UDC 537.9; 621.383.51

ELECTRICAL CHARACTERISTICS OF SEMICONDUCTOR POLYMER FILMS DOPED WITH SILVER NANOPARTICLES

Ibrayev N.Kh.[1], Afanasyev D.A.[1, 2]

[1]Buketov Karaganda State University, Institute of molecular nanophotonics, Karaganda, Kazakhstan

[2]Institute of Applied Mathematics, Karaganda, Kazakhstan, a_d_afanasyev@mail.ru

The electrical properties of composite films based on polymer PEDOT:PSS with a addition of Ag nanoparticles or Ag–TiO2 nanostructures have been studied. A current–voltage characteristic is observed for polymer solar cells. A short circuit current increased after adding of Ag nanoparticles or Ag–TiO2 nanostructures to the PEDOT:PSS polymer. Also, an increase in the recombination rate in cells with silver nanoparticles is observed. An electrical impedance is measured for polymer solar cells. A significant increase in the dielectric constant of a PEDOT:PSS film containing silver nanoparticles was detected.

Keywords: semiconductor polymer, silver nanoparticles, polymer solar cell, core – shell nanostructure

Introduction

Polymer solar cells (PSC) are currently considered as one of the promising areas capable of replacing traditional silicon batteries in a number of practical applications [1]. Industrial production of PSCs is quite low in cost due to the possibility of producing large areas by roll printing methods. Also, the technologies used in the production of polymer cells are less environmentally harmful than the technology of production of silicon cells.

Despite the low cost of manufacturing PSCs they have a number of disadvantages. A low efficiency of PSC is the main drawback. Currently, a number of approaches are used to increase PSCs efficiency. An use of nanoparticles (NPs) of metals in PSCs is one of such approaches [2]. In general, silver or gold NPs with the maximum plasmon effect in the visible region of the spectrum among difference materials can be use [3, 4]. However, there are works suggesting the use of other NPs metals, such as aluminum NPs [5].

A bulk heterojunction is the main element of PSC. The heterojunction consists of materials having donor-acceptor properties in relation to charge transfer. The classical substances used to form heterojunction are polymer poly(3–hexylthiophene–2,5–diyl) (P3HT) and methanofullerene molecules [6,6]phenyl–C61–butane acid methyl ether (PCBM). On the basis of these substances PSCs efficiency reaches ~ 5 % [6]. Other auxiliary elements are the anode, cathode and polymers mixture layer PEDOT:PSS (poly (3,4 – ethylenedioxythiophene): polystyrene sulfonate). The PEDOT:PSS layer lies between the anode and the bulk heterojunction. PEDOT:PSS performs the function of a layer with a p–type conductivity of HOMO (high occupied molecular orbital) whose energy levels are located above the HOMO–levels of the P3HT polymer. This allows charge carriers with P3HT to freely enter the anode of the solar cell. Also, the polymer layer PEDOT:PSS is necessary to obtain a more uniform film of P3HT–PCBM heterojunction on its surface.

The efficiency of PSC depends on conductive properties of the polymer film PEDOT::PSS. Therefore, PEDOT:PSS films with increased conductivity are required to obtain PSC with high efficiency. Increasing the conductivity of PEDOT:PSS films can be achieved by adding Ag or Ag–TiO_2 plasmon nanoparticles to the film [7]. This article presents the results of the study of electrical and photovoltaic properties of PSCs with composite films based on PEDOT: PSS with additives of Ag or Ag–TiO_2 nanoparticles. It is shown that the addition of silver nanoparticles to the PEDOT:PSS film leads to a significant change in the dielectric permeability of the medium (ε).

1. Experimental part

As shown in [8, 9], the specific conductivity of PEDOT:PSS films is affected by the rate of application and the annealing temperature of the films, as well as the addition of extra solvents to the PEDOT:PSS solution. The results of studies of the effect of adding dimethylformamide and dimethylsulfoxide (DMSO) and the conditions of production on the value of the resistivity of the composite films PEDOT:PSS are given in [10]. A minimum resistance of the films is observed for solution PEDOT:PSS with the addition of 2% DMSO. These results are consistent with the results obtained in other papers [8, 9]. Study of effects of the speed of centrifuge rotation at making of films and the temperature of annealing of films showed that 5000 rpm. is the optimal speed, and 150 ° C is the optimum annealing temperature.

