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THE RESEARCH OF PHOTO-ELECTROPHYSICAL PROPERTIES OF COBALT PHTHALOCYANINE FILM

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The paper presents results of a study of photo-electrophysical characteristics in a solid film and nanowires of cobalt phthalocyanine (CoPc). A solid CoPc film on a substrate with a conductive surface ITO (indium tin oxide) was obtained by thermal evaporation in vacuum. CoPc nanowires were obtained by the temperature gradient physical vapor deposition (TG-PVD). Measurements of current-voltage characteristics were carried out using a potentiostat-galvanostat P20X in the linear sweep mode. The study of transport kinetics and carrier recombination was carried out on the impedance meter P45X. A xenon lamp with radiation intensity equal to 100 mW/cm² was used as a solar light simulator.

Keywords: cobalt phthalocyanine, solid film, nanowires, IVC, impedance spectroscopy

Introduction

Organic molecular semiconductors in the last decade have been an area of intensive research aimed at the development of various elements of organic electronics, such as field effect transistors, light emitting diodes, solar cells and memory cells. This is due to the low cost of these materials, the possibility of applying their films to flexible substrates, obtaining films of large areas, etc. Recently, among the variety of organic semiconductors, phthalocyanine complexes, which represent an extensive class of macro-heterocyclic compounds, have become very attractive. Films based on metallo-phthalocyanines have a higher conductivity than other organic compounds. Their electrical and optical properties can vary widely and depend on a number of factors. The high mobility of charge carriers and the efficiency of light energy conversion make it possible to consider metallo-phthalocyanines as promising materials for photoelectric converters [1-2].

The paper presents the results of a study of the current-voltage characteristics (IVC) of a photosensitive cell based on cobalt phthalocyanine (CoPc). The kinetics of transport and recombination of charge carriers in a solid CoPc film were studied using the impedance spectroscopy method.

1. Experimental technique

The preparation of substrates for photosensitive cells on the basis of ITO was carried out according to the method [3]. A solid film of cobalt phthalocyanine (Sigma Aldrich, 99%) ~ 75 nm thick was deposited on the surface of a substrate coated with ITO by thermal evaporation in a vacuum using a Carl Zeiss Jena HBA 120/2 installation. The deposition was carried out in a vacuum of 10⁻⁵Torr at a rate of 0.5 nm/s. Growth of nanowires on the ITO surface was carried out by the temperature gradient physical vapor deposition (TG-PVD) [4].

Measurements of the current-voltage characteristics of an organic photosensitive cell were carried out using a potentiostat-galvanostat P20X in the linear sweep mode on the installation described in detail in [5]. The kinetics of transport and carrier recombination were studied on a P45X impedance meter (Elins). In both cases, the cell surface was illuminated using a 100 mW/cm² xenon lamp. Photovoltaic cell samples were prepared for photoelectrical measurements. They consisted of several layers: 1-glass substrate; 2-transparent conductive layer ITO (anode); 3-photoactive layer; 4-aluminum electrode (cathode). The choice of aluminum and ITO as contact

layers is due to the fact that this produces the best ohmic contacts with the films and the best value of the electron output.

2. Results and discussions

The surface morphology of nanowires and the film thickness were measured using a JSPM–5400 atomic force microscope. Fig. 1 shows the surface morphology of the obtained samples. The average thickness of the solid film obtained by thermal evaporation was ~ 74 nm. The average height of the grown nanowires consisting of stacks of cobalt phthalocyanine molecules was ~ 137 nm.

