UDC 537.632

THE INFLUENCE OF THE MAGNETIC FIELD ON THE CURRENT-VOLTAGE CHARACTERISTICS OF CUPC NANOSTRUCTURES

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The paper presents the results of a study of the role of spin states in the process of charge carrier transfer in copper phthalocyanine (CuPc) nanostructures. It is shown that the film obtained by thermal evaporation has the structure of the α-phase, the CuPc nanowires are in the η-phase. The effect of an external magnetic field on the current-voltage characteristics (IVC) of CuPc nanostructures was studied. It is shown that a decrease in the value of the short-circuit current when an external magnetic field is applied, which is associated with the mechanism of spin polarization in the formation of a bipolaron. It is shown that the effect of "spin blocking" in nanowires is stronger.

Keywords: *copper phthalocyanine, nanowires, IVC, charge carrier mobility, magnetic field, spin state.*

Introduction

The possibility of using individual molecules and molecular ensembles as active elements of electronics attracts the attention of researchers in various fields of science [1]. The definition of the boundaries of potential and the approach to these boundaries of modern semiconductor technologies is heightened interest in building basic elements of molecular electronics. Further prospects for the development of electronics are associated with the creation of devices using quantum phenomena, in which the count goes on units of photons and electrons. Recently, theoretical and experimental studies of artificially created low-dimensional structures have been widely conducted [2]. At the same time, an active search is underway for materials and mechanisms for spintronics, a field of science that considers the possibilities of controlling information transfer processes using a magnetic field [3].

The high mobility of charge carriers and the efficiency of light energy conversion make it possible to consider metal phthalocyanines as promising materials for photovoltaic cells [4–5]. One of the effective ways to increase the optical sensitivity range and improve the photoelectric characteristics is the formation of nanocomposite structures of metal phthalocyanine complexes. The conductive and magnetic properties of phthalocyanines are of great interest.

This paper presents the results of a study of the influence of a magnetic field on the current-voltage characteristics of a solid CuPc film and CuPc nanowires.

1. Experimental technique

Preparation of substrates for a photosensitive cell was carried out as follows: glass conductive plates (ITO, size 20x20mm, R_{ITO} = 60 Ω/cm) were placed in an ultrasonic bath and washed for 10 minutes in acetone, in isopropyl alcohol and in deionized water, then dried in drying cabinet for 20 minutes and then subjected to UV treatment for 30 minutes.

A solid film of copper phthalocyanine (Sigma Aldrich, 99%) ~ 140 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^{-5} Torr at a rate of 0.5 nm/s.

CuPc nanowires on the surface of a substrate with a conductive ITO coating were obtained using temperature gradient physical vapor deposition (TG-PVD) (fig.1). The substrates were

installed inside a quartz tube in the growth zone. The temperature in the reaction zone was 465°C. The temperature control of the working zone was carried out using the PID controller. The high-purity argon flow rate in the reaction zone was ~150 standard-state cubic centimeter per minute (sccm). The deposition time of nanowires was 6 hours.