As shown in [7, 11], the addition of silver and gold NPs reduces the resistance of PEDOT:PSS films. In work [10], the results of studies of the complex effect of silver plasmon NPs and additive of DMSO solvent on the conductive properties of PEDOT:PSS films are presented. Aqueous solutions of silver NPs and nanostructures (NSs) of Ag–TiO_2 with concentration $5\cdot10^{-9}$ mol/L was used. The method of synthesis of silver NPs and Ag–TiO_2 NSs described in detail in [12]. An addition of organic solvents and metal NPs, NSs leads to a decrease in the electrical resistance in PEDOT:PSS films. This, in turn, should lead to an increase in the efficiency of PSC with highly conductive composite polymer film based on PEDOT::PSS.

Optimal conditions for the manufacture of composite films with PEDOT:PSS from [10] were used in this work. These optimal fabrication conditions include the concentrations of NPs or NSs, the optimal deposition rate and the annealing temperature of the PEDOT:PSS composite films, used in [10]. The DMSO solution with the concentration of 8% relative to the PEDOT:PSS solution was added to the original solution to improve the electrically conductive properties of the PEDOT:PSS films. The obtained PEDOT:PSS films with the addition of NPs and NSs were used for the manufacture of photovoltaic cells. The size of NPs in colloidal solutions was determined by the method of dynamic light scattering on the analyzer Zetasizer Nano ZS (Malvern). The size of the used NPs or NSs and their absorption spectra are given in [13]. The technique of manufacturing cells is described in detail in [14]. The thickness of polymer films was determined by scanning electron microscope Tescan Mira 3. Glove box SPECS GB 03-2M (Spectroscopic systems) was used for fabrication of P3HT–PCBM layers. Aluminum electrodes was made by thermal evaporation in a vacuum with a pressure not exceeding 10^{-5} Torr. The thickness of the aluminum electrodes was measured using SI–TM106 Subminiature Film Thickness Tester. The thickness of obtained electrodes wasn't less than 100 nm.

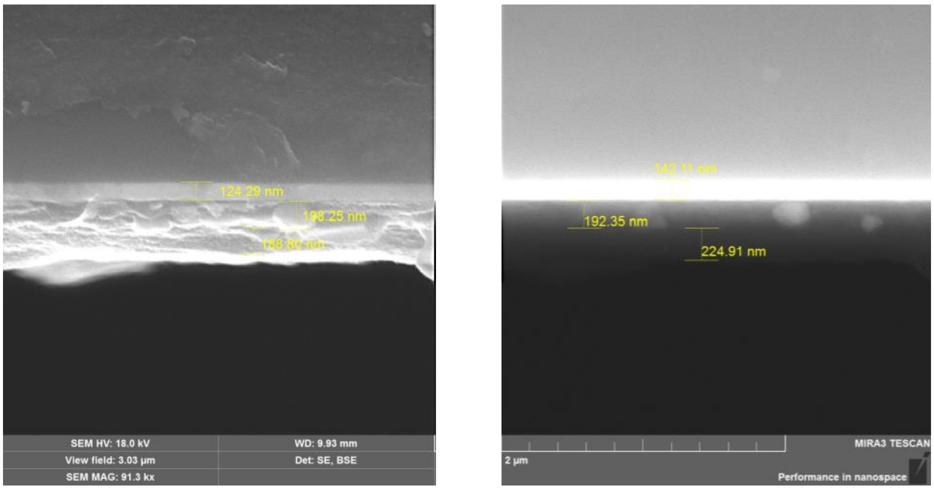
Solar simulator with xenon lamp with 100 mW/cm^2 (Photo Emission Tech Inc.) was used for measured of current-voltage characteristics and an efficiency of PSCs. The impedance of the solar cells was measured using the Z500PRO impedance meter in potentiostatic mode with a given constant potential. The method of measurements corresponds to the method used in [14, 15]. The EIS–analyzer program was used to determine the main parameters of the solar cell chain.

