pre-annealing temperature are observed. The decrease in the photocurrent is due to a change in the relief of the film. Films with a wrinkled structure, due to strong scattering, increase the optical path of light in the photoactive layer and thereby increase the probability of absorption, which leads to an increase in the photocurrent.

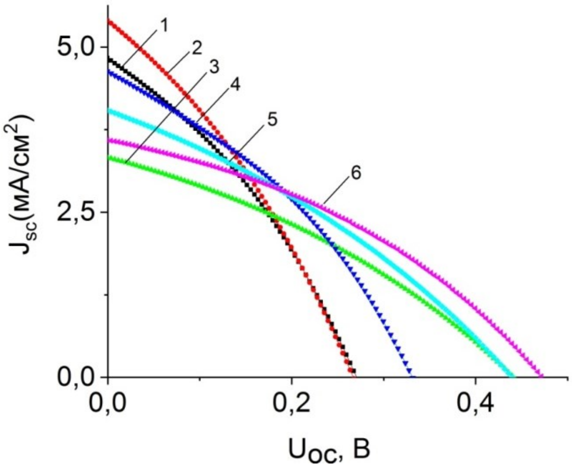


Fig.5. Current-voltage characteristics of inverted polymer solar cells:
1 - 100°C, 2 - 150 °C, 3 - 175°C, 4 - 200°C, 5 – 300 °C, 6 - 450 °C

Table 2. Electrophysical properties of films obtained at different annealing temperatures

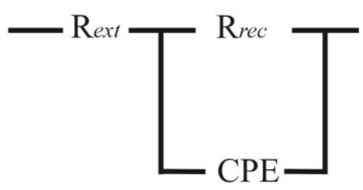
Sample (°C)	U oc, (mV)	Jsc, (mA/cm^2)	FF, (%)	PCE, %
100	260	4.76	30	0.442
150	270	5.45	30	0.456
175	450	3.35	33	0.496
200	330	4.64	35	0.541
300	440	4.08	32	0.577
450	480	3.59	37	0.638

The photovoltage of inverted polymer solar cells is due to the energetics of the photoactive layer and selective electrodes. In our cells, these are molybdenum oxide and zinc oxide. However, molybdenum oxide and the photoactive layer were deposited under the same conditions, and the observed changes in the photovoltage of the cells are due to the influence of the structure of zinc oxide. The position of the quasi-Fermi level of electrons in ZnO determines the cell photovoltage and depends on the density and types of lattice defects. The higher the position of the quasi-Fermi level of electrons to the bottom of the conduction band, the higher the generated photovoltage. It is known that defects forming shallow donor levels shift the Fermi level of electrons to the bottom of the conduction band. Thus, the observed increase in the photovoltage of the cells with an increase in the pre-annealing temperature can be associated with an increase in the density of defects in the ZnO crystal lattice.

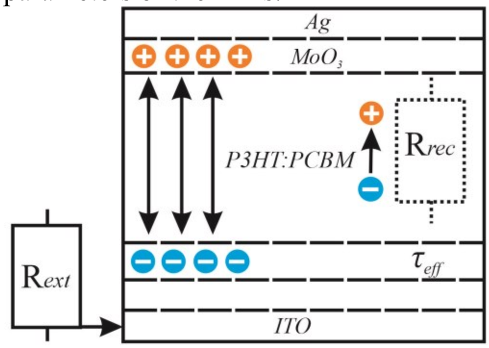
For a detailed understanding of the influence of the electron transport layer of ZnO on the mechanisms of charge carrier transport, we measured the impedance spectra of polymer solar cells. To interpret the impedance spectra, a standard equivalent electrical circuit was used, where R_{rec} is the low-frequency resistance, CPE is the capacitance, and R_{ext} is the high-frequency resistance (figure 6 a).

