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EFFECT OF ALCOHOL SOLVENTS ON THE STRUCTURAL, OPTICAL AND ELECTRICAL CHARACTERISTICS OF PEDOT:PSS POLYMER FILMS ANNEALED AT LOW ATMOSPHERIC PRESSURE

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The paper presents the results of a study of the effect of alcohol solvents on the surface structure, optical and electrical characteristics of a Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate films annealed at a low atmospheric pressure of 10^{-3} millimeters of mercury. It has been found that the modification of the surface of a polymer film with ethyl and isopropyl alcohols leads to a change in the surface morphology, optical and electrical transport properties of the polymer. It is shown that when the Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate film is modified with alcohol solvents, the absorption spectra show a decrease in the absorption of the polystyrene sulfonate aromatic fragment. It is shown that the structural features of the Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate surface morphology affect the electrical transport parameters of films, such as the resistance of the Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate film, the charge carrier transfer resistance at the Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/electrode interface, the effective extraction rate, and the effective time of flight of charge carriers. The optimal technological parameters for the production of films have been determined, at which the electrical transport properties of Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate films annealed at low atmospheric pressure increase.

Keywords: PEDOT:PSS, Izopropanol, Ethanol, low atmospheric pressure, surface morphology, optical spectroscopy, impedance spectroscopy

Introduction

PEDOT:PSS is traditionally used as a hole transport layer in organic solar cells (OSC) due to its high transparency in the visible light range, good film formation during dissolution, and high work function [1,2]. The properties of the PEDOT:PSS layer can definitely affect the performance of the OSC. It can be used as a potential alternative to both traditional solid substrate electrodes such as conductive electrode (ITO, FTO) and metal electrodes (Au, Pt, Cu, etc.) [3-4].

However, defects of microstructure in the PEDOT:PSS film morphology can lead to inefficient hole transport within the PEDOT:PSS layer [5-8], causing unbalanced charge carrier transport, which ultimately results in low FF and high current leakage [9-12]. Thus, the uniformity of the PEDOT:PSS layer is important for PSC performance.

Currently, there are several methods for improving the electrical and optical properties of a PEDOT:PSS film: post-processing, doping and creating composites [5]. One of the main ways to improve the conductivity of PEDOT:PSS is the addition of organic solvents, including alcohol ones [13–17]. It is known that solvents affect the conductivity and structure of the film [18, 19], however, in the works of the authors, due attention is not paid to the processes of generation and transport of charge carriers in films of the modified PEDOT:PSS.

Previously, we studied the effect of modification of the structure of the PEDOT:PSS polymer with hole conductivity on the optical, electrical transport and photovoltaic properties of an organic solar cell based on a P3HT:PC60BM bulk heterojunction [20]. It was shown that thermal treatment with the addition of isopropyl alcohol to the PEDOT:PSS polymer solution leads to a change in the structural and optical properties of the films. It has been established that the efficiency of charge

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carrier transfer and the efficiency of a polymer solar cell depend on the structural features of PEDOT:PSS.

Thus, it can be noted that studies on the effect of structural changes in the PEDOT:PSS polymer on its morphological, optical and electrical transport parameters remain relevant.

In this work, we will investigate the effect of modification of a conductive PEDOT:PSS polymer with organic alcohol solvents on the morphological, optical and electrical transport characteristics of a PEDOT:PSS polymer with hole conductivity annealed at low atmospheric pressure.

1. Experimental

We used PEDOT:PSS (1%, Ossila Al4083), Izopropanol, Ethanol (pure 99.9% Sigma Aldrich). To change the surface morphology, the PEDOT:PSS hole-conducting polymer was diluted with a certain concentration of alcohol (ethyl, isopropyl), placed in a vacuum furnace (YHCHEM, Shanghai Yuanhuai Industrial Co) and annealed at 120°C for 10 minutes. A comparative analysis of the modified PEDOT:PSS film was carried out by comparing the structure of the surface morphology, optical and electrical properties. The structural formulas of the compounds are shown in Figure 1. The preparation of the substrates was carried out according to the procedure [21]. Before starting the experiments, the PEDOT:PSS solution was filtered through a 0.45 micrometer filter. PEDOT:PSS films were obtained on the surface of quartz glass by centrifugation (on a SPIN150i centrifuge manufactured by Semiconductor Production System) at a rotation speed of 5000 rpm.