2. Results and their discussion

Microscopic data were used to estimate the thickness of different layers. The thickness of the produced films was determined at cross-section cells. An example of a cross-section cells with the structure ITO/PEDOT:PSS/P3HT:PCBM with silver NPs in the layer PEDOT:PSS is shown in Figure 1. These results are shown in Table 1. Layer thickness was estimated from 3 to 5 measurements. At Figure 1, on the cross-section cells in the PEDOT:PSS layer, NPs with sizes corresponding to the size of the PEDOT:PSS layer are observed. However, an amount of large particles in the film is small compared to the average particle size used in the work [13].

.

For comparison, in Table 1 are shown the results of surface resistance of films obtained by the four-probe method in [10]. it can be seen that the addition of NPs Ag or NSs Ag–TiO_2 in the film leads to a decrease resistance by 3 times.



a) b)

Fig.1. The thickness of the functional layers of the solar cell, when registering the signal from the detector of secondary electrons (a) and reflected electrons (b)

Table 1. A basic geometrical and electrical characteristics of PEDOT:PSS composite layers with additives of Ag NPs or Ag–TiO_2 NSs

Defined model parameter	Properties of PEDOT::PSS		
	Without NPs	Ag NPs	Ag–TiO^2 NSs
The thickness of the layer of PEDOT:PSS in the cell (d)	200 nm	200 nm	150 nm
The thickness of the active layer of P3HT-PCBM	180 nm	170 nm	140 nm
Resistivity (ρ) of PEDOT:PSS films (resistance per square)	21,3*10^3 Ohm/sq.	6,7*10^3 Ohm/sq.	6,5*10^3 Ohm/ sq.
ε_1	2,2	10	3,7

The obtained composite semiconductor films PEDOT:PSS with the addition of NPs or NSs were used for the manufacture of photovoltaic cells. Photovoltaic properties of PSCs were investigated (Figure 2, Table 2). Adding NPs and NSs to PEDOT:PSS leads to an increase in photocurrent. These results are consistent with the results of measuring the electrical characteristics of PEDOT:PSS composite films (Table 1). The highest efficiency is observed for cells with silver NPs. A high value of short-circuit current (Jsc) is observed for these cells. The high Jsc value indicates good conductive properties of all functional layers in the cell, especially the PEDOT:PSS composite layer. In this case, the value of an open circuit voltage (Uoc) is low. The shape of a volt-ampere curves, a low value of fill factor (FF) and value of efficiency indicates the high value of the rate of recombination in PSCs (Figure 2). The increase in the rate of recombination of charge carriers in the cell may be due to two main reasons. The first reason is due to the large thickness of the PEDOT:PSS layer. In our work the thickness of this layer was ~ 150-200 nm. While, for high-efficiency solar cells, this value is in the range of 50 to 100 nm [2, 3]. The second reason that leads to an increase in the recombination rate may be the presence of large particles in the PEDOT:PSS layer, which lead to a short circuit between the polymer layers or electrodes.

Thus, the addition of NPs to the polymer PEDOT: PSS leads to an improvement in the conductive properties of solar cells. At the same time, there is an increase in the rate of recombination in the cells. Therefore, it is necessary to continue research aimed at reducing the rate of recombination in PSCs.

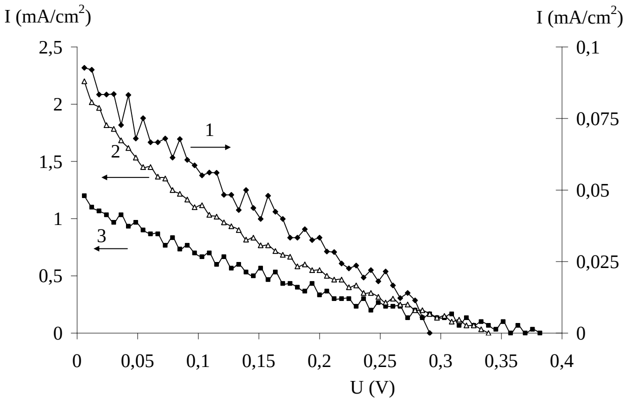


Fig.2. Volt-ampere characteristics of PSC by additives of NPS and NSs Ag or Ag/TiO_2

