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INVESTIGATION OF OPTICAL AND ELECTROPHYSICAL CHARACTERISTICS OF COMPOSITE FILMS NIO/PEDOT:PSS

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This work presents the results of a study of the morphological, optical, and electrophysical parameters of Nickel Oxide/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (NiO/PEDOT:PSS) composite films. It is shown that an increase in the speed of rotation of the substrate leads to a decrease in the surface roughness of NiO films. As the surface roughness of the Nickel oxide decreases, the roughness of the PEDOT:PSS film also decreases. Increasing the speed of rotation of the substrate leads to a decrease in the optical density of the absorption spectra of NiO films, as well of composite films NiO/PEDOT:PSS. It was found that changes in the morphology of NiO/PEDOT:PSS composite films contribute to the rapid transport of injected holes to the external electrode and reduce the probability of reverse recombination.

Keywords: nickel oxide (NiO), PEDOT:PSS, composite film, surface morphology, optical and impedance spectroscopy.

Introduction

Among inorganic hole transport layers (HTL), nickel oxide (NiO) is of considerable interest and has been extensively studied as a selective electrode for PSCs [1, 2]. Nickel Oxide is a well-known semiconductor material with hole conductivity, which has excellent properties: it is thermally and chemically stable, has a wide band gap of 3.6-4.0 eV, providing optical transparency, and is not an expensive material whose films can be obtained by various physical and chemical synthesis methods. Like many oxides, it has a non-stoichiometric composition due to the formation of point defects: Nickel vacancies and interstitial oxygen, which form shallow acceptor levels and contribute p-type conductivity.

NiO-based PSCs usually have a p-i-n structure (inverted structure) [1, 2]. In NiO-based PSCs, they are used as compact NiO layers (c-NiO) so are the mesoporous layers of NiO (mp-NiO). Planar PSCs have a simpler design than mesoporous ones. However, in both types of PSCs, an important role is played by the c-NiO layer, which extracts holes from the active layer, transports them to the TCO anode, and blocks the active layer from contacting the cathode. To further increase the efficiency and stability of NiO-based PSCs, it is necessary to optimize the synthesis of compact NiO films, as well as optimize the processes of modifying the structure and surface of NiO through doping and other modification methods.

One of the disadvantages of using the HTL layer of PEDOT:PSSis the degradation of organic solar cells due to the highly acidic nature of PSS [3]. As a result, the interface between ITO and PEDOT:PSS becomes unstable, and an undesirable chemical reaction occurs. To solve this problem, this paper proposes the use of an HTL NiO layer between ITO and PEDOT:PSS that will block unwanted degradation of ITO. For this purpose, the present paper presents the results of the study of the optical and electrophysical characteristics of composite films NiO/PEDOT:PSS.

Experimental methods

Production of Nickel oxide films on the ITO surface was carried out as follows [4]: Nickel nitrate hexahydrate [$Ni(NO_3)_2\ 6H_2O$] weighing m=145mg (LLC «Polihrom») was dissolved in a volume of ethylene glycol V=1 ml. Monoethanolamine (5 μkl) was added to the resulting solution. The solution was mixed at room temperature for 16 hours and then kept for 24 hours at room temperature. NiO films were obtained by centrifugation (SPIN150i, Semiconductor Production System). To change the film thickness, the substrate rotation speed was changed from 1500 rpm to 2500 rpm. After that, the film was annealed for 10 minutes at

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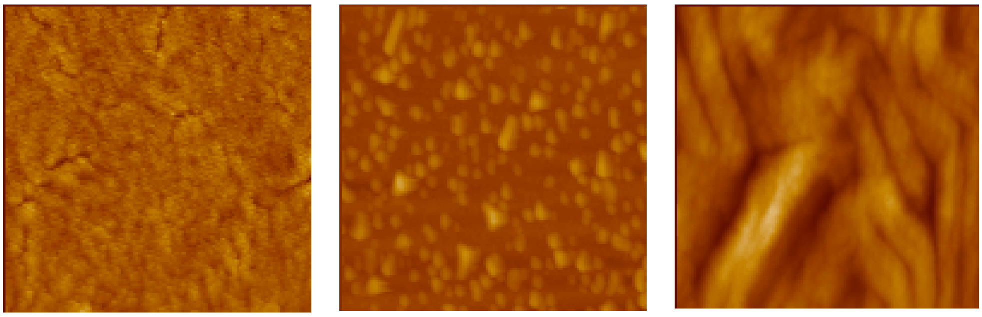
100°C, and then annealed to a temperature of 350°C at a rate of 10°C/min. Ito-based substrates were prepared according to the method [5].

