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Effect of ZnO in various alcohols on photoelectric characteristics of OSC

The paper presents the results of a study of the effect of alcohols on the electron transport of the ETL layer of a ZnO polymer solar cell with an inverted structure. To obtain films, zinc acetate was dissolved under the same experimental conditions in isopropanol, butanol and ethanol. According to the SEM data, it was found that the use of various alcohol solvents in the synthesis of the film shows a change in the morphology of the surface. The observed changes in the interface of the surface of the films are associated with the formation of ZnO aggregates depending on the polarity used of the alcohols. It is shown that the optical width of the ZnO band gap also depends on alcohol solvents. It is shown that the aggregation of ZnO has an effect on the electron transport and efficiency of the polymer solar cell. The voltage characteristics of the solar cells FTO/ ZnO/P3HT: IC60MA/PEDOT: PSS/Ag were measured. It is shown that the smallest aggregation of ZnO is observed in Isopropanol, in which the organic cell showed the highest efficiency of converting solar energy into electrical energy. The polymer solar cell has been the efficiency 2.5 %. From the obtained ETL impedance measurement data, the ZnO based layer obtained in Ethanol has the lowest electron transport parameters. This is due to the high degree of aggregation of ZnO, as a result of which the resistance to increases of the interface ZnO/FTO. The solar cells based ZnO in Ethanol demonstrated an efficiency value of 0.9 % compared to ZnO in Butanol with an efficiency of 1.6 %.

Keywords: ZnO, Isopropanol, Ethanol, Butanol, surface morphology, thermal annealing, optical spectroscopy, impedance spectroscopy.

Introduction

Obtaining electrical energy from the sun is one of the ways that in the near future can provide a rapidly growing demand for clean energy. Among the currently existing various phototransverters, organic solar cells are of great interest. Currently, the efficiency of organic solar cells (OSC) already exceeds 15 % [1-3]. The photoactive OSC layer is a volumetric heterojunction in which electron and acceptor materials are mixed in the active layer, forming an interfacial region where excitons are separated. To minimize charge recombination at both interfaces and increase the efficiency of charge extraction, a volumetric heterojunction is placed between the electron transfer transport layer (ETL) and the hole transfer layer (HTL). The inverted structure is widely used in OSC due to the simple manufacturing technology, good stability and efficient phase separation [4].

The ETL layer based on metal oxides has attracted great attention due to its high transparency in the visible spectral region, as well as the possibility of changing energy levels and electrical properties by doping or chemical modification [5]. Among the known metal oxides used in OSC, ZnO [6], TiO2 [7], etc. can be distinguished. In inverted OSCs, the morphology and structure of ZnO have a strong influence on the efficiency of organic solar cells [8].

ZnO is a multifunctional semiconductor with a straight wide band gap (3.37 eV for ZnO wurtzite). ZnO has a fairly high exciton binding energy (60 MeV), which makes the semiconductor thermally and chemically stable [9]. However, the high reactivity in water leads to a rapid growth of ZnO crystallites, which makes it difficult to control the synthesis of nanometer-scale particles. Alcohol solvents are used to prevent the growth of ZnO nanoparticles [10]. It is known that the morphology of the surface of ZnO films depends on the length of the alkyl chain of alcohols [11].

In this work, the influence of alcohol solvents of different polarities on the morphology, optical and electrophysical characteristics of ZnO films was studied. The results of the study of the effect of ZnO films obtained in alcohols of different polarities on the efficiency of OSC are presented.

