DOI 10.31489/2023No1/20-26

UDC 538.9; 535.215; 539.23; 535.3

THE EFFECT OF MOLYBDENUM DISULFIDE NANOPARTICLES ON THE PROPERTIES ZINC OXIDE ELECTRON TRANSPORT LAYER OF ORGANIC SOLAR CELLS

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In this work, the effect of molybdenum disulfide nanoparticles on the properties zinc oxide electron transport layer of organic solar cells is studied. molybdenum disulfide nanoparticles were obtained by laser ablation of MoS2 powder in isopropyl alcohol. To form composite films, nanoparticles were added to a sol–gel zinc oxide solution with different concentrations. According to scanning electron microscope study, as the concentration of nanoparticles in the film increases, the thickness of the molybdenum disulfide layer on the zinc oxide surface changes. molybdenum disulfide nanoparticles in the film structure gradually fill the bulk and surface voids in zinc oxide. However, when the concentration exceeds 1%, holes and voids are formed in the film. The absorption spectra of composite films showed that as the concentration of nanoparticles in the film increases, the absorption intensity enhances due to the increase of the overall thickness. At the same time, zinc oxide optical band gap width does not change, which means the molybdenum disulfide nanoparticles do not affect the electronic structure of zinc oxide. It was shown that the observed changes in the volt-ampere characteristic *of organic solar cells with composite films electron transport layer composite films was associated with the influence of molybdenum disulfide nanoparticles on electron transport in* organic *solar cells. According to impedance spectroscopy study, it was found that molybdenum disulfide nanoparticles at concentration below critical value increases the lifetime of charge carriers and the diffusion coefficient in composite film.*

Keywords: zinc oxide, molybdenum disulfide, composite film, surface morphology, optical and impedance spectroscopy.

Introduction

In inverted organic solar cells (OSCs), ZnO is used as electron transport layer (ETL) because of its high electron mobility, high visible light transmittance, stability in air and possibility to control electrical and optical properties. One of the reasons of the low power conversion efficiency of OSCs is the presence of bulk and surface defects in the ETL based on ZnO. Defects intensify the charge recombination, impede the charge transfer and reduce the efficiency of electron collection at electrodes [1]. To solve this problem, a number of researchers propose to use interfacial layers between the ZnO and the photoactive layer. For example, a two-layer ETL with conjugated polyelectrolyte was used [1], ZnO was doped with perylene bisimides [2-4], aluminum [5-7], fullerene derivatives [8,9] and Sn [10], which leads to the decrease in the electron work function, and to the improvement in electron transport in ZnO due to the decrease in the defect density.

Two-dimensional transition metal dichalcogenides (2D TMDs) can be also combined with ETL. The band gap, physical and chemical properties of 2D TMDs can be easily tuned by developing varies van der Waals structures in combination with other materials. In these materials, due to the special single-layer structure, the unshared pairs of electrons in the atoms of S and Se can provide rapid transport and as result increase the mobility of charge carriers. Graphene-like 2D materials have great potential and are alternatives to traditional hole transport layer (HTL) and ETL materials for organic solar cell (OSC), Fig.1. J.-M. Yun et al. [11] showed the possibility to use transition metal dichalcogenide nanosheets as HTL and ETL layers in direct and inverted OSCs. However, nanosheets can not form a continuous layer, so they developed hybrid composite structures based on them. The authors of the work [1] reported that the increase of MoS2 nanosheet density in ZnO up to 0.5 wt.% led to the decrease in the interfacial resistance and the suppression

of the leakage current in devices, and as a result, power conversion efficiencies (PCE) boosted from 8.8% to 10.1%.

In our work to suppress bulk and surface defects in ZnO ETL, we doped ZnO ETL with MoS2 nanoparticles. MoS2 nanoparticles were added in ZnO solution and then composite ETLs were deposited. The effect of MoS2 nanoparticles on electron transport mechanisms in OSCs was studied in detail.