For obtaining the composite films of NiO/PEDOT:PSS solution was used PEDOT:PSS (1%, Ossila Al4083). Before applying the solution of PEDOT:PSS was filtered through a 0.45 micrometer filter. Films of PEDOT:PSS were obtained on the NiO film by centrifugation at a speed of 4000 rpm. After film of PEDOT:PSS on the surface of NiO annealed in air atmosphere at a temperature of 120°C for 15 min.

The surface topography of the samples was studied using the JSPM -5400 atomic force microscope (ASM) JSPM-5400 (JEOL, Japan). A special modular program for analyzing scanning probe microscopy data (Win SPMII Data-ProcessingSoftware) was used to process images obtained on the ASM. Surface morphology, roughness of NiO films, and composite NiO/PEDOT:PSS films were analyzed from ASM images. Images of the film surface were obtained using the semi-contact scanning method. The absorption spectra of the studied samples were recorded using a CM-2203 Solar spectrofluorometer. The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode on the installation described in detail in [6].

Results and discussion

Images of the surface morphology of NiO films obtained at different speeds of rotation of the substrate are shown in figure 1. From figure 1, it can be seen that the NiO film obtained at the substrate rotation speed of 1500 rpm /min has a granular structure, the surface roughness is 7,44 nm. As the substrate rotation speed increases, the film surface roughness decreases (figures 1, b and 1, c).



a b c

Fig.1. Images of the surface morphology of NiO films:
a) – NiO – 1500 rpm /min; b) – NiO – 2000 rpm /min; c) – NiO – 2500 rpm /min.

The roughness of the film at the speed of rotation of the substrate 2000 rpm/min is 5.19 nm, and at 2500 rpm is 3.51 nm. Table 1 shows the roughness values of NiO films obtained at different speeds of rotation of the substrate. After that, PEDOT:PSS films were applied to the surface of the NiO films by spincoating. Figure 2 shows images of the surface morphology of PEDOT:PSS films on the NiO surface. The figure shows that the PEDOT:PSS film on the surface of the NiO film obtained at a rotation speed of 1500rpm/min has an inhomogeneous surface structure with a roughness of 5.56 nm.

Table 1- Surface roughnessof NiO films with different rotation speeds

Sample	R_a, nm
NiO – 1500 rpm /min	7.44
NiO – 2000 rpm /min	5.19
NiO – 2500 rpm /min	3.51

As can be seen from the figure, when the surface roughness of the Nickel oxide film decreases, the roughness of the PEDOT:PSS film also decreases (figure 2, b). Further reduction in the roughness of the NiO film also leads to a reduction in the roughness of the PEDOT:PSS film (figure 2, c). PEDOT film roughness PEDOT:PSSon the surface of NiO films are shown in table 2.

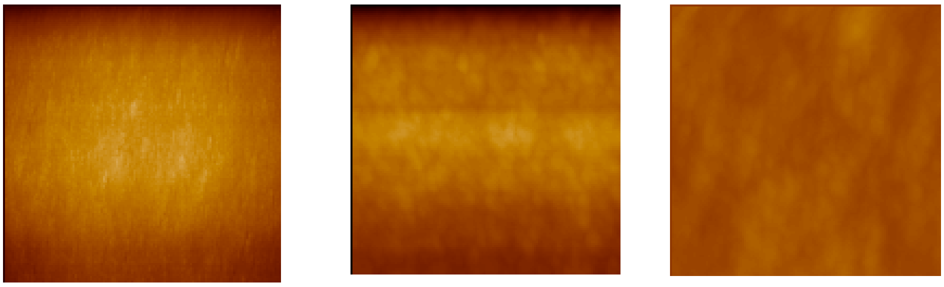

a b c

Fig.2. Images of the surface morphology of NiO/PEDOT:PSS films:
a) – NiO – 1500 rpm/min /PEDOT:PSS; b) – NiO – 2000 rpm/min /PEDOT:PSS;
c) – NiO – 2500 rpm/min / PEbOT:PSS.