Experimental

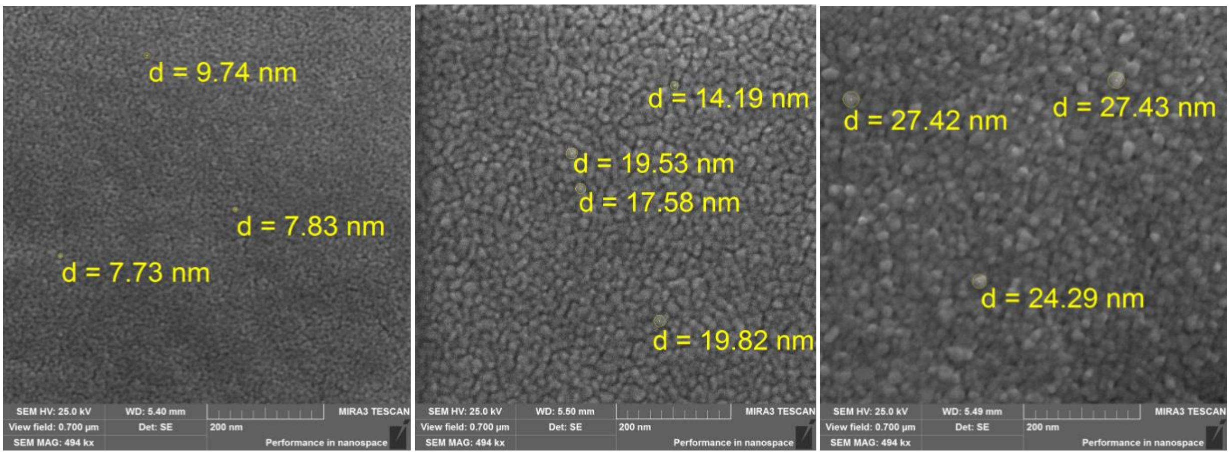
To obtain compact layers of ZnO, the following materials were used: $Zn_5(OH)_8Cl_2$, Isopropanol, Ethanol, Butanol (pure 99.9 % Sigma Aldrich). At first the FTO covered glass substrates were rigorously cleaned [12]. The preparation of solutions was carried out in accordance with the method. For this $Zn_5(OH)_8Cl_2$ (weighted m =49.3 mg) was dissolved separately in volume (V= 0.5 ml) in Isopropanol, Ethanol, Butanol. After Monoethanolamine (Sigma Aldrich) was added to the obtained solutions after 20 minutes in an amount (V = 38 μl). Further, the solutions were mixed at a temperature of T = 60 °C for 2 hours, and then kept for 24 hours at room temperature.

At the next stage, the solutions were applied to the FTO surface by spin-coating at a speed of 4000 rpm. After the film was annealed in an air atmosphere at a temperature of 200 °C for 15 minutes, then annealed at a temperature of 450 °C for one hour. A photoactive layer of P3HT: IC60MA (pure 97 % Sigma Aldrich) at a concentration of 1:0.8 was applied to the surface of the resulting ZnO film by spin-coating. After that, the samples were annealed in an air atmosphere at a temperature of 140 °C for 10 minutes, then PEDOT: PSS was applied to the surface of the photoactive layer by spin-coating in volume (V=25 μl) after annealing in an air atmosphere at a temperature of 115 °C for 10 minutes, then to the surface of the film by thermal deposition silver electrode was sprayed on the CY-1700x-spc-2 installation (Zhengzhou CY Scientific Instruments Co., Ltd).

Microstructural characterization of the obtained samples was carried out using a scanning electron microscope MIRA 3 LMU(TESCAN). The absorption spectra of the studied samples were recorded using an AvaSpec-ULS2048CL-EVO spectrometer manufactured by Avantes, which registers absorption spectra in the range of 200-1100 nm and has an optical resolution of 0.04 nm. Measurements of the impedance spectra were carried out using in the impedance mode a potentiostat-galvanostat P45X. The VAC of photosensitive cells was determined by the Sol 3A Class AAA Solar Simulators (Newport) with the PV IV-1A IV Test Station.

Results and Discussion

Figure 1 shows SEM images of ZnO films obtained in isopropanol (a), butanol (b) and ethanol (c). It can be seen from the figures that the surface interfaces of the films differ. This is due to the influence of alcohol solvents such as isopropanol, butanol, and ethanol. So, in isopropanol, the grain sizes on the surface of the film are about 10 nm. Further, it can be seen that the ZnO grains obtained in butanol are less than 20 nm (Fig. 1b). At the same time, the coarse-grained structure of ZnO is obtained in ethanol with a size greater than 20 nm (Fig. 1c).



a) b) c)

Figure 1. SEM images of a) Isopropanol; b) Butanol; c) Ethanol

The influence of alcohol solvents of different polarities is associated with the aggregation of ZnO nanoparticles due to non-covalent interactions, such as hydrogen bonding, which provides a weaker electrostatic interaction in the film.

