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Study of the effect of an external magnetic field on the photoelectric properties of a copper phthalocyanine film

In the article the results of a study of the influence of a magnetic field on the change in current-voltage characteristics and charge carrier mobility in a solid film of copper phthalocyanine (CuPc) are presented. A solid CuPc film on a substrate with a conductive ITO surface (Indium Tin Oxide) was obtained by thermal evaporation in a vacuum. The absorption spectrum of CuPc was measured; as a result, copper phthalocyanine molecules on the substrate surface were found to be in the metastable α-phase. Measurements of current-voltage characteristics (IVC) were carried out using a potentiostat-galvanostat P20X in the linear sweep mode. To study the effect of a magnetic field on the photoelectric characteristics, a sample was placed between the poles of an electromagnet. A xenon lamp with radiation intensity of 50 mW/cm^2 was used as a simulator of sunlight. As a result of experiments, it was found that the external magnetic field affects the value of the short-circuit current, at the same time, the charge carrier mobility in a magnetic field does not change. The studied effect of a change in the current-voltage characteristics in a solid CuPc film upon application of an external magnetic field can be used as a high-speed magnetic field sensor.

Keywords: copper phthalocyanine film, IVC, magnetic field, charge carrier mobility.

Currently, semiconductor silicon solar cells are leaders in the field of converting light energy into electrical energy (a record makes ~ 46 %). However, the complexity of the technology, the high cost of production, the requirement for the purity of the materials used and the fragility limit their widespread distribution [1].

An alternative replacement for silicon solar cells is organic polymer batteries. These devices have several advantages, such as the simplicity of the used technology, the low cost of materials, the possibility of obtaining a large area with flexibility [2]. In this regard, the actual task is the study and application of semiconductor organic photovoltaic devices.

To clarify the mechanism of formation of charge carriers and other processes involving excited singlet and triplet states in organic solids, along with traditional optical and electrical methods, new methods have been widely used based on the influence of an external magnetic field on specific stages of non-equilibrium electronic processes and related to reactivity paramagnetic particles. Changes in the speed of these stages are detected by changes in photoconductivity, fluorescence intensity, optical density, etc. With the help of these effects, the specificity of the influence of the magnetic field allows to judge the mechanism of the processes and the presence of magnetically sensitive stages.

The aim of the work is to study the effect of an external magnetic field on the processes of generation and separation of charges in a solid film of copper phthalocyanine. The tasks are to measure the influence of an external magnetic field on the current-voltage characteristics of a solid CuPc film; on the basis of existing measurement methods, calculate the charge carrier mobility in a thin-film solar cell.

The high charge carrier mobility [3] and high photovoltaic parameters allow us to consider metal phthalocyanines as promising materials for photovoltaic devices [4, 5]. The structural formula of the compound based on copper phthalocyanine is shown in Figure 1.

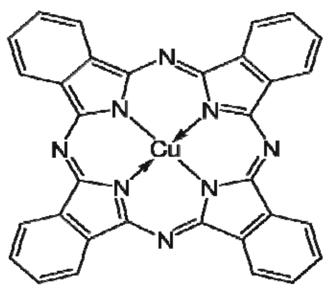


Figure 1. The structural formula of copper phthalocyanine

Thermal evaporation is the most rational way of applying phthalocyanines to the surface, because most of them are able to sublimate. These compounds are susceptible to sublimation in vacuum at temperatures up to 573 K [6].

A solid film of organic CuPc molecules was deposited on the surface by thermal evaporation in a vacuum (10^{-5}Torr) using a Carl Zeiss Jena HBA 120/2 appliance.

The thickness of the precipitated layer was calculated by the Formula 1.

$$T = \frac{M \sin\theta}{4\pi\rho R^2}, \tag{1}$$

where M is the mass of the material to be evaporated; T is the thickness of the deposited layer; θ is the angle of inclination of the substrate to the evaporator; *ρis* is the density of the material to be evaporated; R is the distance from the evaporator to the substrate.