The spectra were simulated using the EIS-analyzer software package and the main electrical transport properties of the films were calculated (table 3), where: D_{eff} is the effective diffusion coefficient of electrons, k_{eff}

is the effective rate of electron recombination, τ_{eff} is the effective lifetime of an electron. Resistance to electron transport in the zinc oxide film R_{ext}, charge transfer resistance R_{rec} associated with electron recombination were calculated from the central arc of the impedance spectra. The charge transfer mechanism and the transport of electrons in the IPSC are shown in figure 6b. The analysis of the impedance measurement results was carried out according to the diffusion – recombination model. Figure 6c shows the impedance spectra of the films under study. It can be seen from the figure that the hodograph diameter of a film with a smooth surface is smaller than that of a wrinkled film. This means that the sample annealed at 450^0C has a lower value of the charge transfer resistance. Table 3 shows the values of the electrophysical parameters of the films.



a)



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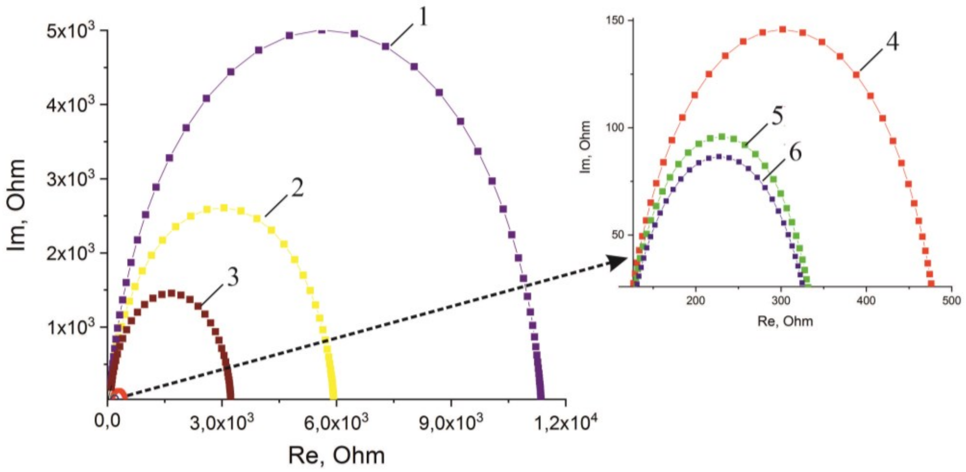

c)

Fig.6. Equivalent electrical circuit (a), charge transfer mechanism (b) and impedance hodographs (c) of inverted polymer solar cells: 1 - 100°C, 2 - 150 °C, 3 - 175°C, 4 - 200°C, 5 – 300 °C, 6 - 450 °C

Table 3. The value of the electrophysical parameters of the ZnO film.

t, ^{0}C	D_{eff}, (cm^2s^{-1})	k_{eff}, (s^{-1})	τ_{eff}, (ms)	R_{rec}, (Ohm)	R_{ext}, (Ohm)	Con,(Ohm*cm*s^{-1})	L, (nm)
100^0C	$4.67*10^{-6}$	0.4	678	11304	57	66.6	40
150^0C	$5.17*10^{-6}$	0.87	318	5873	57	73.8	40
175^0C	$2.92*10^{-6}$	1.21	230	3156	75	54.8	40
200^0C	$2.1*10^{-7}$	1.17	236	366	118	6.19	40
300^0C	$5.21*10^{-7}$	2.28	122	242	61	7.95	40
450^0C	$3.47*10^{-7}$	1.74	159	238	69	5.99	40

Using the EIS-analyzer software package, R_{rec} and R_{ext} are calculated, and k_{eff} is determined from the maximum of the hodograph arc by the formula $\omega_{max} = k_{eff}$. The thickness of the films was determined using a scanning probe microscope. It can be seen from table 3 that with an increase in the pre-annealing temperature, the effective diffusion coefficient D_{eff} decreases, as does the resistance R_{rec}., which characterizes the recombination channels. This dynamic is due to an increase in the density of crystal lattice defects with an increase in the pre-annealing temperature. The lower the temperature, the slower the crystallization process

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occurs and a less defective structure is formed, and at higher temperatures the crystallization process is accelerated, which leads to an increase in the density of defects. The defects of the crystal lattice serve as traps of charge carriers and centers of recombination, and with an increase in their density, D_{eff} and R_{rec}, the recombination of charge carriers is enhanced.

Conclusion

Thus, the characteristics of inverted organic solar cells based on ZnO have been investigated at different temperatures of preliminary annealing from 150°C to 450°C. As a result of studies, it was found that preliminary annealing leads to a change in the morphology, optical properties, and structural features of ZnO films. The temperature of preliminary annealing of the zinc acetate solution film controls the rate of formation of the ZnO film and also affects the relief of the film surface. With an increase in temperature, a decrease in the surface relief and an increase in the density of ZnO lattice defects are observed. Thus, preliminary annealing of films of zinc acetate solution at temperatures below 200°C followed by annealing at 450°C leads to the formation of a highly relief (wrinkled) morphology with a lower density of ZnO lattice defects. Whereas the films obtained at a pre-annealing temperature above 200°C have a smooth surface, but with a high density of defects.