Table 2. Photovoltaic and electrical properties of cells based on a mixture of polymers P3HT: PCBM

Layer properties of PEDOT:PSS	Jsc, mA/ cm^2	Umax, (V)	Uoc, (V)	η, %	RSER, kOhm/ cm^2	RSH, Ohm/ cm^2
Without NPS	0.09	0.29	0.073	0.005	151	687
Ag NPs	2.14	0.28	0.121	0.05	0.0	$4 \cdot 10^{-5}$
Ag–TiO_2 NSs	1.23	0.35	0.164	0.02	3.4	579

Additional information about processes of transport and recombination of charge carriers in PSCs can be obtained from electrical impedance measurements of cell. The real (Z’) and imaginary (Z') parts of the electrical resistance of solar cells were measured. The method of measurements corresponds to the method used in [14, 16].

The EIS–analyzer program interface is shown in Figure 3. For extract the basic electrical characteristics of solar cell was used electrical model of PSC, which is given in the upper right part of Figure 3, a. It is R1– resistance layer ITO layer; R2 – resistance of a layer of PEDOT:PSS; R3 – resistance of the P3HT-PCBM active layer; R4 – resistance of the interface of P3HT-PCBM and aluminum electrode; C1 – capacitance of a layer of PEDOT::PSS; C2 – capacity of the active layer of P3HT-PCBM; C3 – capacitance of the interface of P3HT-PCBM and aluminum electrode, in this model, in accordance with article [16]. The results of determining the circuit parameters are given in Table 3. Comparison of R2 values for all cells shows that the cells with PEDOT:PSS with silver NPs has the least resistance. The remaining cells have a higher resistance value of the PEDOT:PSS layer.

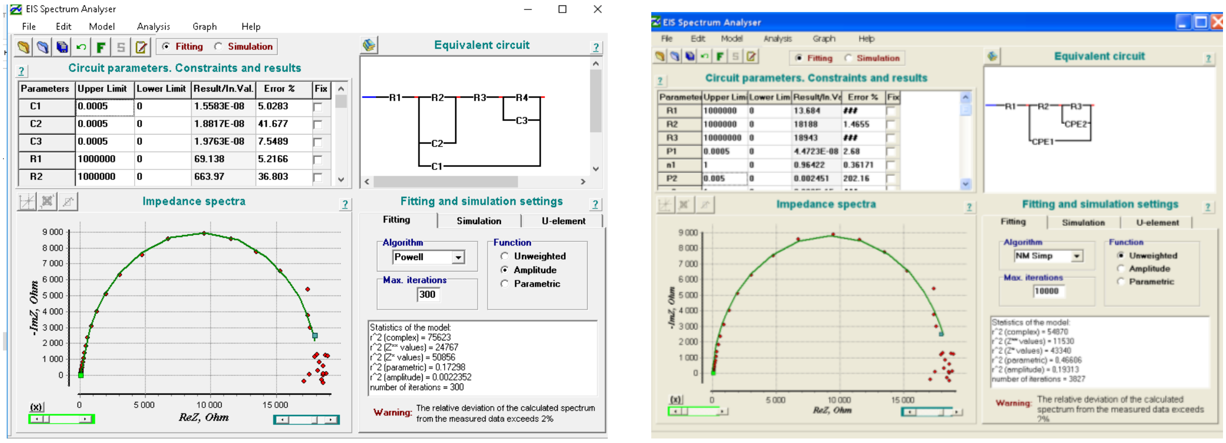
The capacitance of the C2 layer can be used to estimate the dielectric constant (ε) without addition and with addition of NPs and NSs. For this purpose, the formula (1) given in [16]:

$$C = \frac{\varepsilon_1 \varepsilon_0 A}{d} \tag{1}$$

For calculations it is necessary to know the thickness of PEDOT:PSS films. These values were obtained from the scanning electron microscope measurements of PSCs (Table 1).