With the help of thermal vacuum evaporation, a solid film of copper phthalocyanine with a thickness of ~ 140 nm (Fig. 2) was sprayed onto the surface of an ITO (Indium Tin Oxide) coated substrate. Further, an electrode of aluminium with a thickness of ~ 150 nm was deposited on the surface of the deposited layer of organic molecules of CuPc. The layer thickness was measured using a Hitachi S-4800 scanning electron microscope (Tomsk city).

Before thermal evaporation the surface of glass substrates with a transparent conductive ITO coating (resistance R_{ITO} = 60 Ω/cm) must be thoroughly cleaned. In the process of cleaning, the samples were vertically placed in an ultrasonic bath and washed for 10 minutes in acetone, in isopropyl alcohol and in dionized water, and then dried in a drying cabinet for 20 minutes. At the end, in order to remove organic residues from the surface and increase wettability, they were subjected to UV-ozone treatment for 1 hour.

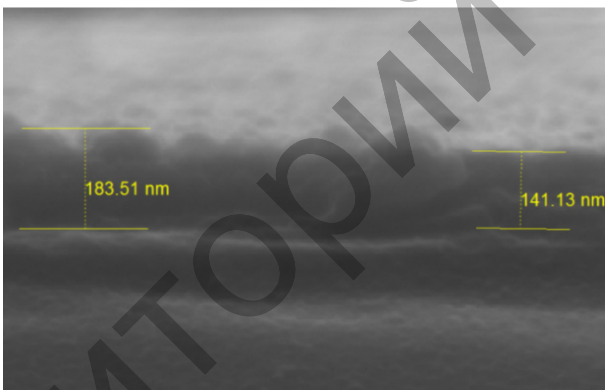


Figure 2. SEM image of the cleaved quartz substrate with a solid CuPc film

The absorption spectrum of copper phthalocyanine was measured using a CM2203 spectrofluorometer (Fig. 3). As can be seen in Figure 3, the absorption spectrum has 3 maxima. The first absorption maximum is observed in the ultraviolet region with a wavelength of λ=335 nm and an optical density of 0.59. This area is called the B-range. 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 of λ=615 nm and λ=695 nm, there are second and third absorption maxima in the visible region of the spectrum (Q-band). The optical density is 0.63 and 0.56, respectively. This spectrum coincides with the studies of the authors [8]. The characteristic splitting of the Q-band into two absorption peaks is a consequence of the crystalline form of phthalocyanine and is called Davidov splitting [9].

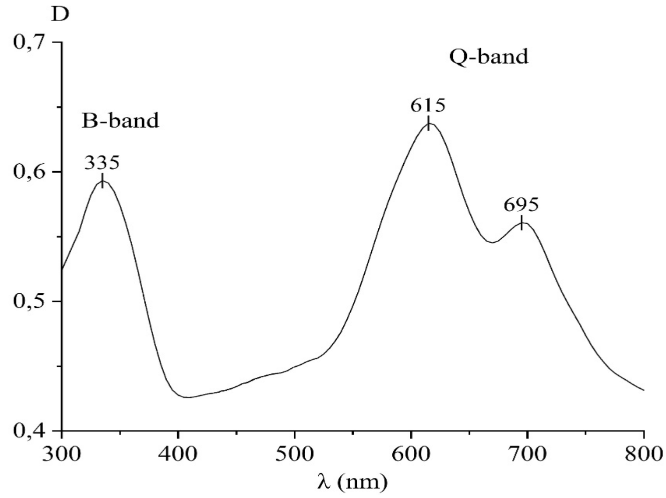


Figure 3. Absorption spectrum of Cu-phthalocyanine film on quartz substrate

Figure 4 (a) shows a diagram of the energy levels of a sample of a photovoltaic cell with a layered structure ITO/CuPc/Al. From Figure 4 (b) it follows that the sample consists 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.