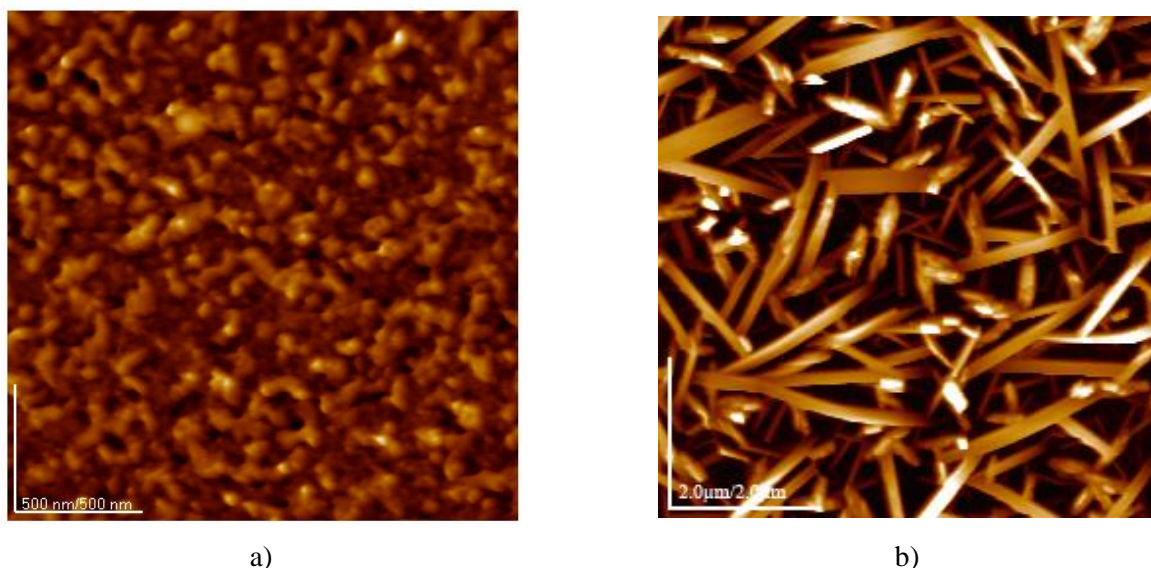


Fig.1. AFM image of the surface of a solid film (a) and CoPc nanowires (b)

The absorption spectra of the studied samples were recorded on a CM2203 spectrophotometer (Solar). Fig. 2 (curve 1) shows the absorption spectra of cobalt phthalocyanine films obtained by thermal evaporation.

In the absorption spectra there are two very intense bands in the region of 350 nm (the Soret band or B-band), which corresponds to the mixed $\pi - \pi^*$ and $n - \pi$ transitions $a_{2u} \rightarrow ^2e_g$ and $b_{2u} \rightarrow ^2e_g$, and the absorption band in the region 550–750 nm (Q-band), which corresponds to the $\pi - \pi^*$ transition $a_{1u} \rightarrow ^2e_g$ [11]. The absorption spectrum of CoPc film obtained by thermal evaporation (fig.2) in the Soret region has a maximum at $\lambda=320$ nm and in the Q-band there are two bands with maxima at $\lambda=616$ nm and $\lambda=678$ nm. The characteristic splitting of the absorption of nanostructures in the Q-band into two peaks is associated with the Davydov splitting [6].

In the spectrum of CoPc nanowires (Fig. 2, curve 2) the absorption band is broadened in the Soret region. The absorption band in the Q-band is also broadened, in addition, there is a bathochromic shift of the maxima in this spectral region in comparison with the film obtained by the method of thermal evaporation.

Table 1. Spectral characteristics of cobalt phthalocyanine

Sample	B-band			Q-band		
	Adsorption peak, nm	D	FWHM, nm	Adsorption peak, nm	D	FWHM, nm
Evaporated	$\lambda=315$	0.51	80	$\lambda=616, \lambda=678$	0.44	150
Nanowires	$\lambda=324$	0.85	125	$\lambda=612, \lambda=700$	0.48	225

The current-voltage characteristic of a CoPc-based photosensitive cell was determined by illuminating the sample from the ITO side with a xenon lamp in the wavelength range of 350-800 nm and a power of 100 mW/cm^2 . Fig. 3 shows the IV characteristics of the samples obtained. It can be seen from Fig. 3 that the IVCs are non-linear. The values of open-circuit voltage U_{oc} , short-circuit current J_{sc} , maximum voltage and maximum current density U_{max} and J_{max} , and fill factor FF were determined according to the method [7].

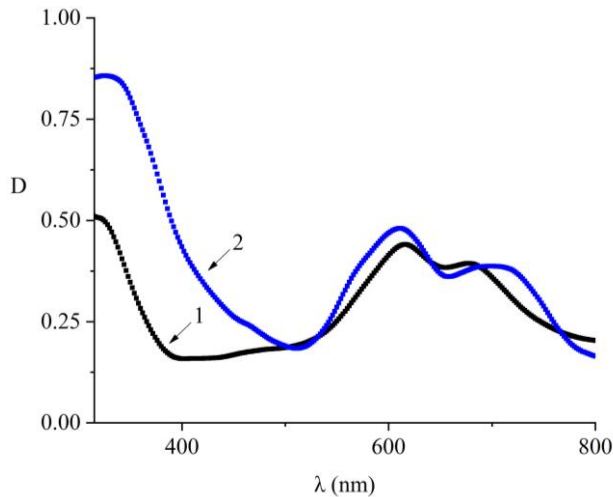


Fig.2. Absorption spectrum of CoPc:
1 – CoPc film obtained by thermal evaporation;
2 – CoPc nanowires.