Table 2 - The surface roughness of the films, the NiO/PEDOT:PSS

Sample	**R_a, nm**
NiO - 1500 rpm/min / PEDOT:PSS	5.56
NiO – 2000 rpm/min /PEDOT:PSS	4.92
NiO – 2500 rpm/min /PEDOT:PSS	1.15

Figure 3 shows the absorption spectra of NiO films obtained at different speeds of rotation of the substrate: 1500 rpm, 2000 rpm, 2500 rpm.

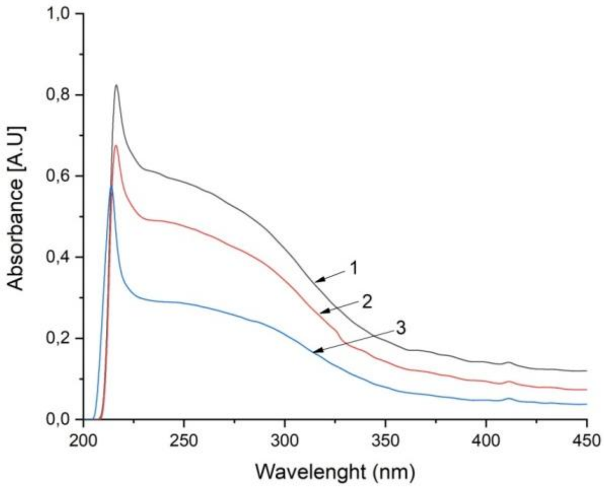


Fig.3. Absorption spectra of NiO films:
1 – NiO – 1500 rpm/min; 2 – NiO – 2000 rpm/min; 3 – NiO – 2500 rpm/min.

The absorption spectrum has two peaks at 216 nm and 237 nm. The figure shows that the optical density of the absorption spectra of NiO films decreases as the substrate rotation speed increases. The positions of the maxima of the absorption spectrum do not change. Table 3 shows the characteristics of the absorption spectra of NiO films. The decrease in the optical density in the absorption spectra with an increase in the rotation speed of the substrates is associated with a decrease in the thickness of the NiO films.

Table 3 - Characteristics of the absorption spectra of NiO films

Sample	D1, (λ =216 nm)	D2, (λ =237 nm)
NiO – 1500 rpm/min	0.82	0.60
NiO –2000 rpm/min	0.67	0.49
NiO –2500 rpm/min	0.56	0.29

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Figure 4 shows the absorption spectra of NiO/PEDOT:PSS composite films. The absorption spectrum of the films has two max at 216 nm and 237 nm.

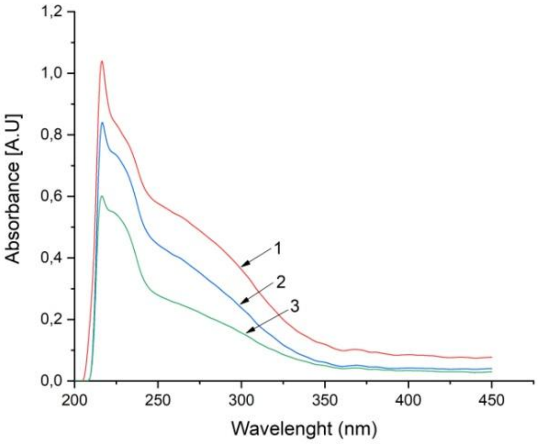

Fig.4. Absorption spectra of films: NiO/PEDOT:PSS:
1 – NiO - 1500 rpm /min/PEDOT:PSS; 2 – NiO – 2000 rpm /min/PEDOT:PSS;
3 – NiO – 2500 rpm /min/PEDOT:PSS.