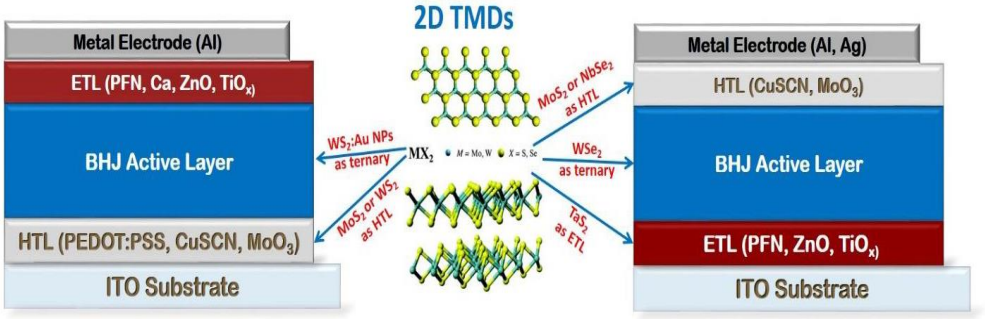

Fig. 1. Schematic diagram showing both the direct (left) and inverted OPVs structure. In the center the structure of various 2D TMDs are shown, and the blue arrows show the various layers in which TMDs were added [1].

1. Experimental part. Methods and materials

At first the FTO covered glass substrates were rigorously cleaned [12].The preparation of ZnO:MoS2 solution had the following steps: firstly, 98.7 mg of Zn5(OH)8Cl2 (pure 99.9% Sigma Aldrich) was dissolved in 1 ml of isoproponol (pure 99.9% Sigma Aldrich), then 75 µl of monoethanolamine (Sigma Aldrich) was added to the solution, after that, the solution was stirred at 60 °C for 2 hours, and then kept for 24 hours at room temperature, finally MoS2 nanoparticles were added to the solution with different concentrations. MoS2 nanoparticles were obtained by laser ablation of MoS2 powder by the second harmonic of a solid-state Nd:YAG laser (SOLAR LQ).

After, ZnO:MoS2 solution was spin-coated on clean FTO glass substrates by spin-coating techniques at the rotation speed of 4000 rpm. SPIN150i SPS was used for the spin-coating. Then the film was preheated in air at temperature of 200 °C for 15 minutes and immediately annealed at the temperature of 450 °C for one hour to form crystalline structure. Further, P3HT:IC60MA chlorobenzene solution (P3HT and IC60MA is pure 97% from Sigma Aldrich) with the ratio of 1:0.8 was spin-coated on ZnO:MoS2/FTO glass substrate to form the photoactive layer and annealed in air at a temperature of 140 °C for 10 minutes. Before creating inverted structure solar cells, P3HT:IC60MA solution was filtered using a syringe filter with a pore diameter of 0.45 microns. The rotation speed of the centrifuge was 2000 rpm, the rotation time at this speed was at least 30 seconds. After thermal annealing, a part of the photoactive layer was removed to provide access to the electrode on the surface of the FTO. Further, PEDOT:PSS solution was spin-coated to the substrates to form HTL [13]. Finally, silver electrodes was sputtered on PEDOT:PSS layer surface by thermal deposition (CY-1700x-spc-2 evaporator). The residual pressure in the working volume during operation did not exceed 10^{-4} Pa. The tantalum boat was used as a silver vaporizer. The current flowing through the boat during the spraying process varied in the range of 60-65 A [14].

2. Results and discussion

Morphology of ZnO:MoS2 nanocomposite ETLs was studied by a MIRA 3 LMU scanning electron microscope (TESCAN). In Fig.2 the surface morphologies and cross-sections of ZnO:MoS2 nanocomposite films with different concentrations of MoS2 nanoparticles are presented. As the concentration of nanoparticles increases, the thickness of the MoS2 layer changes. The morphology of the surface of composite films becomes smoother (Figure 2 a, b, c, d, e). The addition of MoS2 nanoparticles to ZnO enhances the generation and transport of charge in the mixture under study. This leads to an increase in the efficiency of solar energy conversion. A more efficient process of transporting charge carriers in the studied systems. It is worth noting that samples of nanocomposite films demonstrate various photoelectric and electrophysical characteristics.