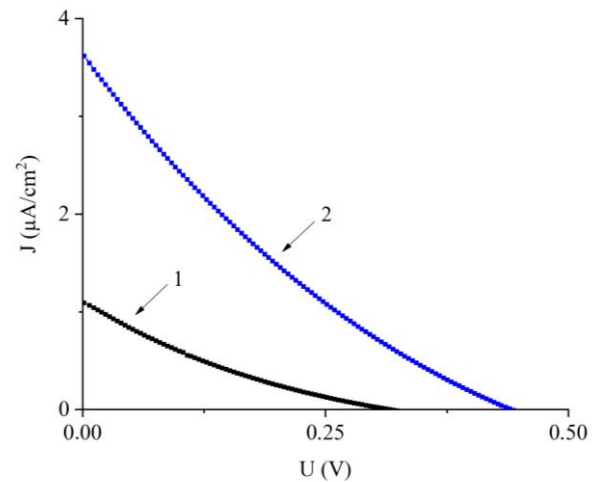


Fig.3. Comparison of current-voltage characteristics: 1 – IVC of CoPc film obtained by thermal evaporation; 2 – IVC of CoPc nanowires.

Thus, it can be concluded that the photosensitive cell based on cobalt phthalocyanine has lower values of voltage and current density compared to the photocell based on copper phthalocyanine, investigated by the authors in the paper [8]. Table 2 shows the parameters of the photoelectric characteristics of cobalt phthalocyanine nanostructures.

Table 2. Photoelectric characteristics of cobalt phthalocyanine nanostructures

Sample	U_{oc} (V)	J_{sc} ($\mu\text{A/cm}^2$)	U_{max} (V)	J_{max} ($\mu\text{A/cm}^2$)	FF
Evaporated	0.31	1.07	0.13	0.43	0.17
Nanowires	0.44	3.63	0.19	1.58	0.19

The efficiency of generation of charge carriers in a CoPc solid film obtained by thermal evaporation is low compared to nanowires. This fact is due to weak broadening of the absorption band, in contrast to nanowires. This is evidenced by the low value of the short-circuit current of the current-voltage characteristic of the cell (Figure 3, curve 1). In nanowires, CoPc molecules line up in a lamellar structure. As a result, the interaction of molecules in the unit cell increases. In this case, the broadening of the absorption bands in the Q and B ranges is more pronounced in comparison with the film obtained by thermal evaporation. Thus, this leads to an increase in the number of charge carriers in the cell (Fig. 3, curve 2).

Investigation of the mechanisms of transport and recombination of charge carriers of a cobalt phthalocyanine solid film was carried out by impedance spectroscopy. To interpret the impedance spectra, we used the equivalent circuitry of the photovoltaic cell (Fig. 4), where R1 (R_w) is the equivalent resistance of the multilayer film ($R_{ITO} + R_{Al}$ + resistance of the photoactive layer), R2 (R_{rec}) is the resistance characterizing the recombination of localized electrons with holes. CPE1 is an

element with a constant phase, which is an equivalent component of an electric circuit, modulating the behavior of the active layer, but being an imperfect capacitor.

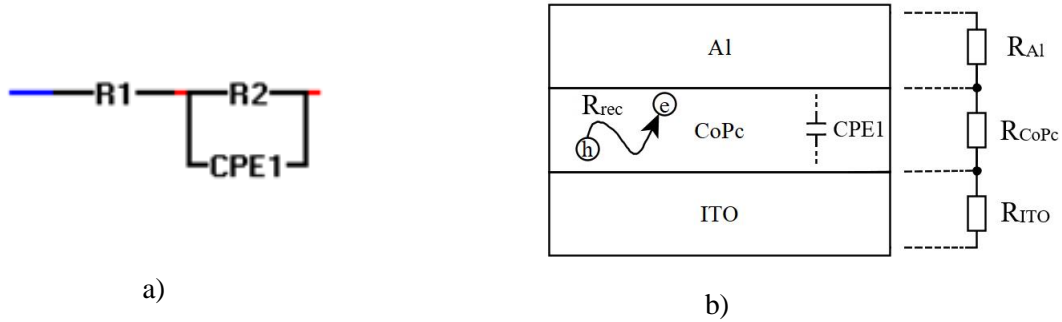


Fig.4. An equivalent electrical circuit (a) and a schematic representation (b) of the photosensitive cell.