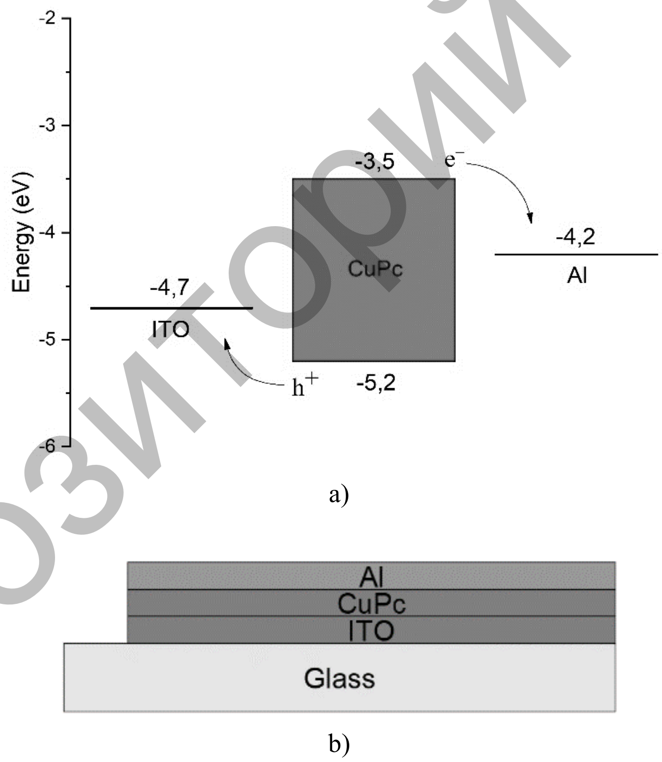


Figure 4. Diagram of energy levels (a) and cell structure (b)

Measurements of current-voltage characteristics (IVC) were carried out using a potentiostat-galvanostat P20X in the linear sweep mode. A xenon lamp with a study intensity of 50 mW/cm^2 was used as a simulator of sunlight. The installation diagram is shown in Figure 5.

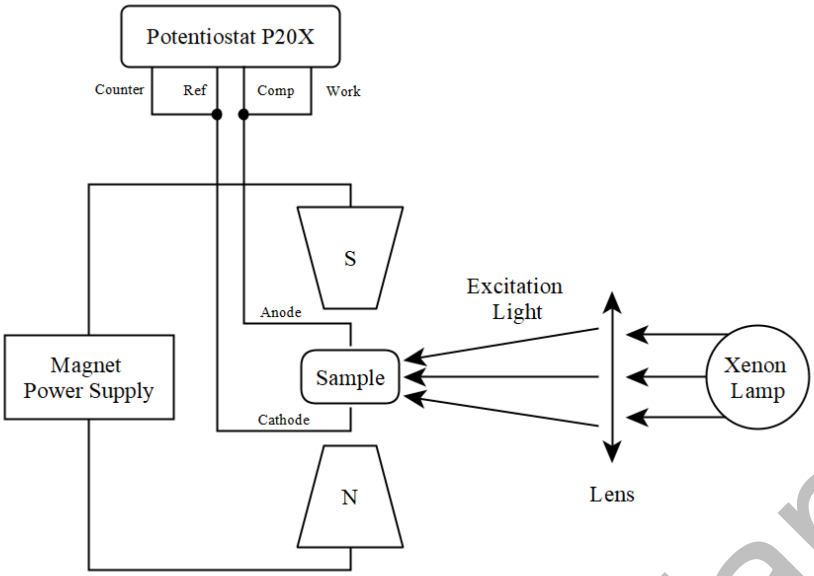
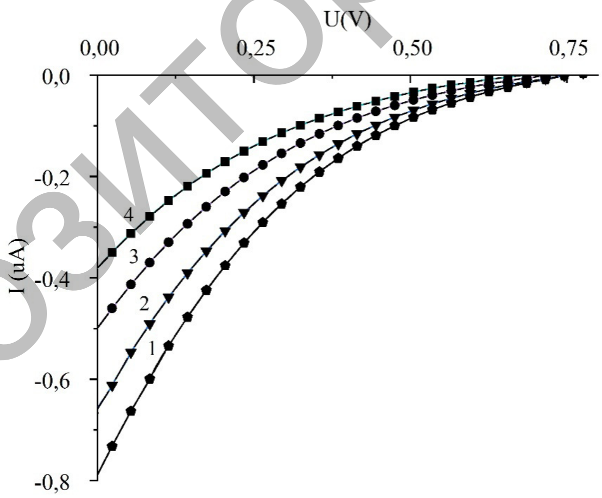


Figure 5. Diagram of the experimental installation for measuring the IVC in an external magnetic field

The maximum open circuit voltage of the organic cell was 0.75 V at a short-circuit current density of 2.020 μA/cm^2. Based on the dependence of the current on voltage, the current density, the filling factor (FF) and the efficiency of conversion of solar energy into electrical energy were calculated according to the method described in [10].