.

The results of determining the dielectric permittivity of PEDOT:PSS films are given in Table 1. As can be seen from the Table 1, the addition of NPs and NSs leads to an increase in the dielectric constant of the film (ε_1). Comparison of the value of ε_1 for the film PEDOT:PSS with the results given in other works shows their compliance [17]. For example, in [18] for composites based on a dielectric polymer polyvinyl alcohol, a decrease in the dielectric permittivity of the film ε_1 was observed. A change in the dielectric characteristics of cells based on PEDOT:PSS and P3HT-PCBM when silver NPs were added to various PSC layers was detected in [19]. An increase in ε_1 is observed in this case. However, the increase of ε_1 for PEDOT:PSS films with NPs requires additional studies.



a)

Parameters	Upper Limit	Lower Limit	Result/In.Val.	Error %	Fix
C1	0.0005	0	1.5583E-08	5.0283	☐
C2	0.0005	0	1.8817E-08	41.677	☐
C3	0.0005	0	1.9763E-08	7.5489	☐
R1	1000000	0	69.138	5.2166	☐
R2	1000000	0	663.97	36.803	☐

Algorithm: Powell

Max. iterations: 300

Function: ○ Unweighted ● Amplitude ○ Parametric

Statistics of the model:
r^2 (complex) = 75623
r^2 (Z** values) = 24767
r^2 (Z* values) = 50856
r^2 (parametric) = 0.17298
r^2 (amplitude) = 0.0022352
number of iterations = 300

Warning: The relative deviation of the calculated spectrum from the measured data exceeds 2%

b)

Parameter	Upper Lim	Lower Lim	Result/In.Va	Error %	Fix
R1	1000000	0	13.684	###	☐
R2	1000000	0	18188	1.4655	☐
R3	10000000	0	18943	###	☐
P1	0.0005	0	4.4723E-08	2.68	☐
n1	1	0	0.96422	0.36171	☐
P2	0.005	0	0.002451	202.16	☐

Algorithm: NM Simp

Max. iterations: 10000

Function: ● Unweighted ○ Amplitude ○ Parametric

Statistics of the model:
r^2 (complex) = 54870
r^2 (Z** values) = 11530
r^2 (Z* values) = 43340
r^2 (parametric) = 0.46606
r^2 (amplitude) = 0.19313
number of iterations = 3827

Warning: The relative deviation of the calculated spectrum from the measured data exceeds 2%

Fig.3. EIS–analyzer program interface with electric models of PSC (upper right corner of the program) within the models given in [16] (a) and [20] (b)

Table 3. Electrical characteristics of PSCs with PEDOT:PSS films with additives of NPs or NSs

Defined model parameter	Properties of PEDOT::PSS		
	Without NPS	Ag NPs	Ag–TiO$_2$ NSs
R1, (Ohm)	69.0	80	86
R2, (Ohm)	664.0	231	8742
C2, (nF)	18.8	82	23
R3, (Ohm)	197.0	$1.9 \cdot 10^{-4}$	187
C1, (nF)	15.5	$1.8 \cdot 10^{-3}$	6.97
R4, (Ohm)	$1.7 \cdot 10^{4}$	$1.8 \cdot 10^{4}$	181
C3, (nF)	19.7	35	94

For comparison also the analysis of the impedance of the cells in the model of Biscuit [20]. The electrical diagram of the model is shown in Figure 3, b. The simulation results are given in Table 4. In this model, R1 is the resistance of the electrical contacts and the bulk material; R2 – the resistance to charge transfer in the active region and on the boundary of electrode–active area; R3 – resistance associated with recomenaria electron-hole pairs in the active region; CPE1 is the total capacity of the cell; CPE2 – diffusion capacity.