Solar cells based on ZnO films with a wrinkled morphology generally have a greater value of the photocurrent density due to the effect of light scattering, while cells with a smooth morphology have a large photovoltage value, which is caused by a high density of defects that raise the position of the quasi-Fermi level of electrons. Thus, this study has shown the possibility of optimizing the photovoltaic parameters of solar cells by varying the pre-annealing temperature of ZnO films.

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REFERENCES

1 Lin Y., Adilbekova B., Firdaus Y., et al. 17% Efficient Organic Solar Cells Based on Liquid Exfoliated WS2 as a Replacement for PEDOT:PSS. *Adv. Mater*. 2019, Vol.31, No. 46, pp. 1902965 - 1902965

2 Liu Q., Jiang Y., Jin K., Qin J., Xu J., Li W., Xiong J., Liu J., Xiao Z., Sun K., Yang S., Zhang X., and Ding L. 18% Efficiency organic solar cells. *Sci. Bull.* 2020, Vol.65, No 4, pp.272 -275.

3 Sun Y., Seo J. H., Takacs C. J., Seifter J., et al. Inverted Polymer Solar Cells Integrated with a Low-Tempera-ture-Annealed Sol-Gel Derived ZnO Film as an Electron Transport Layer. *Adv. Mater.* 2011, Vol.23, pp.1679–1683.

4 Sekine N., Chou C.-H., Kwan W.L., Yang Y. ZnO Nano-Ridge Structure and Its Application in Inverted Polymer Solar Cell. *Org. Electron*. 2009, Vol.10, pp. 1473 – 1477.

5 Srinivasan G., Gopalakrishnan N., Yu Y. S., Kesavamoorthy R. and Kumar J. Influence of post-deposition annealing on the structural and optical properties of ZnO thin films prepared by sol-gel and spin-coating method. *Superlattices and Microstructures.* 2008, Vol.43, No. 2, pp. 112–119.

6 Aimukhanov A.K., Zeinidenov A.K., Zavgorodniy A.V., Ilyassov B.R., Pazyl B.M. The research of photo-electrophysical properties of cobalt phthalocyanine film. *Eurasian phys. tech. j.* 2019, Vol. 16, pp. 16 – 20.

7 Yang T.B., Cai W.Z., Qin D.H., et al. Y. Solution-processed zinc oxide thin film as a buffer layer for polymer solar cells with an inverted device structure. *Journal of Physical Chemistry C*. 2010, Vol.114, pp. 6849-6853.

8 Richardson B. J., Wang X., Almutairi A., et al. High Efficiency PTB7-Based Inverted Organic Photovoltaics on Nano-Ridged and Planar Zinc Oxide Electron Transport Layers. *J. Mater. Chem. A.* 2015, Vol.3, pp. 5563–5571.

9 Lim D. C., et al. Spontaneous Formation of Nanoripples on the Surface of ZnO Thin Films as Hole-Blocking Layer of Inverted Organic Solar Cells. *Sol. Energy Mater. Sol. Cell*. 2011, Vol.95, pp. 3036–30409.

10 Kim M.S., Yim K.G., Lee D., et al. Effect of cooling rate and post heat treatment on properties of ZnO thin films deposited by sol–gel method. *Appl. Surf. Sci.* 2011, Vol.257, pp 9019–9023.

11 Ilyassov B. R., Ibraev N. Kh., Abzhanova D. B. Effect of morphology of ZnO nanowire arrays on photovoltaic and electron transport properties of DSSC. *Proceeding of the IOP Conf. Series: Materials Science and Engineering*. 2015, Vol. 81, pp. 012046 – 012046.

12 Khanam Jobeda J., Foo Simon Y. Modeling of High-Efficiency Multi-Junction Polymer and Hybrid Solar Cells to Absorb Infrared Light. *Polymers.* 2019, Vol.11, No. 2, pp. 2323-2325.

13 Bisquert J., Mora-Sero I., Fabregat-Santiago F. Diffusion–Recombination Impedance Model for Solar Cells with Disorder and Nonlinear Recombination. *ChemElectroChem.* 2014, Vol.1, No. 1, pp. 289-296.

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