Figure 6 demonstrates the effect of a magnetic field. Curve 1 corresponds to the current-voltage characteristic of a CuPc-based photovoltaic cell without an external magnetic field. When solar cells are placed in a magnetic field, the short-circuit current is more than halved, which indicates a negative effect of the magnetic field on the current-voltage characteristic (curves 2–4).



1 — 0T; *2* — 0,2T; *3* — 0,4T; *4* — 0,6T

Figure 6. The influence of the magnetic field on the current-voltage characteristics

Table shows the calculations of the characteristics of a photovoltaic cell with the ITO/CuPc/Al structure when the magnetic field varies from 0 to 0.6T.

Table

Photovoltaic cell characteristics

B (T)	U_{max} (V)	U_{oc} (V)	J_{max} (μA /cm^2)	J_{sc} (μA/cm^2)	FF	η (%)
0	0,269	0,75	0,725	2,020	0,128	3,878E-06
0,1	0,29	0,764	0,628	1,910	0,124	3,619E-06
0,2	0,287	0,755	0,546	1,682	0,123	3,124E-06
0,3	0,287	0,740	0,482	1,479	0,126	2,758E-06
0,4	0,26	0,723	0,458	1,276	0,129	2,38E-06
0,5	0,255	0,704	0,402	1,117	0,130	2,045E-06
0,6	0,25	0,683	0,356	0,976	0,133	1,773E-06

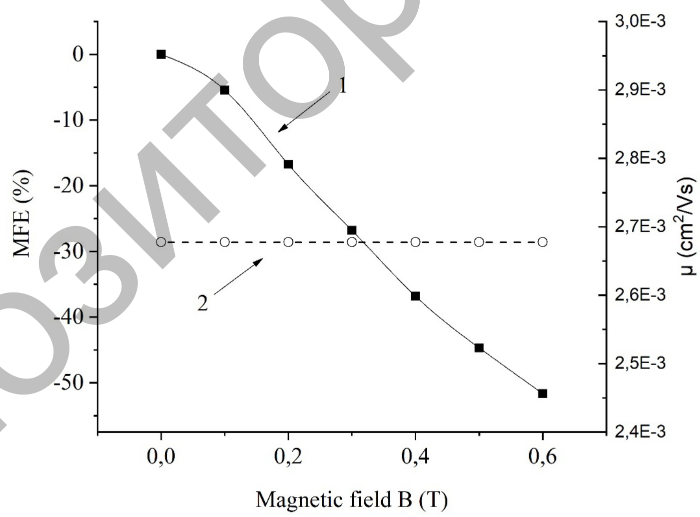
Based on the data obtained in Table, it can be concluded that with an increase in the magnetic field (from 0 to 0.6T) the maximum current density (J_{max}) and short-circuit current density (J_{sc}) decreases more than 2 times, while, maximum voltage (U_{max}) and open circuit voltage (U_{oc}) practically do not change. Also, the efficiency of the photovoltaic cell decreased by more than 2 times at the maximum value of the applied external magnetic field (0.6T).

Also, during the experiments, the effect of a magnetic field (MFE — Magnetic Field Effect) on the short circuit current of an organic semiconductor cell was revealed. MFE was calculated according to the method [11]. This graph is shown in Figure 7.

The formula (2) for calculating the effect of a magnetic field is given below.

$$MFE = \frac{I_B - I_0}{I_0} \cdot 100\ \%, \quad (2)$$

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



1 — MFE; *2* — carrier mobility

Figure 7. The effect of the magnetic field (MFE) and the charge carrier mobility

According to the above graph, it can be concluded that with an increase in the magnetic field, the short-circuit current changes in a negative direction. The reduction of the short circuit current was more than 50 % with an increase in the magnetic field from 0 to 0.6T.