A comparison of the circuit parameters obtained from results of modeling of electrical circles with used the two models (Tables 3, 4) shows similar values of the circuit characteristics. Effective carrier transfer time (τ_d) and electron mobility (μ) were estimated using the Bisquerts model in accordance with the formulas:

$$\tau_d = R3 \cdot C2, \qquad \mu = \frac{eL^2}{k_B T \tau_d} \tag{2}$$

where e – electron charge, L – thickness of the active layer, k_B – Boltzmann constant, T – temperature.

Table 4. Electrical characteristics of PSCs with PEDOT:PSS films with additives of NPs and NSs (modeling by the Bisquerts model)

Defined model parameter	Properties of PEDOT:PSS		
	Without NPS	Ag NPs	Ag–TiO_2 NSs
R1, (Ohm)	160	85	71
R2, (Ohm)	3768	224	1596
C1, (nF)	85.0	17.2	39
n1	1	0.94	0.95
R3, (Ohm)	5340	9342	16902
C2, (nF)	14.0	26.0	8.7
n2	1	0.96	1
τ_d (μs)	75.0	243	147
μ ($cm^2{*}V^{-1}{*}s^{-1}$)	$1.6{*}10^{-4}$	$0.5{*}10^{-4}$	$0.5{*}10^{-4}$

The obtained results indicate an increase the time of charge transfer in films with additives of NPs or NSs and a decrease in the mobility of charge carriers in the active layer of these cells. The decrease in the mobility of charge carriers in films with NPs or NSs in the PEDOT:PSS layer contradicts the results obtained by measuring the current-voltage characteristics of the cells (Table 2). In cells with NPs or NSs, a higher current density Jsc is observed. It may be necessary to take into account possible changes in the dielectric properties of polymers when metal NPs are added to them when used modeling by the Bisquerts model.

Conclusion

According to the results of the research we can get a number of conclusions:

- the addition of organic solvents and metal NPs leads to a decrease in the electrical resistance of PEDOT:PSS films, which in turn leads to an increase in the efficiency of PSCs;
- the electrical properties of PSCs with composite films based on PEDOT:PSS were investigated. The high conductivity of PEDOT:PSS composite films leads to an improvement in the conductivity of solar cells, which is manifested in an increase in short circuit current. Along with an increase in the short-circuit current, the open-circles voltage decreases, which is associated with an increase in the rate of recombination of charge carriers observed in cells with PEDOT:PSS composite films. A high resistance value is observed for some cells at the interface of the P3HT-PCBM active layer and an aluminum electrode. This result indicates the need to improve the technology of deposition of the aluminum electrode on the P3HT-PCBM layer;
- using the method of impedance spectroscopy, solar cells containing PEDOT:PSS composite films with additions of Ag NPs or Ag–TiO_2 NSs were investigated. A significant increase in the dielectric constant of a PEDOT: PSS film containing Ag NPs has been found. To explain the result obtained, continuation of the research is necessary. A change in the dielectric characteristics of the medium will affect such important properties as the intensity of light absorption by the material, the excitonic transport in the material, and the transport of charge carriers. This, in turn, can significantly change the efficiency of transformation of light energy into electrical energy in PSCs.

.

Acknowledgements

This work was carried out with the financial support of the Ministry of Education and Science of the Republic of Kazakhstan.

REFERENCES

1 Pavlov N. What Barriers Will Overcome Printed Solar Elements. *Vector of High Technologies*. 2013, No.3 (3), pp. 8 – 14. [in Russian]

2 Chan K., Wright M., Elumalai N. Uddin A., Pillai S. Plasmonics in Organic and Perovskite Solar Cells: Optical and Electrical Effects *Adv. Optical Mater.* 2017, Vol. 5, No.6. pp. 1600698(1-19).

3 Pillai S., Catchpole K.R., Trupke T., Green M. J. Surface plasmon enhanced silicon solar cells *Appl. Phys.* 2007, Vol.101, No.9, pp. 093105(1) - 093105(8).

4 Schaadt D.M., Feng B., Yu E.T. Enhanced semiconductor optical absorption via surface plasmon excitation in metal nanoparticles *Appl. Phys. Lett.* 2005, Vol. 86, No.6, pp. 063106(1-3).