Figure 2 shows the absorption spectra of ZnO films obtained with different alcohols.The absorption spectrum is typical of the absorption spectrum of wide-band semiconductors.The edge of the fundamental absorption band falls at 380 nm, which corresponds to the optical transition of the ZnO band gap. The figure shows the dependences of the ZnO band gap width depending on alcohol solvents. The graph shows that the aggregation of ZnO in the film leads to a decrease in the optical band gap from 3.2 eV to 2.8 eV. A decrease in the optical band gap leads to a decrease in the degree of crystallinity of ZnO.

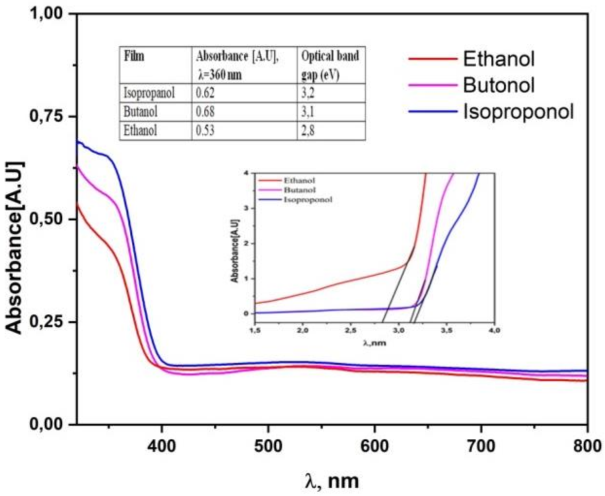
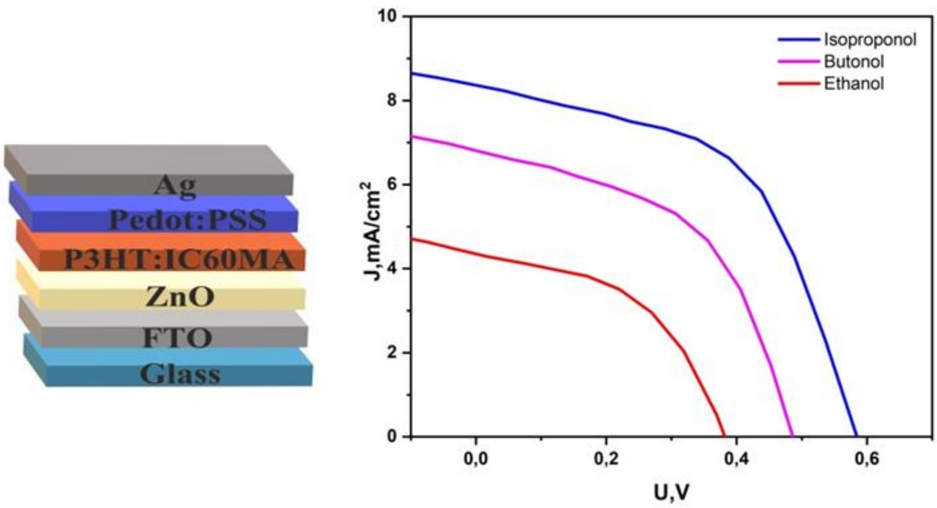


Figure 2. Absorption spectra and Tauc plots (the inset) of films

To determine the effect of alcohol solvents on the transport and recombination of charges in the ZnO of a polymer solar cell, an organic cell FTO/ZnO/P3HT: IC60MA/PEDOT: PSS/Ag was assembled. The voltage characteristics of ZnO in different alcohols are shown in Figure 3. Photovoltaic parameters of organic solar cells are presented in Table 1.



a) b)

Figure 3. a) the architecture of the inverted PSC; b) current – voltage characteristics of FTO/ZnO/P3HT: IC60MA/PEDOT: PSS/Ag devices

Data analysis showed that the values of short-circuit current densities vary depending on alcohol solvents, so for Isoproponol (*J_{sc})* 8.6, Butanol (*J_{sc})* 7.1 and Ethanol (*J_{sc})* 4.7 mA/cm^2, respectively. The no-load voltage (U_{oc}) also depends on alcohol solvents (Table 1). The change in the values of the current density is associated with the process of aggregation of ZnO depending on alcohol solvents. The lowest aggregation of ZnO is observed in Isopropanol, in which the organic cell showed the highest efficiency of converting solar energy into electrical energy.