These results indicate that MoS2 nanoparticles in the film structure gradually fill the bulk and surface voids in ZnO [15]. When nanoparticles are added in concentrations above 1%, holes and voids are formed in

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the film (Fig.2f). Obviously, in this case, a uniform film is not formed. The quantitative content of MoS2 nanoparticles in ZnO was determined based on EDX analysis (Fig. 3). The composition of the composite film includes elements such as Mo, S, Zn and O (Table 1). As the concentration of nanoparticles increases, so does the concentration of related elements.

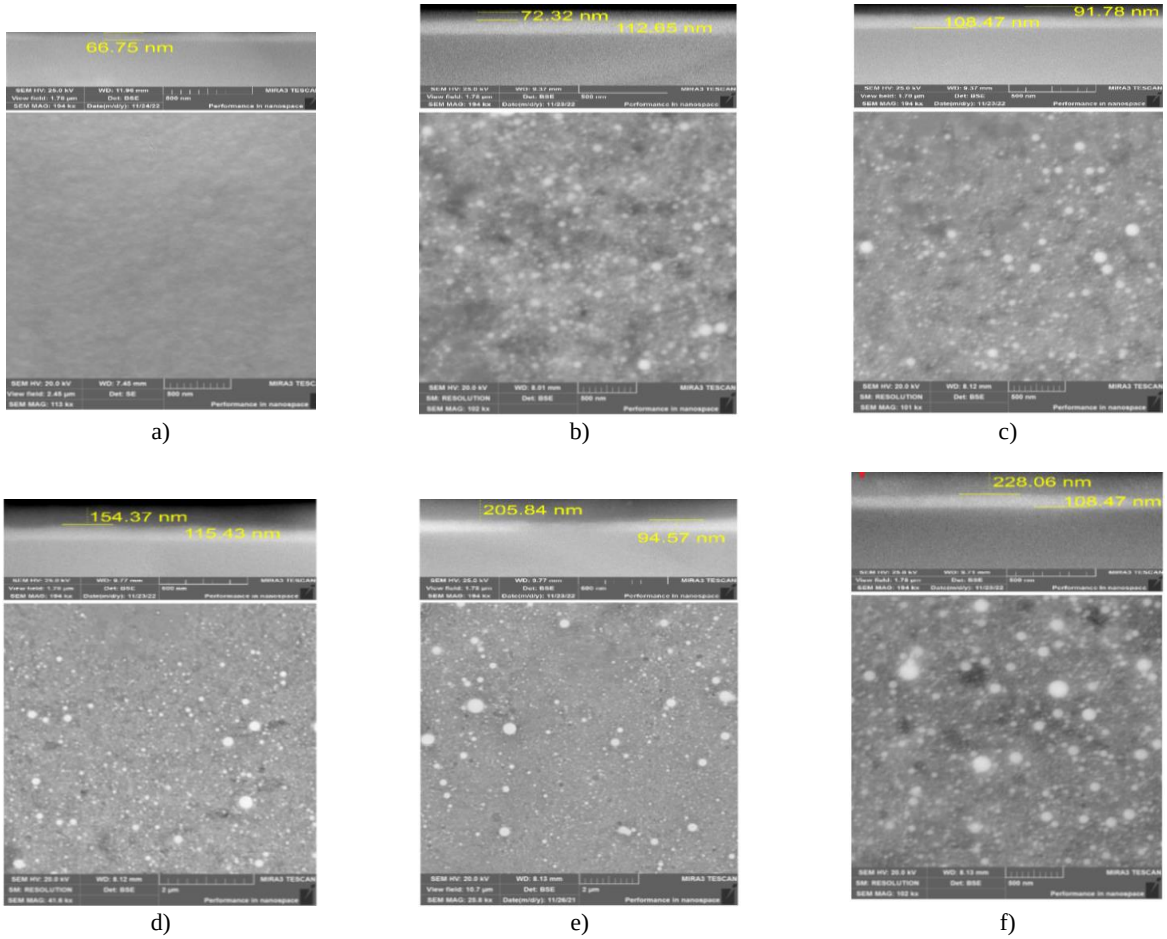


Fig. 2. Images of surface morphology of ZnO:MoS2 composite films

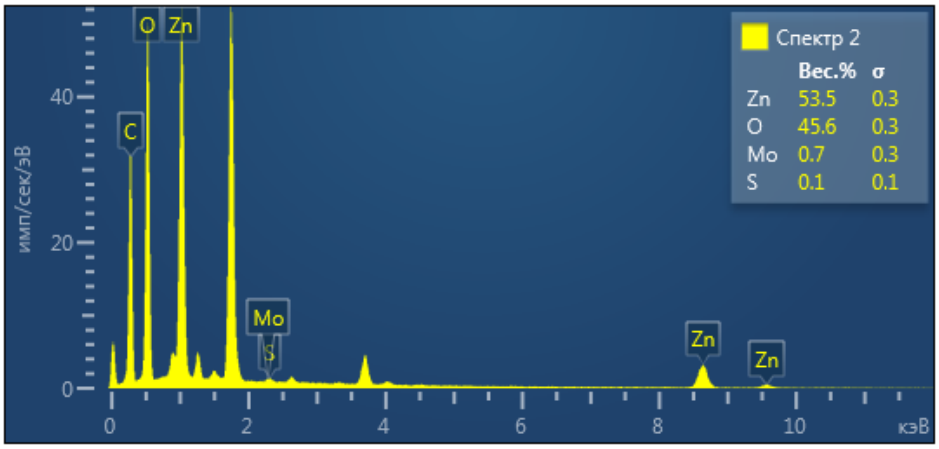


Fig.3. EDX analysis

Absorption spectra of ZnO and ZnO:MoS2 is shown in Fig. 4. As can be seen from the figure, as the concentration of nanoparticles in the film increases, the absorption of the film increases, which is associated with a change in the overall thickness. Using the Tauc graph, it was found that the values of the optical band gap width do not change, which indicates that the addition of MoS2 does not affect the electronic structure of

ZnO. The figure shows that the absorption spectrum of ZnO:MoS2 of the film is located in the range of 320-400 nm with peaks at 360 nm. When adding MoS2 nanoparticles, an increase in the optical density is observed.

Table 1. Elemental composition of ZnO:MoS2 composite films (Atomic percentages)

Weight %	Mo, weight %	S, weight %	Zn, weight %	O, weight %
0.2	0,7	0,1	53,5	45,6
0.4	1,6	0,8	54,4	43,2
0.6	2,1	2,0	53,6	42,3
0.8	3,7	2,5	51,9	41,8
1	4,7	2,7	51,9	40,7