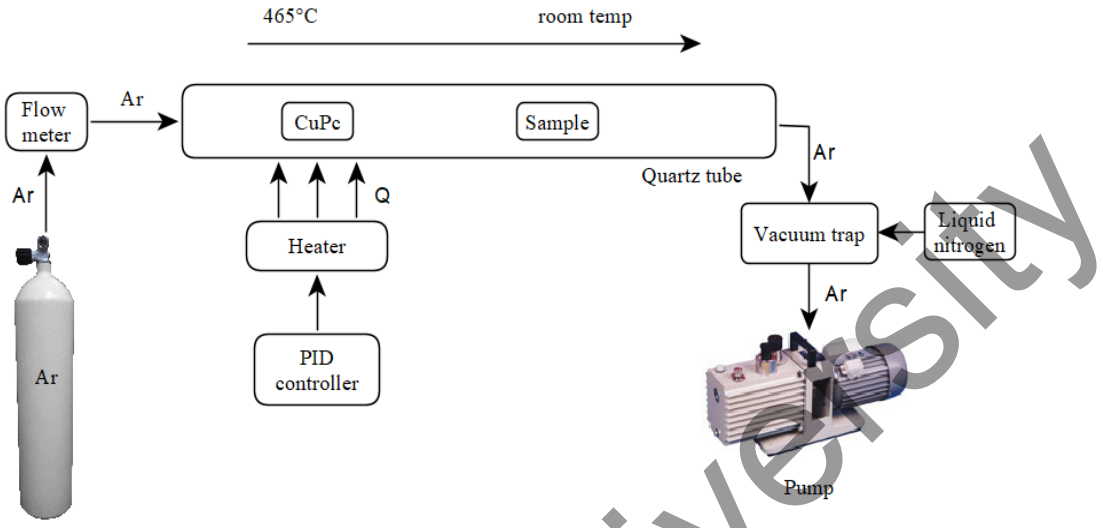

Fig.1. The diagram of the experimental installation TG-PVD

An aluminum electrode with a thickness of ~ 150 nm was deposited on the surface of an organic film by thermal evaporation in a vacuum of 10^{-5} Torr at a rate of 1 nm/s. The choice of ITO as an electrode is due to the fact that this produces the best ohmic contacts with the films and the best values of the electron work function (Figure 2). Aluminum is used as a cathode, since the electron work function for it is – 4.2 eV, which is in good agreement with the LUMO energy for CuPc equal to – 3.5 eV.

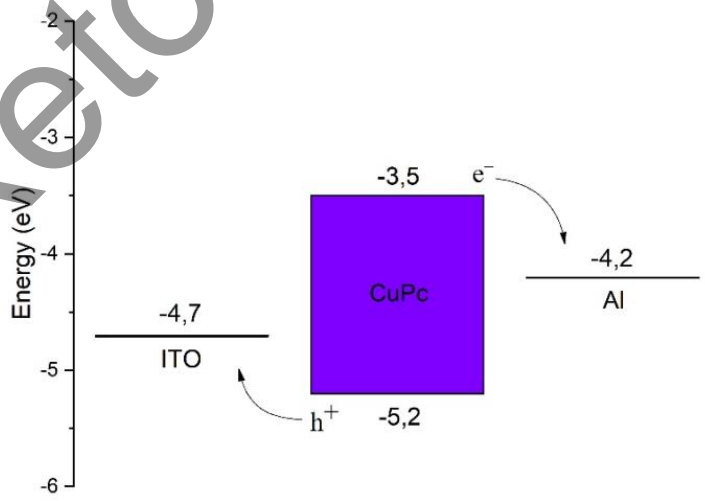

Fig.2. Energy level diagram

The surface morphology of nanostructures (figure 3) was measured using an MIRA 3 LMU electron microscope. The average thickness of the solid film obtained by thermal evaporation was ~ 140 nm.

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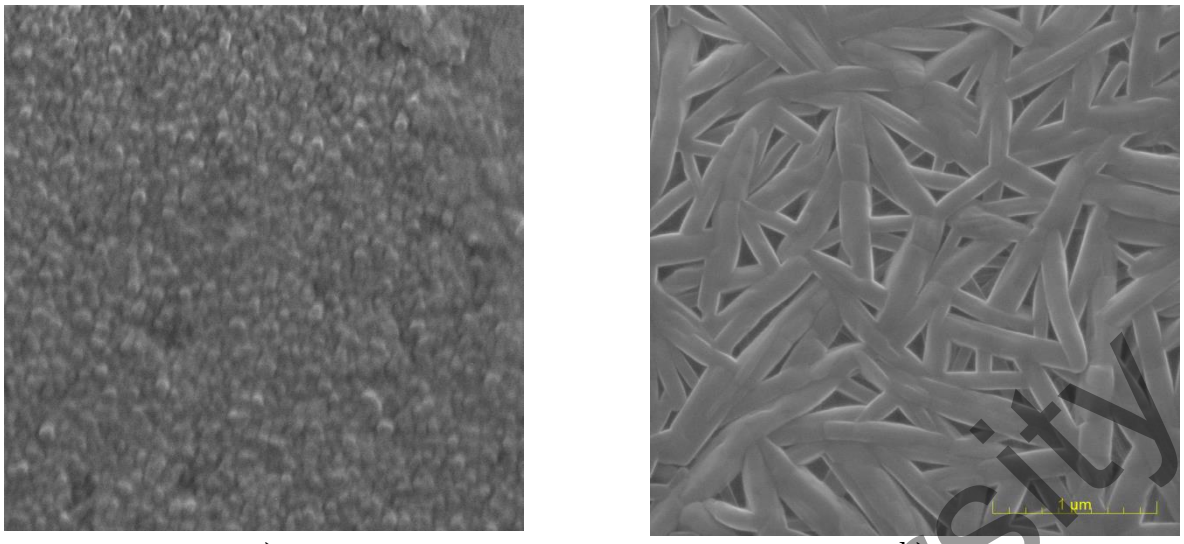

a) b)

Fig.3. SEM images of the obtained samples:
a) solid CuPc film; b) CuPc nanowires.