Table 1

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 %
Isopropanol	0.58	8.6	0.40	6.33	0.50	2.5
Butanol	0.48	7.1	0.32	5.04	0.47	1.6
Ethanol	0.38	4.7	0.24	3.2	0.43	0.9

Studies of the mechanisms of transport and recombination of charge carriers of the electron transport layer of the ZnO film in different alcohols were carried out by the method of impedance spectroscopy. The impedance spectra of the ETL layer in Nyquist coordinates based on solid films are shown in Figure 4. Table 2 shows the electron transport parameters of the ETL layer calculated using the EIS-analyzer software package, where (R_w) is the equivalent resistance of the film; (R_{rec}) is the resistance characterizing the recombination of localized electrons with holes; (k_{eff}) is the effective recombination rate of charge carriers; (τ_{eff}) is the effective lifetime of charge carriers; (D_{eff}) is the diffusion coefficient.

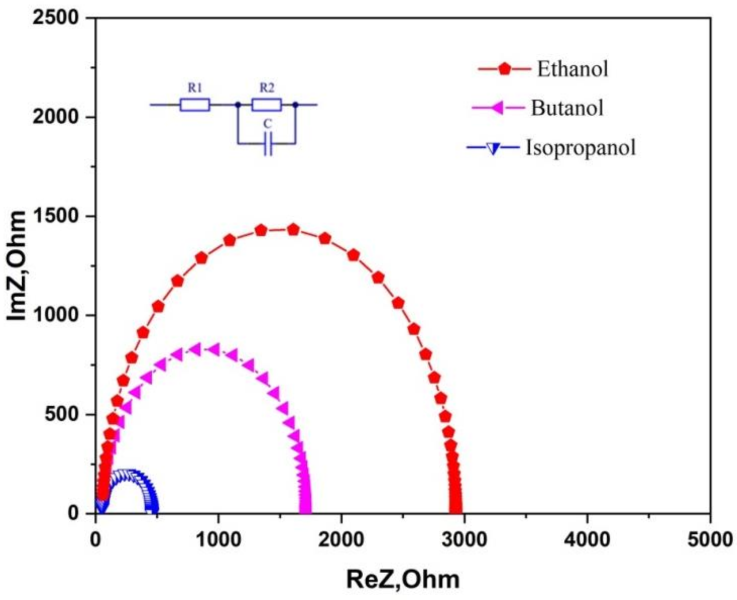


Figure 4. Impedance spectra of ZnO

From the obtained impedance measurement data, it follows that the ETL layer based on ZnO obtained in Ethanol has the lowest electron transport parameters. This is due to the high degree of aggregation of ZnO, as a result of which the resistance to increases interface of the ZnO/FTO.

In polymer solar cell with ZnO in Isoproponol, due to the low degree of aggregation, rapid electron transfer to the cathode (FTO) and a decrease in recombination of injected electrons at the boundary with the photoactive layer are observed, as a result, the photovoltaic characteristics of the polymer solar cell increase compared to other alcohols.

Table 2

The value of electrophysical parameters of films

Sample	R_1, (ohm)	R_2, (ohm)	R_2 / R_1	τ_{eff}, (ms)	k_{eff}, (s^{-1})	D_{eff}, (cм$^2 \cdot$c^{-1})
Isopropanol	51	406	7.9	10.2	807	$1.7 \cdot 10^{-7}$
Butanol	59	1662	28.1	5.1	1937	$1.5 \cdot 10^{-8}$
Ethanol	82	4020	49.0	4.2	2329	$3.3 \cdot 10^{-8}$

Conclusions

The paper presents the results of a study of the effect of different alcohols in the synthesis of ZnO films on the electron transport of a polymer solar cell. The analysis of experiments showed that depending on alcohols, there is a change in the morphology of ZnO, which in turn affects the efficiency of electron transport. It is established that the optical band gap of ZnO in isopropanol is 3.2 eV and in ethanol decreases to 2.8 eV. It is shown that changes in the morphology of the ZnO surface affect the parameters of the VAC polymer solar cell. So for Isopropanol (J_{sc} -8.6 mA/cm^2), Butanol (J_{sc} -7.1 mA/cm^2) and Ethanol (J_{sc} -4.7 mA/cm^2) respectively. ZnO based photocells in Isopropanol have shown the highest efficiency of converting light energy into electrical energy.