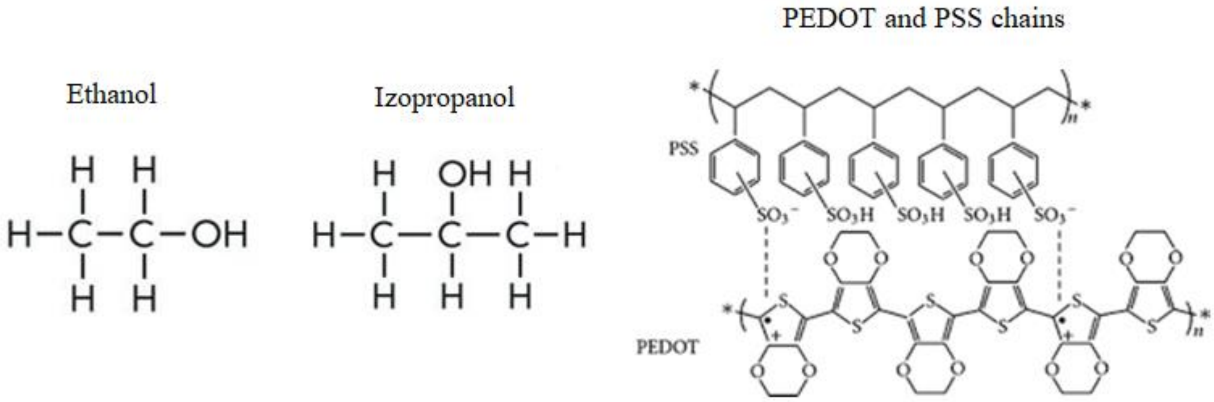

Fig. 1. Chemical structure of Ethanol, Izopropanol, PEDOT and PSS

The surface topography of the samples was studied using a high-resolution atomic force microscope (AFM) JSPM-5400 (JEOL, Japan). The AFM images were processed using a special modular program for analyzing scanning probe microscopy data (Win SPMII Data-Processing Software). The surface morphology and roughness of PEDOT:PSS thin films were analyzed from AFM images. The images of the surface of the PEDOT:PSS films were obtained in the mode of the semicontact scanning method. The absorption spectra of the studied samples were recorded 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 0.04 nm. The impedance spectra were measured using a measuring system P-45X (Elins) with an additionally installed FRA-24M frequency analyzer module. Fitting and analysis of the spectrum parameters were carried out using the EIS-analyzer software package, according to the procedure [22].

2. Results and Discussion

Images of the surface morphology of PEDOT:PSS films with different ratios of ethyl and isopropyl alcohols are shown in Figure 2. Table 1 shows the roughness values of PEDOT:PSS films. Figure 2 shows that the PEDOT:PSS film without the addition of alcohols after thermal annealing has a rather pronounced relief. In this case, the surface morphology has a pronounced heterogeneity, the surface roughness is 0.64 nm. In a PEDOT:PSS film prepared in ethanol in a ratio of 80% PEDOT:PSS/20% ethanol, after thermal annealing at a temperature of 120°C, a decrease in surface roughness to a value of 0.58 nm is observed. A further increase in the concentration of alcohol in a ratio of 70% PEDOT:PSS/30% ethanol leads to a reduction in the surface roughness of the film to 0.54 nm. At a ratio of 50% PEDOT:PSS/50% ethanol, the surface roughness of the film is reduced to a value of 0.45 nm.