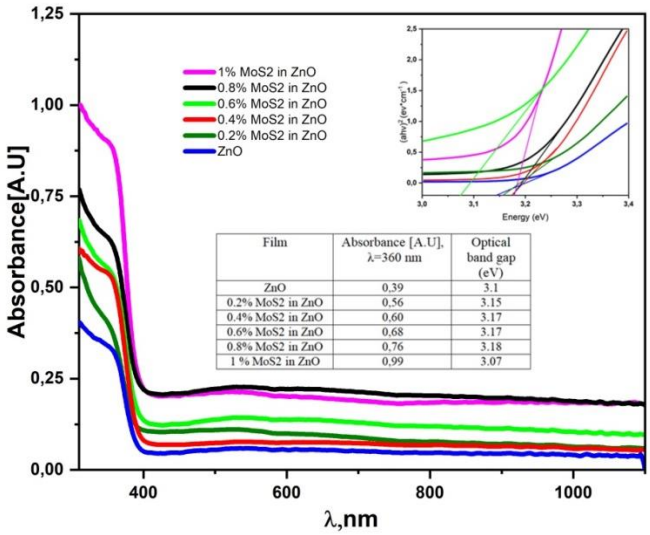
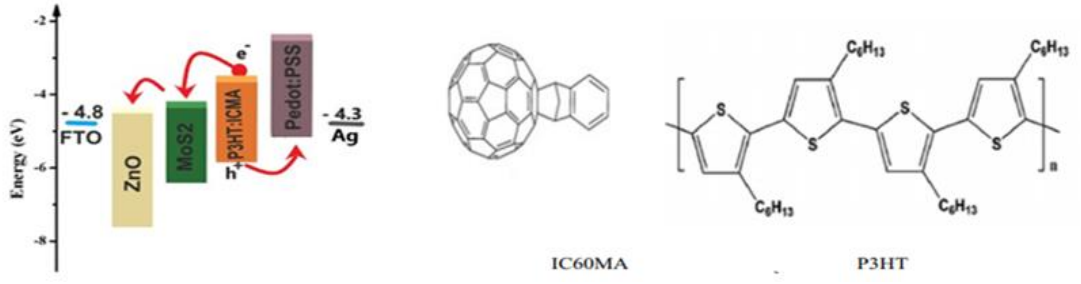


Fig. 4. Absorption spectra and Tauc plots (the inset) of ZnO:MoS2 composite films

In order to determine the effect of MoS2 nanoparticles on electron transport, a polymer solar cell with an inverted structure was assembled in a polymer solar cell. Upon photoexcitation of the photoactive layer P3HT:IC60MA, an electron-hole pair is formed, which then at the interface ZnO:MoS2/P3HT:IC60MA and P3HT:IC60MA/PEDOT:PSS decay into free charge carriers (Fig. 5). Electrons are injected into the ETL layer of ZnO:MoS2, and a hole is injected into the HTL layer of PEDOT:PSS.



a) b)

Fig.5 (a) Energy level diagram of ZnO:MoS2 and (b) chemical structures of BHJ compounds

Samples of solar cells were prepared for the study of photovoltaic measurements, such as voltage characteristics and impedance spectra FTO/ZnO:MoS2/P3HT:IC60MA/PEDOT:PSS/Ag. Figure 6b shows that the addition of MoS2 nanoparticles affects the parameters of the VAC cells. For example, the filling factor of the composite cell 08% MoS2 in ZnO was FF = 0.42, and the value of the short-circuit current

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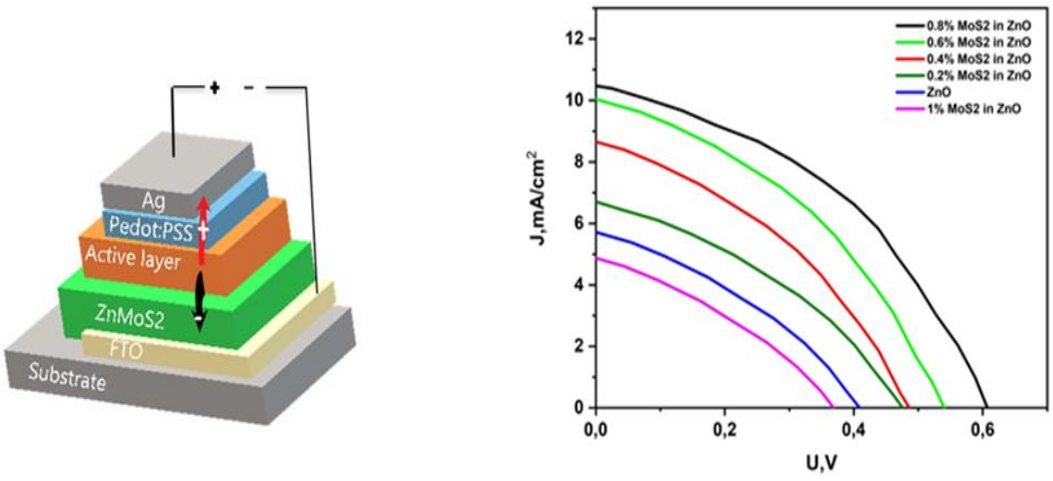
density is equal to J_{sc} = 10.5 mA/cm^2. The maximum value of the increase in the VAC parameters is observed for the composite cell 08% MoS2 in ZnO, so the short-circuit current density increased by 3 times, the efficiency value was 2.6%.