Due to the small thickness of the PEDOT:PSS film compared to the NiO film, no absorption bands of PEDOT:PSS are observed in the absorption spectrum, except for an increase in the optical density. Reducing the thickness of the NiO film leads to a decrease in the optical density of the absorption spectrum of the composite film. However, it should be noted that the absorption of the composite film remains high compared to the NiO film. The characteristics of the absorption spectra of NiO/PEDOT:PSS composite films areshown in table 4.

Table 4 - Characteristics of the absorption spectra of films NiO/PEDOT: PSS

Sample	D1, (λ =21 nm)	D2, (λ =222 nm)
NiO - 1500 rpm/min / PEDOT:PSS	1.03	0.85
NiO – 2000 rpm/min / PEDOT:PSS	0.83	0.74
NiO – 2500 rpm/min /PEDOT:PSS	0.59	0.55

The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode. For this purpose, an aluminum electrode with a thickness of 200 nm was applied to the surface of the films in a vacuum at a pressure of 10^{-5} Torr on the CY-1700x- spc-2 spray plant (Zhengzhou CY Scientific Instruments Co., Ltd). Fitting of the impedance spectra was performed using the EIS-analyzer software package. The analysis of the impedance measurement results was carried out according to the diffusion-recombination model and the equivalent circuit shown in figure 5 was used for the fitting. The figure shows the following parameters for obtaining a hodograph of semiconductor films: R1 and R2 are the resistances corresponding to R_h and R_{ext}; CPE1 is a constant phase element, which is an equivalent component of an electrical circuit that simulates the behavior of a double layer, but is an imperfect capacitor.

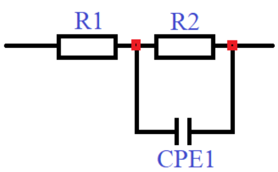

Fig.5. Equivalent electrical circuit

Light impedance spectra of the cells of the structure ITO/PEDOT:PSS/Al and ITO/ NiO/PEDOT:PSS/Al on voltage -500 mV and frequencies from 100 kHz to 0.5 Hz is shown in figure 6. Fitting of impedance spectra was performed using the software package EIS–analyzer, it was calculated the basic charge transport properties of the films (table 5), where: k_{eff} is the effective rate of extraction of charge carriers from PEDOT:PSS or NiO/PEDOT:PSS, τ_{eff} is effective time of flight of charge carriers through PEDOT: PSS or NiO/ PEDOT:PSS, R_h-resistance of the film PEDOT:PSS or NiO/PEDOT:PSS, Rext – resistance of transfer of charge carriers at the border PEDOT:PSS/electrode or NiO/PEDOT:PSS/electrode associated with the extraction of charge carriers with PEDOT:PSS or NiO/PEDOT: PSS.

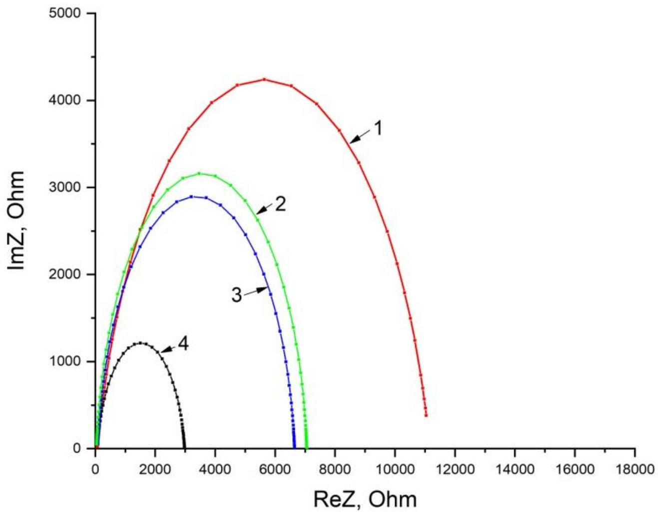

Fig.5. Light impedance spectra of NiO/PEDOT: PSS films with voltage parameters of -500 mV and frequency from 100 kHz to 0.5 Hz: 1 – PEDOT: PSS; 2 – NiO - 1500 rpm /min/ PEDOT:PSS; 3 – NiO – 2000 rpm /min/PEDOT:PSS; 4 – NiO – 2500 rpm /min/PEDOT:PSS.