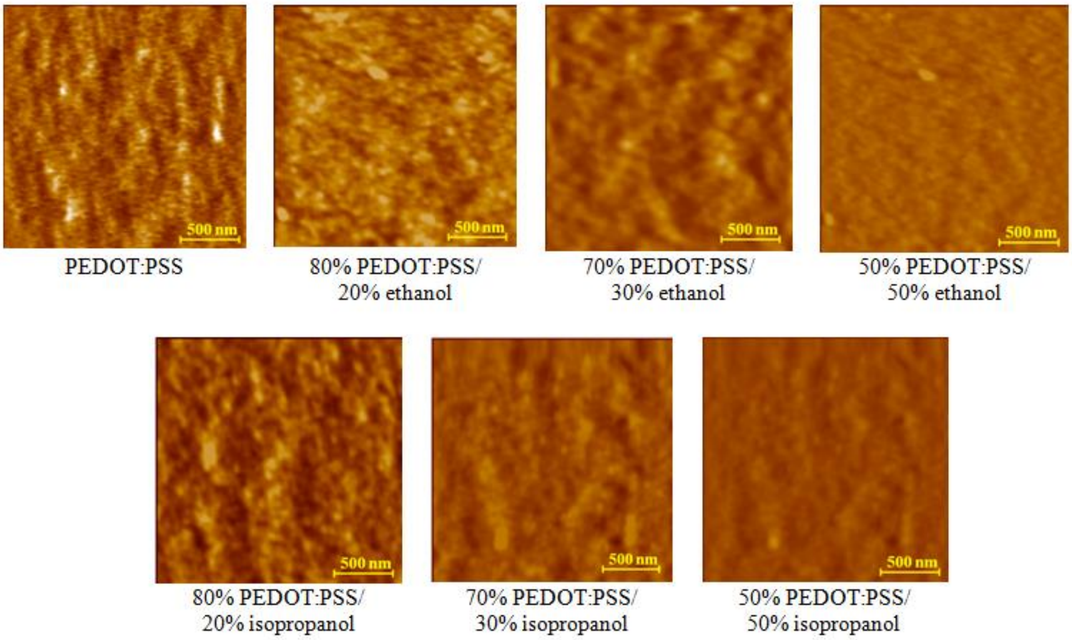

Fig. 2. Surface morphology images of PEDOT:PSS films

For a qualitative analysis of studies, the effect of the ratio of isopropyl alcohol on the morphology of the PEDOT:PSS polymer was studied. From the obtained results it can be seen that the roughness of the PEDOT:PSS film in a ratio of 80% PEDOT:PSS/20% isopropanol was 0.54 nm. This value is not very different from the roughness value obtained for ethyl alcohol. At a ratio of 70% PEDOT:PSS/30% isopropanol, the film roughness also decreases to a value of 0.49 nm. Increasing the proportion of isopropyl alcohol to 50% in the film resulted in smoothing of the film surface with a roughness of 0.43 nm. Comparative analysis of changes in surface roughness showed that in the process of film preparation with the addition of various concentrations of ethyl alcohol, the surface roughness decreases by 1.4 times, and isopropyl alcohol by 1.5 times.

Table 1. Surface roughness of PEDOT:PSS films with different concentrations of alcohols

Sample	R_a, nm
PEDOT:PSS	0.64
80% PEDOT:PSS/20% ethanol	0.58
70% PEDOT:PSS/30% ethanol	0.54
50% PEDOT:PSS/50% ethanol	0.45
80% PEDOT:PSS/20% isopropanol	0.54
70% PEDOT:PSS/30% isopropanol	0.49
50% PEDOT:PSS/50% isopropanol	0.43

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Figure 3 shows the absorption spectra of PEDOT:PSS films with different ratios of ethyl and isopropyl alcohol, annealed at low atmospheric pressure at *T*=120C°. It can be seen from the figure that the initial PEDOT:PSS film has a maximum at a wavelength of λ_1 = 214 nm with a spectral half-width of 10.2 nm. In the absorption spectra of all films, a shoulder λ_2 is observed with a maximum at 227 nm, which is associated with the absorption of the PSS - poly(styrenesulfonate) [20,23]. When ethyl alcohol is added to the film during preparation, the positions of the maxima in the absorption spectra do not change, only a decrease in the optical density values and a decrease in the half-width are observed (Figure 3a). The value of the maximum at a wavelength of 214 nm decreased by 1.2 times, and at a wavelength of 227 nm - by 1.6 times.