The average grain size on the surface of a solid film was ~ 57 nm. The average height of the grown nanowires consisting of stacks of copper phthalocyanine molecules was ~ 137 nm, with an average diameter of ~ 4.5 nm.

2. Results and discussion

The absorption spectrum of copper phthalocyanine was measured on a CM2203 spectrofluorometer (Figure 4). Figure 4 (curve 3) shows the absorption spectrum of CuPc in an alcohol solution. The data obtained show that the absorption spectrum of CuPc has 4 maxima. The first absorption maximum is observed in the ultraviolet region with a wavelength equal to λ = 324 nm. It is known [6] that copper phthalocynine molecules can be in one of three crystalline phases: η-CuPc, α-CuPc, β-CuPc. In accordance with this, the observed band with a maximum at 324 nm can be attributed to the Soret band or the B-band. In the B-range, a large absorption peak is observed, which indicates that CuPc has the structure of the metastable α-phase, since during thermal annealing, a sharp decrease in absorption is observed in this range [7]. Also, at wavelengths λ = 604 nm and λ = 692 nm, there are second and third absorption maxima in the visible region of the spectrum (Q-band). This spectrum coincides with the studies of the authors [8]. The characteristic splitting of the Q-range into two absorption peaks is a consequence of the crystalline form of phthalocyanine and is called Davydov splitting [9].

The absorption spectrum of a solid film obtained by thermal evaporation (Figure 4, curve 1) has a shift in the long-wavelength region by 2 nm in the Soret region and 14 nm in the Q-band. An increase in the absorption intensity by 1.75 times is also observed. The CuPc molecules in the solid film are in the α-phase.

Figure 4 (curve 2) shows the absorption spectrum of nanowires. As can be seen from the figure, the spectrum has 4 maxima. The maxima in the Q-range at 622 nm and 764 nm indicate that copper phthalocynine molecules are in the η-phase. The CuPc nanowires in the B-range are characterized by the presence of a wide absorption band up to 540 nm, which is associated with the ordering of the CuPc molecules in the nanowires.

Based on the above data, it can be concluded that the absorption spectrum of copper phthalocyanine nanowires in the region of 400-500 nm is wider compared to the absorption spectrum of CuPc molecules in alcohol and the film obtained by thermal evaporation.