a) b)

Fig.6. a) the architecture of the inverted PSC b) J–V characteristics of inverted solar cells

As the concentration of MoS2 increases to 0.8%, an increase in the parameters of the VAC is observed. A further increase in the MoS2 concentration leads to a decrease in the values of the VAC parameters. The obtained data correlate with the results of the morphology of the surface of composite films. 1% MoS2 in ZnO this sample has the lowest value of the fill factor and the lowest value of the maximum voltage. The inverted composite cell with added MoS2 nanoparticles has a low no-load voltage (U_{oc} = 0.30 V) among all the samples obtained. At the same time, this sample shows the lowest efficiency value among nanocomposites, equal to 0.5%.

Table 2. Photovoltaic characteristics of organic solar cells.

Sample	U_{oc} (V)	J_{sc} (mA/cm^2)	U_{max}(V)	J_{max} (mA/cm^2)	FF	PCE %
ZnO	0.4	5.7	0.24	3.37	0.35	0.7
0.2% MoS2	0.4	6.6	0.25	4.4	0.35	0.9
0.4% MoS2	0.4	8.6	0.30	5.2	0.37	1.3
0.6% MoS2	0.5	10.2	0.35	6.5	0.42	2.1
0.8% MoS2	0.6	10.5	0.39	6.9	0.42	2.6
1% MoS2	0.3	4.7	0.21	2.7	0.33	0.5

The observed changes in the IV curve are associated with the effect of MoS2 nanoparticles on electron transport in OSCs. To study in detail the effect of MoS2 nanoparticles on the kinetics of electron transport and recombination in OSCs, the impedance spectra of OSCs were measured. Fitting and analysis of spectrum parameters were carried out using the EIS-analyzer software package. With the using of this software, the values of capacity C and the values of R_1 and R_2 were calculated. The analysis of the impedance measurement results was carried out according to the diffusion-recombination model.

Fig. 7b shows the measured impedance spectra (points) of OSCs. The impedance spectra are described by an equivalent electrical circuit shown in the inset of Fig. 6a, where R_1 is the equivalent resistance of the external electrodes (R_{FTO} + $R_{ZnO:MoS2}$ + PEDOT:PSS +Ag), R_2C is characterized by the photoactive layer/ZnO:MoS2 interface.

Since the films were obtained under the same conditions, the observed changes are associated with a change in the photoactive layer/ZnO:MoS2 interface. The greater the R_2, the lower the recombination rate at the phase interface. As can be seen from Table 3, an increase in the concentration of MoS2 nanoparticles also leads to a decrease in recombination resistance, which indicates an increase in recombination processes.