The absorption spectra of PEDOT:PSS films annealed at *T*=120C° with different ratios of isopropyl alcohol are shown in Figure 3b. A comparison of the shapes and positions of the absorption spectra maxima of films with isopropyl and ethyl alcohol showed no visible changes. The half-width of the absorption spectrum remained within the same range as for ethyl alcohol. The values of the optical density at the absorption maxima decrease. The value of the maximum at a wavelength of 214 nm decreased by a factor of 1.7, and at a wavelength of 227 nm, by a factor of 2.2. Table 2 lists the characteristics of the absorption spectra of PEDOT:PSS films prepared with various concentrations of alcohol solvents and annealed at low atmospheric pressure.

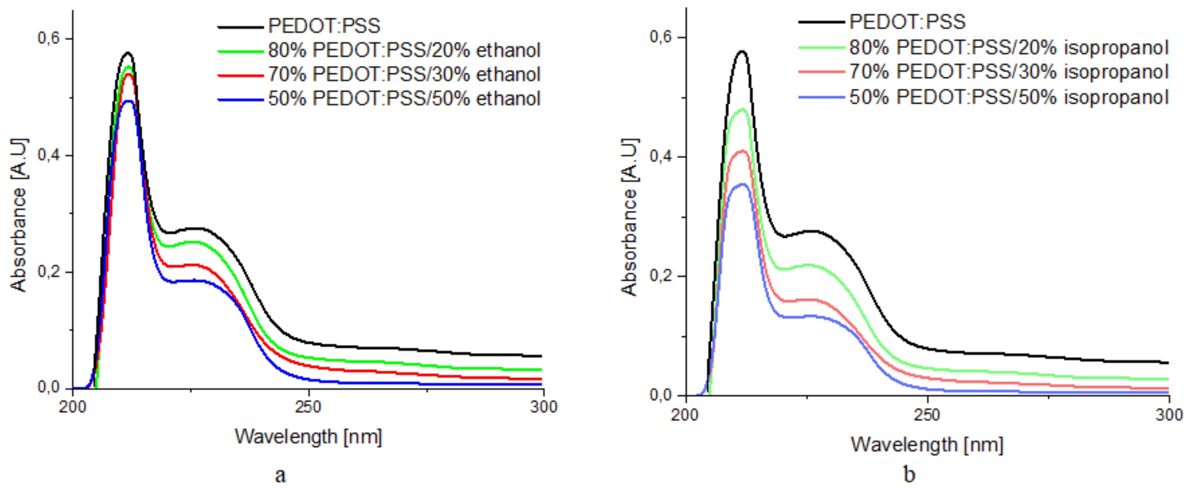

Fig. 3. The absorption spectra of PEDOT:PSS/ethanol (a) and PEDOT:PSS/isopropanol (b) films

It should be noted that a comparative analysis of the change in the values of optical density at the absorption maxima of the films shows that for isopropyl alcohol a greater decrease in absorption is observed than for ethyl alcohol.

Table 2. Characteristics of absorption spectra of PEDOT:PSS films

Sample	Absorption peaks		D_1	D_2	FWHM, nm
	λ_1, nm	λ_2, nm			
PEDOT:PSS	214	227	0.58	0.28	10.2
Ethanol					
80% PEDOT:PSS/20% ethanol	214	227	0.55	0.25	9.5
70% PEDOT:PSS/30% ethanol	214	227	0.54	0.21	9.1
50% PEDOT:PSS/50% ethanol	214	227	0.49	0.18	8.5
Isopropanol					
80% PEDOT:PSS/20% isopropanol	214	227	0.48	0.22	10.1
70% PEDOT:PSS/30% isopropanol	214	227	0.41	0.16	10.1
50% PEDOT:PSS/50% isopropanol	214	227	0.35	0.13	9.7