The impedance spectra in the Nyquist coordinates based on CoPc films are presented in Fig. 5. The spectra were fitted using the EIS-analyzer software package. The main electric transport properties of solar cells were calculated (Table 3), where k_{eff} is the effective recombination rate of charge carriers, and τ_{eff} is the effective electron lifetime. The analysis of impedance measurements was carried out according to the diffusion-recombination model [9].

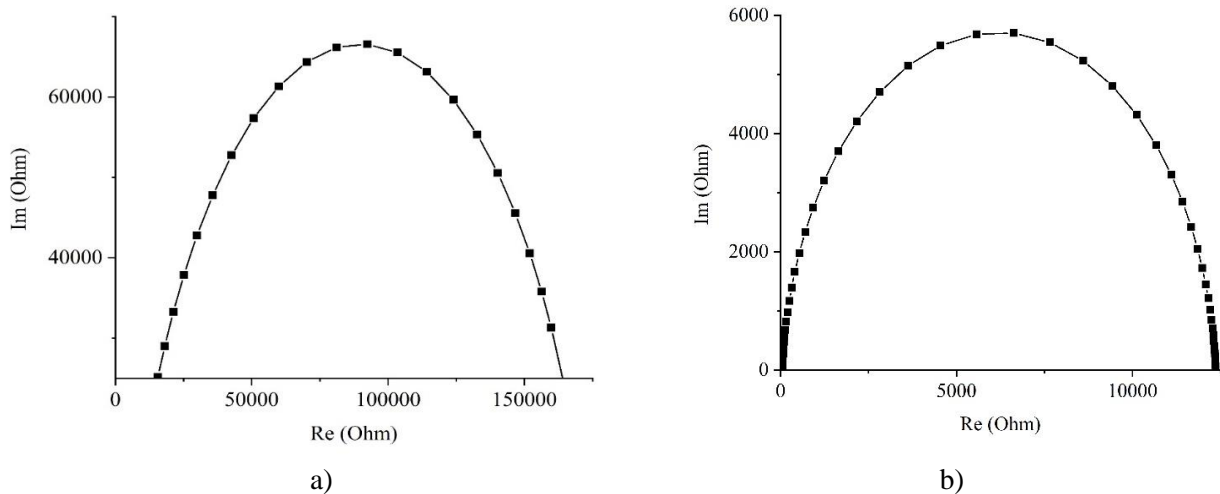


Fig. 5. Impedance spectra of CoPc solid film (a) and CoPc nanowires (b)

An analysis of the impedance spectra shows that the addition of CoPc nanowires improves the conductivity of the film, which is determined by the value of R_w . Table 3 shows that, in nanowires, the effective mean free path of charge carriers (D_{eff}) is higher than the film obtained by thermal evaporation.

Table 3. Electric transport properties of CoPc cells

Sample	D_{eff} , (cm^2s^{-1})	k_{eff} , (s^{-1})	τ_{eff} , (ms)	R_k , (Ohm)	R_w , (Ohm)	C_{on} , (Ohm cms^{-1})	L ,(cm)
CoPc Evaporated	4.08×10^{-8}	22.3	44.8	1.7×10^5	5093.4	28.1	7.4×10^{-6}
CoPc Nanowires	1.38×10^{-5}	277.8	3.6	12321	46.53	46.9	13.7×10^{-6}

Using the EIS – analyzer software package, R_{rec} and R_w are calculated; k_{eff} value is determined by the maximum of the hodograph arc according to the formula $\omega_{max} = k_{eff}$. The value of the effective lifetime of charge carriers τ_{eff} in the films is calculated by the formula $\tau_{eff} = \frac{1}{k_{eff}}$.

The observed effect is associated with an increase in the structuring of molecules in the film, because CoPc nanowires form a lamellar structure. A lower R_w value in cells with CoPc nanowires also suggests that nanowires contribute to better carrier transfer to the electrode. Also, the effective carrier lifetime in nanowires (τ_{eff}) is shorter. The parameter τ_{eff} determined by the method of impedance spectroscopy takes into account the time spent by charge carriers in traps. A lower value of τ_{eff} indicates a lower density of localized states in nanowires.

Conclusion

Researches have shown that in the cell based on CoPc nanowires, broadening of the B and Q bands and a shift of the maxima in the spectra are observed. The structuring of CoPc molecules with the formation of nanowires affects the value of the short-circuit current of the cell. Using the method of impedance spectroscopy, it was found that transport properties are improved in nanowires.

Acknowledgements

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