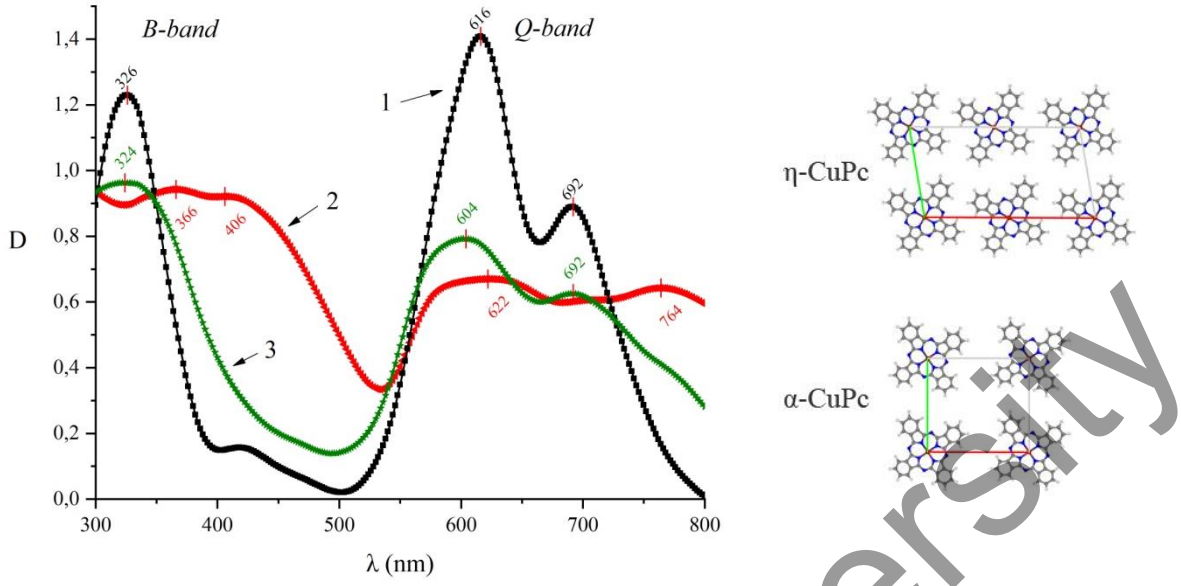

Fig.4. Absorption spectrum of CuPc:
1 – CuPc film obtained by vacuum thermal evaporation; 2 – CuPc nanowires; 3 – CuPc in ethanol

After that, samples of photovoltaic cells were prepared, consisting of several layers: 1 – glass substrate; 2 – a transparent conductive layer of ITO (indium tin oxide), which serves as the anode; 3 – a layer of copper phthalocyanine organic molecules; 4 – aluminum electrode serving as a cathode (Figure 5).

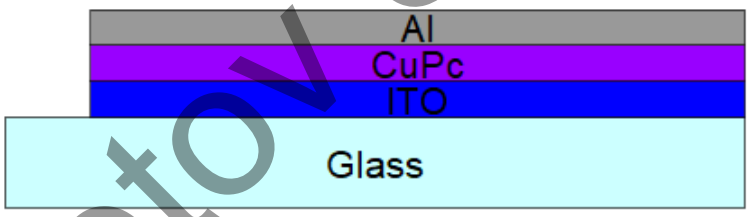

Fig.5. Photovoltaic cell structure

3. The influence of the magnetic field

Measurements of the influence of the magnetic field on the IVC of an organic photosensitive cell were carried out using a P20X potentiostat-galvanostat in the linear sweep mode. The setup diagram is shown in Figure 6. A sample is placed between the poles of a permanent electromagnet. The cell surface was illuminated using a xenon lamp with a power of 100 mW/cm^2. The IVC of the photosensitive cell was determined by illuminating the sample from the ITO side with a xenon lamp in the wavelength range of 350–750 nm and a power of 100 mW/cm^2 (Figure 6).

Figure 7 shows the IV characteristics of the samples obtained. From figure 6 it is clear that the IVCs are non-linear. The values of idling U_{oc}, short circuit current I_{sc}, filling factor FF and efficiency were determined according to the method [10].

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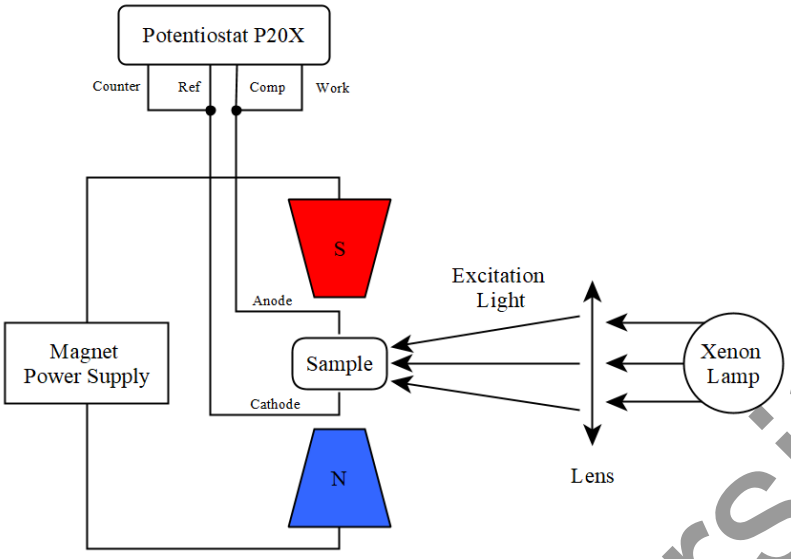


Fig.6. Diagram of the experimental setup for measuring the IVC in an external magnetic field.