The values of the electrophysical parameters of the films are shown in table 5. As can be seen from the data in table 5, the thickness of the NiO film significantly affects the resistance of the NiO/PEDOT:PSS (R_{ext}) film and the resistance of charge carrier transfer at the NiO/PEDOT:PSS/electrode interface (R_{ext}). The resistance of the NiO-1500 rpm/min / PEDOT:PSS film has the highest resistance, and the resistance of the NiO-2000 rpm /min/ PEDOT:PSS film is less than the resistance of the PEDOT:PSS film by about 30%. Nio-2500 rpm/PEDOT:PSSfilm resistance shows the best value. A lower film resistance should improve the solar cell fill factor and generally increase photovoltaic performance

The dynamics is observed in the change in the charge carrier transfer resistance at the interface between PEDOT: PSS/electrode and NiO/PEDOT:PSS /electrode (R_{ext}). The R_{ext} resistance value of the PEDOT:PSS film has the highest value. The resistance of the NiO-1500 rpm/min/PEDOT:PSS and NiO-2000rpm/min/PEDOT:PSS films is significantly less than the R_{ext} resistance of the PEDOT:PSS film. The Rext resistance of the NiO film is 2500 rpm/min/PEDOT: PSS shows the lowest value. The R_{ext} value determines the efficiency of charge carrier recovery from PEDOT:PSS and NiO/PEDOT:PSS films, and the lower the R_{ext}value, the greater the efficiency of charge carrier accumulation and photocurrent of the cell. The values k_{eff} and τ_{eff} characterize the efficiency of charge carrier extraction with PEDOT: PSS,NiO/PEDOT:PSS and the effective time of charge carrier flight in PEDOT:PSS, NiO/PEDOT:PSS. As can be seen from table 5, the NiOfilm significantly affects the PEDOT:PSS film, and there is a positive dynamics in the coefficients k_{eff} and τ_{eff}.

Table 5 - Value of the electrophysical parameters of the film PEDOT:PSS and composite films NiO/PEDOT:PSS

Sample	R_h, Ω	R_{ext}, Ω	k_{eff}, s^{-1}	τ_{eff}, ms
PEDOT:PSS	95.5	11097	46.8	21.36
NiO - 1500 rpm/min /PEDOT:PSS	81.41	6571.2	56.37	17.13
NiO – 2000 rpm/min /PEDOT:PSS	44.17	7016	79.83	12.52
NiO – 2500 rpm/min /PEDOT:PSS	35.49	2917.2	118.12	8.46

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The efficiency of charge carrier extraction from NiO – 2500 rpm/min/ PEDOT:PSS films increased approximately twice as compared to the film PEDOT:PSS, and the effective time of charge carrier flight decreased inversely. Holes injected into NiO/PEDOT:PSS diffuse to the electrode, where they recombine with electrons. Fast transport of the injected holes to the external electrode is very important, as this reduces the probability of their reverse recombination.

Conclusion

As a result of research, it was found that the surface roughness of NiO films decreases with increasing substrate rotation speed. It is shown that when the surface roughness of Nickel oxide decreases, the roughness of the PEDOT:PSS film also decreases. It is found that with increasing substrate rotation speed, the optical density of the absorption spectra of NiO films and the absorption of composite NiO/PEDOT:PSS films decreases. It is shown that optimization of the surface structure of NiO//PEDOT:PSS composite films promotes rapid transport of injected holes to the external electrode and reduces the probability of reverse recombination. The results obtained open up the prospect of using NiO//PEDOT:PSS composite films as an HTL Layer of organic solar cells.

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