5 Ikhsanov Sh., Protsenko I.E., Uskov A.V. Increasing the efficiency of organic solar cells using plasmonic nanoparticles *Tech. Phys. Letters.* 2013, Vol.39, No.5, pp. 450 – 453.

6 http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

7 Kukhta A.V., Pochtenny A.E., Misevich A.V. et. al. Optical and electrophysical properties of nanocomposites based on PEDOT: PSS and gold/silver nanoparticles *Phys. of the Sol. St.* 2014, Vol. 56, No.4, pp. 827 – 834.

8 Lee C.S., Kima J.Y., Lee D.E. et. al. Flexible and transparent organic film speaker by using highly conducting PEDOT/PSS as electrode *Synthetic Metals.* 2003, Vol.139, pp. 457–461.

9 Wang G.-F., Tao X.-M., Xin J.H., Fei B. Modification of conductive polymer for polymeric anodes of flexible organic light-emitting diodes *Nanoscale Res. Lett.* 2009, No.4, pp. 613 – 617.

10 Afanasyev D.A., Ibraev N.Kh. Increasing the conductivity of composite semiconductor polymer films based on Pedot: PSS *Solid State Physics, Functional Materials and New Technologies (FTT-2018): Materials of the XIV International Scientific Conference.* Bishkek- Karaganda, 2018, pp. 11 – 13. [in Kazakh]

11 Stratakis E., Kymakis E. Nanoparticle-based plasmonic organic photovoltaic devices. *Materials Today*. 2013, Vol.16, Issue 4, pp. 133 – 146.

12 Afanasyev D.A., Ibrayev N.Kh., Serikov T.M., Zeinidenov A.K. Effect of the titanium dioxide shell on the plasmon properties of silver nanoparticles *Russian Journal of Physical Chemistry A.* 2016, Vol. 90, No.4, pp. 833 – 837.

13 Afanasyev D.A., Ibraev N.Kh. The Effect of Ag-TiO_2 Nanostructures on Photoprocesses in Poly [3-Hexylthiophene] Polymer *Mat. Res. Scientific-Practical Conference.* Karaganda, 2018, pp. 148–151. [in Kazakh]

14 Ibrayev N.Kh., Afanasyev D.A., Zhapabaev K.A. Effect of potassium iodide on luminescent and photovoltaic properties of organic solar cells P3HT-PCBM *IOP Conf. Series: Mat. Sc. and Eng.* 2016, Vol.110, pp. 012067 (1-5).

15 Ibrayev N.Kh., Nurmakhanova A., Afanasyev D. Role of spin states in the process of electron energy transformation in P3HT films, doped KI salt IOP *Conf. Series: Materials Science and Engineering.* 2017, Vol.168, pp. 012060.

16 Knipper M., Parisi J., Coakley K. et al. Impedance Spectroscopy on Polymer-Fullerene Solar Cells *Zeitschrift für Naturforschung A.* 2007, Vol. 62, No 9, pp. 490 – 494.

17 Aleksandrova M., Kolev G.I. et. al. Characterization of Piezoelectric Microgenerator with Nanobranched ZnO Grown on a Polymer Coated Flexible Substrate *Appl. Sc.* 2017, Vol. 7(9), pp. 1 – 11.

18 Ghanipourand M., Dorranian D. Effect of Ag-Nanoparticles Doped in Polyvinyl Alcohol on the Structural and Optical Properties of PVA Films *J. of Nanomat.* 2013, Vol. 2. pp. 1 – 10.

19 N. Kalfagiannis, P. G. Karagiannidis, et. al. Plasmonic silver nanoparticles for improved organic solar cells *Sol. Energy Mater. Sol. C.* 2012, Vol. 104, pp.165–174.

20 G. Garcia-Belmonte, A. Munar, E.M. Barea, J. Bisquert, I. Ugarte, R. Pacios Charge carrier mobility and lifetime of organic bulk heterojunctions analyzed by impedance spectroscopy *Organic Electronics.* 2008, Vol. 9(5), pp. 847 – 851.

Article accepted for publication 10.12.2018