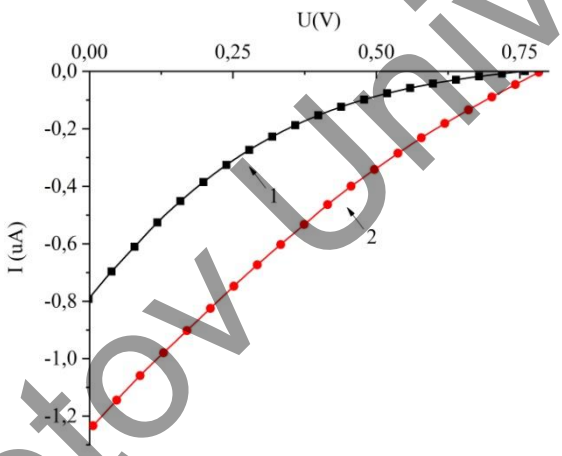
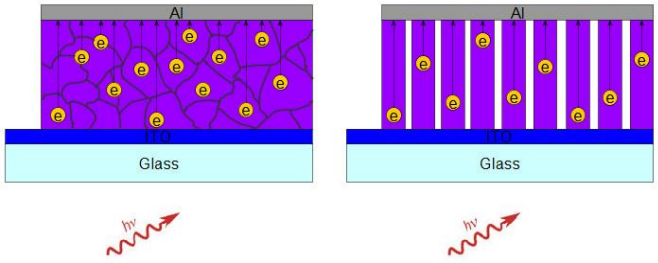


Fig.7. Comparison of current-voltage characteristics:
1 - IVC of CuPc film obtained by the method of vacuum thermal evaporation;
2 - IVC CuPc nanowires.

Figure 8 shows the flow patterns of charge carriers in a solid CuPc film obtained by thermal evaporation in vacuum (a) and in CuPc nanowires (b). The solid film obtained by thermal evaporation (Figure 8, a) is amorphous and does not have a clear structure. The presence of an amorphous film structure increases the probability of charge carrier recombination, preventing their movement in the film. This is indicated by the low value of the filling factor and short-circuit current of the IVC cell (Figure 7, curve 1). In nanowires, CuPc molecules have a lamella structure (Figure 8, b). According to [11], the main charge carriers in metal phthalocyanines are positively charged polarons (holes). Due to the imperfection of the film structure, local electronic states are present on the surface of nanowires – electron and hole traps. This is indicated by the observed wide absorption spectrum of nanowires. The traps can capture two polarons, as a result of which a bipolaron will be formed, which subsequently moves along the nanowires, carrying out charge transfer. As the structure becomes more defective, the number of bipolarons will increase, thus increasing the cell current (Figure 7, curve 2).



a) b)

Fig.8. Cell Structure:
a) - CuPc film obtained by vacuum thermal evaporation; b) - CuPc nanowires

The charge carrier mobility of copper phthalocyanine structures was determined according to the procedure [12]. The calculation of the charge carrier mobility was carried out as follows:

$$\mu = \frac{d^2}{V \cdot t_{tr}}, \quad (1)$$

where μ – charge carrier mobility, *d*– film thickness, *V*– applied voltage, t_{tr}– transient time.

Transient time is calculated by the formula 4, where τ_{peak} is the time of rise of the peak current from the moment the voltage is applied.

$$\tau_{peak} = 0.786 \cdot t_{tr}, \quad (2)$$

Table 1 shows the parameters of the photoelectric characteristics of copper phthalocyanine nanostructures.

Table 1. Photoelectric characteristics of copper phthalocyanine nanostructures

Sample	U_{oc}(V)	I_{sc} (μA)	U_{max} (V)	I_{max} (μA)	FF	η (%)	μ (cm^2/Vs)
Evaporated	0.75	0.79	0.27	0.28	0.13	7.7E-11	2.6E-3
Nanowires	0.78	1.25	0.35	0.57	0.2	1.95E-10	2.85E-3

To study the effect of a magnetic field on the parameters of the current – voltage characteristics, the samples were placed between the poles of an electromagnet. The effect of the magnetic field (MFE) was determined by changing the value of the short-circuit current of an organic cell when the magnitude of the magnetic field changes from 0 to 0.6 T. MFE was calculated according to [13]:

$$MFE = \frac{I_B - I_0}{I_0} \cdot 100\%, \quad (3)$$

where I_B – short-circuit current in a magnetic field; I_0 – short-circuit current without exposure to a magnetic field.