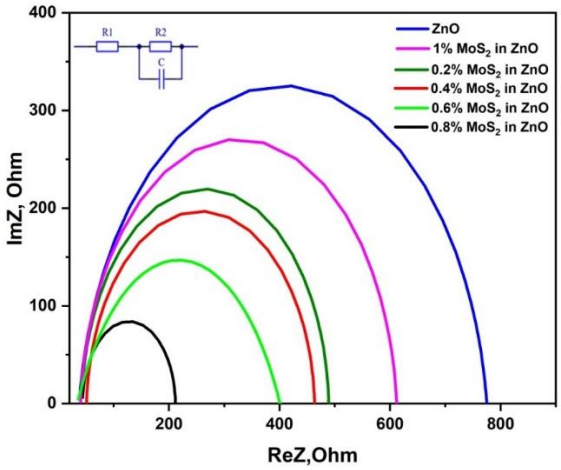


Fig.7. Impedance spectra of PSCs

Table 3 shows the obtained values of R_1 R_2 and C. As can be seen from Table 3, the value of R_1 represents the total resistance of the external electrodes and adjacent ETL and HTL layers. Since all functional layers except ZnO are in the cells under ZnO:MoS2 were obtained under the same conditions, the observed changes in R_1 are associated with a change in the resistance of ZnO:MoS2 films. R_1 has a minimum value at the cell with the maximum concentration of MoS2. R_2, the resistance characterizing electron recombination at the photoactive layer/ZnO:MoS2 interface, varies depending on the concentration of MoS2 nanoparticles.

Table 3. The value of the electrophysical parameters of ZnO:MoS2 composite films

Sample	R_1, (ohm)	R_2, (ohm)	R_1 / R_2	τ_{eff}, (ms)	k_{eff}, (s^{-1})	D_{eff}, ($см^2 \cdot с^{-1}$)
ZnO	47	737	15.7	2.4	404	$1.1 \cdot 10^{-5}$
0.2% MoS2	27	383	14.1	2.6	373	$1.9 \cdot 10^{-7}$
0.4% MoS2	30	449	14.9	3.1	319	$2.6 \cdot 10^{-7}$
0.6% MoS2	30	432	14.4	3.7	264	$3.5 \cdot 10^{-7}$
0.8% MoS2	16	178	11.1	8.6	115	$4.1 \cdot 10^{-7}$
1% MoS2	37	569	15.4	2.6	372	$1.4 \cdot 10^{-6}$

After photoexcitation, electrons from the photoactive layer are injected into ZnO:MoS2 and diffuse to the external electrode. At the same time, the reverse process occurs - the recombination of an electron with a hole into a photoactive layer. Usually, recombination occurs through surface defect levels in ZnO. Impedance spectroscopy also allows us to calculate the time constant $\tau = RC$, which characterizes the lifetime of charge carriers in ZnO:MoS2. It follows from the fitting data of the impedance spectra that τ has the maximum value for ZnO:MoS2 with a concentration of 0.8% nanoparticles. The impedance analysis data is correlated with the VAC data. OSCs with ZnO:MoS2 0.8% of nanoparticles form ETL films with improved conductivity and less structural defects. A sharp deterioration in the photovoltaic parameters of OSCs with ZnO over 0.8% of the MoS2 nanoparticle may be due to a infringement of the integrity of the film, which causes holes and voids to form in the film, through which current leakage occurs.

Conclusions

In this paper, the effect of MoS2 nanoparticles on the morphology, optical and electric properties of ZnO electron transport layer of polymer solar cells is investigated. In the absorption spectra of ZnO:MoS2 composite films, an increase in the absorption intensity is observed. An increase in the absorption of the film

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is associated with a change in the overall thickness. At the same time, the nanoparticles do not affect the electronic structure of ZnO. It is shown that the addition of MoS2 nanoparticles has an effect on the photoelectric and electrophysical parameters of the film in the polymer solar cell. It has been shown that the changes in the IV characteristic of OSCs based on ZnO:MoS_2 ETL are associated with the influence of MoS2 nanoparticles on electron transport. It was found that MoS2 nanoparticles at a concentration of 0.8% increase the lifetime of charge carriers and the diffusion coefficient in composite ETL ZnO:MoS2 and also the maximum value of the increase in the parameters of the VAC is observed for the composite cell 0.8%. As a result, the short-circuit current density increased by 3 times, the efficiency value was 2.6%.

Acknowledgments

This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19679109**).**

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Article accepted for publication 20.03.2023