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Әр түрлі спирттердегі ZnO-нің OSC фотоэлектрлік сипаттамаларына әсері

Жұмыста инверттелген құрылымы бар ZnO полимерлі күн элементінің ETL қабатының электрон тасымалдауына спирттердің әсерін зерттеу нәтижелері берілген. Пленкаларды алу үшін мырыш ацетаты изопропанолда, бутанолда және этанолда бірдей тәжірибелік жағдайларда ерітілді. СЭМ мәліметтері бойынша пленка синтезінде әртүрлі спиртті еріткіштерді қолдану беттік морфологияның өзгеруіне әкелетіні анықталды. Пленка бетінің интерфейсінің өзгеруі қолданылатын спирттердің полярлығына және ZnO агрегаттарының пайда болуымен байланысты. ZnO тыйым салынған аймақтың оптикалық ені спирт еріткіштерінен тәуелді екендігі көрсетілген. ZnO агрегациясы электронды тасымалдауға және полимерлі күн элементінің тиімділігіне әсер ететіні дәлелденген. ZnO:P3HT:IC60MA/PEDOT:PSS/Ag күн ұяшықтарының вольтамперлік сипаттамалары өлшенді. Көрсетілген ең аз ZnO агрегациясы Isopropanol-да байқалады, онда органикалық ұяшық күн энергиясын электр энергиясына айналдырудың ең жоғары тиімділігін көрсетті. Полимерлі күн ұяшықтарының тиімділігі 2.5% құрады. Алынған импедансометрия мәліметтері көрсеткендей Ethanol-да ZnO негізіндегі алынған ETL қабат ең төменгі электр тасымалдау параметрлеріне ие. Бұл ZnO агрегациясының жоғары деңгейіне байланысты, нәтижесінде ZnO / FTO интерфейсінің кедергісі

артады. Ethanol-дағы ZnO негізіндегі күн элементтері 1,6% болатын ПӘК Butanol-дағы ZnO-мен салыстырғанда ПӘК мәні 0,9%-ға тең болатынын көрсетті.

Кілт сөздер: ZnO, изопропанол, этанол, бутанол, беттік морфология, термиялық күйдіру, оптикалық спектроскопия, импеданс спектроскопиясы.

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Влияние ZnO в различных спиртах на фотоэлектрические характеристики OSC

В статье представлены результаты исследования влияния спиртов на электронный транспорт ETL слоя ZnO полимерного солнечного элемента с инвертированной структурой. Для получения пленок ацетат цинка растворяли при одинаковых условиях эксперимента в изопропаноле, бутаноле и этаноле. По данным СЭМ, было установлено, что использование различных спиртовых растворителей при синтезе пленки ведет к изменению морфологии поверхности. Наблюдаемые изменения интерфейса поверхности пленок связаны с образованием агрегатов ZnO в зависимости от полярности используемых спиртов. Показано, что оптическая ширина запрещенной зоны ZnO также зависит от спиртовых растворителей, и агрегация ZnO оказывает влияние на электронный транспорт и эффективность полимерного солнечного элемента. Измерены вольтамперные характеристики солнечных ячеек ZnO:P3HT:IC60MA/PEDOT:PSS/Ag. Обнаружено, что наименьшая агрегация ZnO наблюдается в Isopropоnol, в которой органическая ячейка показала наибольшую эффективность преобразования солнечной энергии в электрическую. КПД полимерного солнечного элемента составил 2,5 %. Из полученных данных импедансометрии ETL слой на основе ZnO, полученном в Ethanol, имеет самые низкие электротранспортные параметры. Это связано с высокой степенью агрегацией ZnO, в результате чего возрастает сопротивление интерфейса ZnO/FTO. Солнечные элементы на основе ZnO в Ethanol продемонстрировали значение КПД, равное 0,9 %, по сравнению с ZnO в Butanol (КПД 1,6 %).

Ключевые слова: ZnO, изопропанол, этанол, бутанол, морфология поверхности, термический отжиг, оптическая спектроскопия, спектроскопия импеданса.