Figure 9 shows the dependence of the effect of the magnetic field of a cell on the induction value of an external magnetic field. It can be seen from the figure that at the maximum value of the field induction, the short-circuit current of the photosensitive cell based on CuPc nanowires decreases by 61%.

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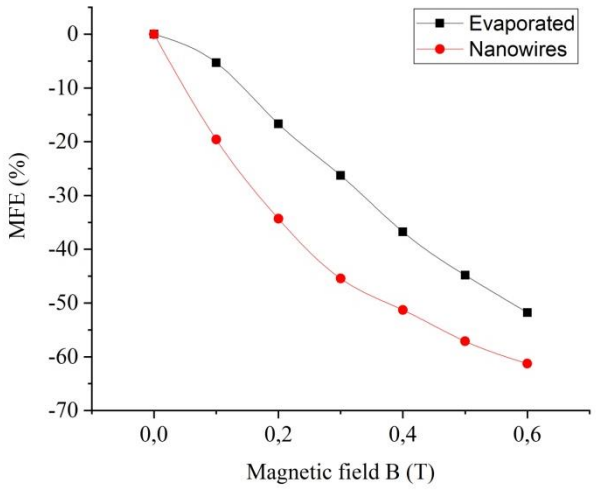

Fig.9. Magnetic Field Effect (MFE)

An external magnetic field affects the spin state of polarons. In the absence of an external magnetic field, two polarons with different spin components can be trapped by a trap, resulting in the formation of a bipolaron - a temporary intermediate quasistationary state (Figure 10, a).

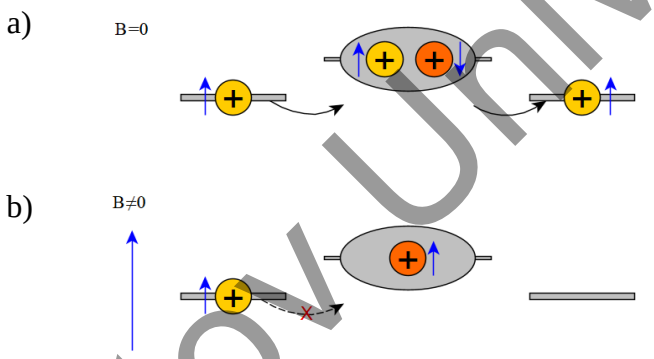

Fig.10. Schematic representation of the formation of a bipolaron at B = 0 on the trap of capture (a) and "spin blocking" at B≠0 (b)

After the collapse of the bipolaron, the hole is able to jump onto the adjacent trap, forming a new bipolaron. Thus, as a result of jumping to nearby defects with the formation of bipolarons, a charge transfer process occurs in the system under study. Due to the hyperfine interaction, the singlet and triplet states of polarons can be mixed [14]. When applying an external magnetic field, the spins of two positively charged polarons are oriented in the same direction (Figure 10, b). The channel of formation of the bipolaron is blocked. This mechanism is called "spin blocking" [15]. As a result, a decrease in the short-circuit current of the photosensitive cell is observed.

The probability of the formation of a bipolaron depends on the rate constant for the repetition of previously uninteracting polarons. In turn, the rate constant of repulsion depends on the dimension of the system in which the reagents are located. With a decrease in the dimension of the system, the rate constant of repulsion increases, which leads to an increase in the probability of the formation of bipolarons. It is obvious that the probability of polaron repulsion in nanowires is higher compared with the film obtained by thermal evaporation. Modulation by an external magnetic field reduces the likelihood of bipolaron formation. Consequently, in nanowires, due to the high probability of polaron repulsion, the effect of "spin blocking" is more pronounced when modulated by an external magnetic field.

Conclusion

Thus, studies have shown that a solid film obtained by thermal evaporation has the structure of the α-phase; CuPc nanowires are in the η-phase. It is shown that the defect structure of the film has a significant effect on the value of the short circuit current of the cell. The effect of a magnetic field on the short-circuit current of the IVC CuPc is investigated. A decrease in the value of the short circuit current is observed when an external magnetic field is applied, which is associated with the mechanism of "spin blocking" in the process of formation of a bipolaron. It has been established that in nanowires, due to the high probability of polaron repetition, the effect of “spin blocking” is more pronounced.

Acknowledgment

This work was supported by the grant of the academician E.A. Buketov Karaganda State University

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Article accepted for publication 15.05.2019