Next, using the method of impedance spectroscopy, we studied the effect of modification of the PEDOT:PSS structure annealed at low atmospheric pressure with alcohol solvents on the parameters of charge carrier transport in the cells of the ITO/PEDOT:PSS/Al structure. The analysis of the results was carried out according to the diffusion-recombination model with an equivalent chain, shown in Figure 4a [24]. Here R_1 is the PEDOT:PSS film resistance, R_2 is the charge carrier transfer resistance at the PEDOT:PSS/Al interface, CPE is a constant phase element, is an equivalent electrical circuit component that simulates the behavior of a double layer, but is an imperfect capacitor. From the impedance spectra, the main electrical transport parameters were calculated (Table 3), where: R_h and R_{ext} correspond to R_1 and R_2, τ_{eff} is the effective transit time through PEDOT:PSS, k_{eff} is the effective charge carrier extraction rate from PEDOT:PSS. The scheme of charge transport in the ITO/PEDOT:PSS/Al cell is shown in Figure 4b.

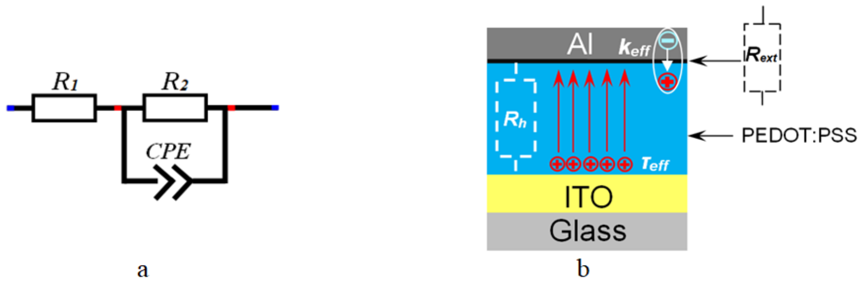

Fig. 4. Equivalent electrical circuit (a) and circuit of charge transport in the cell (b)

The impedance spectra of PEDOT:PSS films with different concentrations of alcohol solvents annealed at low atmospheric pressure are shown in Figure 5. Table 3 shows the values of the electrical transport parameters of the films. As can be seen from Table 3, the modification of PEDOT:PSS with organic solvents affects the transport of charge carriers in PEDOT:PSS. Table 3 shows that cells based on films obtained from solutions with alcohol solvents have better electrical transport properties compared to the original PEDOT:PSS film. The best transport parameters are achieved with a maximum concentration of 50% alcohol solvent. The addition of ethanol significantly reduces the resistance of the PEDOT:PSS (R_h) film by a maximum of 1.8 times and the resistance of the PEDOT:PSS/Al (R_{ext}) interface by a factor of 3.8, which increases the efficiency of hole transport from ITO to Al through PEDOT:PSS. However, when using isopropyl alcohol, the decrease in R_h and R_{ext} is more significant: R_h decreased by 2.7 times, while R_{ext} by 4.2 times compared to the original PEDOT:PSS.

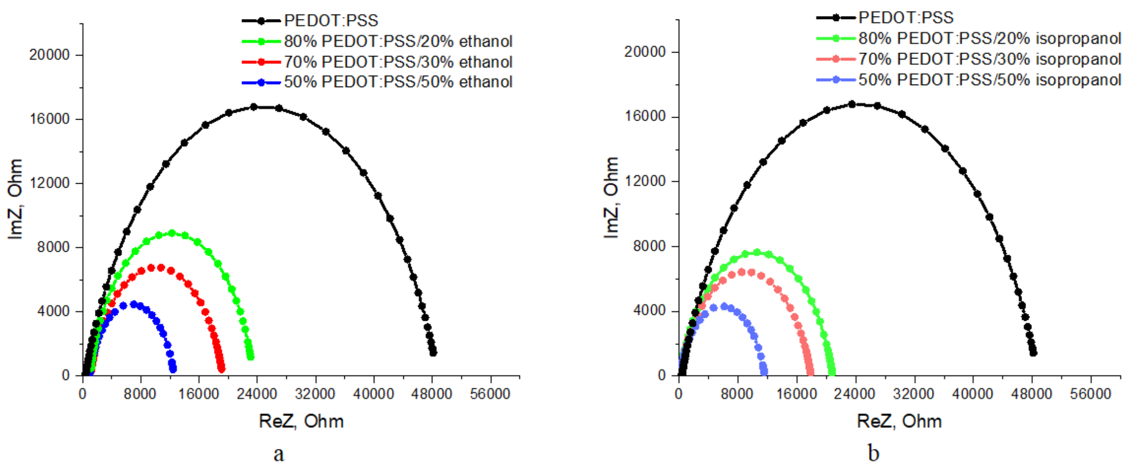

Fig.5. The impedance spectra of PEDOT:PSS/ethanol (a) and PEDOT:PSS/isopropanol (b) films

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The values k_{eff} and τ_{eff} characterize the efficiency of carrier extraction with PEDOT:PSS and the effective charge transit time in PEDOT:PSS. As can be seen from Table 3, the addition of ethyl and isopropyl alcohol to PEDOT:PSS has a noticeable positive dynamic in k_{eff} and τ_{eff}. However, the best results are shown by films prepared with the addition of isopropyl alcohol.

Effective charge carrier extraction rate from PEDOT:PSS films obtained from a solution with isopropyl alcohol increased by more than three times, and the effective transit time decreased inversely. Holes injected into PEDOT:PSS diffuse to the electrode where they recombine with electrons. Fast transport of injected holes to the outer electrode is very important, since this reduces the probability of their reverse recombination. In our case, fast hole transport is provided by improving the structure of PEDOT:PSS after adding isopropyl alcohol to the initial solution, which leads to an improvement in the quality of the PEDOT:PSS/ITO interface [20].

Table 3. Electrical transport parameters of PEDOT:PSS films annealed at low atmospheric pressure

Sample	R_h, Ω	R_{ext}, Ω	k_{eff}, s^{-1}	τ_{eff}, ms
PEDOT:PSS	268.7	48745	157.5	6.4
Ethanol				
80% PEDOT:PSS/20% ethanol	248.3	23854	259.4	3.9
70% PEDOT:PSS/30% ethanol	204.7	19887	348.1	2.9
50% PEDOT:PSS/50% ethanol	148.5	12769	425.1	2.4
Isopropanol				
80% PEDOT:PSS/20% isopropanol	197.8	21748	357.2	2.8
70% PEDOT:PSS/30% isopropanol	104.2	18374	483.9	2.1
50% PEDOT:PSS/50% isopropanol	98.5	11478	601.8	1.7

Conclusions

An analysis of the experiments showed that the addition of an alcohol solvent affects the surface structure of PEDOT:PSS films annealed at low atmospheric pressure, which, in turn, affects the process of charge carrier transport. It has been found that the addition of alcohol to the PEDOT:PSS polymer leads to a decrease in surface roughness. Upon modification of the PEDOT:PSS surface, a decrease in the absorption of the PSS aromatic fragment is observed in the absorption spectra. It is shown that changes in the structure and morphology of the PEDOT:PSS surface affect the electrical transport parameters of the films. It has been found that the surface of the PEDOT:PSS film annealed at low atmospheric pressure and modified in isopropyl alcohol has the lowest resistance parameters R_h and R_{ext} and the highest k_{eff}, at which, due to the change in the PEDOT:PSS surface structure, the fastest charge carriers transport is ensured.

Solar cells based on modified PEDOT:PSS films, as a rule, have lower resistance values compared to the original films, which is due to the faster transport of injected holes to the outer electrode. Thus, this study showed the possibility of optimizing the electrical transport parameters of solar cells by modifying the PEDOT:PSS hole-transport layer.The electrical transport characteristics of the modified PEDOT polymer can be used in the development of organic light-emitting devices and photoconverters.

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