The charge carrier mobility (Fig. 7) of copper phthalocyanine was obtained using the DI-SCLC technique (Dark injection space-charge-limited current) described in [12]. The charge carriers in CuPc are holes, since this compound belongs to *p*-type semiconductors. Below is a formula for calculating the charge carrier mobility (formula 3).

$$\mu = \frac{d^2}{Vt_{tr}}, \tag{3}$$

where μ is the charge carrier mobility; d is the film thickness; V is the applied voltage, t_{tr} is the 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.

$$\tau_{peak} = 0.786 t_{tr}. \tag{4}$$

The calculated charge carrier mobility in a solid semiconductor film consisting of organic molecules of copper phthalocyanine (at an applied voltage of ~ 620 mV) was $2.6 \cdot 10^{-3}$ cm^2/Vs. According to the authors, the mobility of CuPc charge carriers ranges from ~ $3.9 \cdot 10^{-4}$$cm^2$/Vs up to ~ $2.5 \cdot 10^{-3}$$cm^2$/Vs, depending on the annealing temperature [13]. According to the data obtained from the experiment (Fig. 7), a change in the magnetic field from 0 to 0.6T does not affect the charge carrier mobility in an organic photovoltaic cell.

Based on the experiments performed, it can be concluded that the organic molecules of copper phthalocyanine are sensitive to the magnetic field, which was proved by measuring the current-voltage characteristics of the photovoltaic cell. The effect of the influence of the magnetic field showed a decrease in short-circuit current by more than 2 times. Potentially, the studied effect of a change in the current-voltage characteristics in a solid CuPc film upon application of an external magnetic field can be used as a high-speed magnetic field sensor.

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Мыс фталоцианині қабыршағының фотоэлектрлік қасиеттеріне сыртқы магнит өрісінің әсерін зерттеу

Мақалада мыс фталоцианинінің (CuPc) қатты қабыршағындағы заряд тасымалдаушылардың қозғалғыштығы мен вольтамперлік сипаттамаларының өзгерісіне магнит өрісінің әсерін зерттеу нәтижелері келтірілген. Беті ток өткізетін ITO (индий оксиді қалайы) төсемедегі CuPc қатты қабыршағы вакуумда термиялық буландыру әдісі арқылы алынды. CuPc жұтылу спектрлері өлшенді, соның нәтижесінде төсеме бетіндегі мыс фталоцианинінің молекулалары метастабильді α-фазада болатыны анықталды. Вольтамперлік сипаттамаларға (ВАС) P20X потенциостат-гальваностаттың көмегімен сызықтық қашау күйінде өлшем жүргізілді. Фотоэлектрлік сипаттамаларға магнит өрісінің әсерін зерттеу үшін үлгі электрмагнит полюстерінің арасына орналастырылды. Күн жарығының ұқсатқышы ретінде сәуле шығару қарқындылығы 50 мВт/см^2 болатын ксенон шамы қолданылды. Тәжірибе нәтижесінде сыртқы магнит өрісінің қысқа тұйықталу тогының мәніне әсер ететіні, сонымен бірге магнит өрісіндегі заряд тасымалдаушылар қозғалғыштығының өзгермейтіндігі анықталды. CuPc қатты қабыршағындағы ВАС өзгерісі сыртқы магнит өрісіне салған кезде зерттелген әсері магнит өрісінің тез әсер ететін құрылғысы ретінде пайдалануы мүмкін.

Кілт сөздер: мыс фталоцианин қабыршағы, ВАС, магнит өрісі, заряд тасымалдаушыларының қозғалғыштығы.

А.В. Завгородний, А.К. Аймуханов, А.К. Зейниденов, Ж.Ж. Ахатова

Исследование влияния внешнего магнитного поля на фотоэлектрические свойства пленки фталоцианина меди

В статье представлены результаты исследования влияния магнитного поля на изменение вольтамперных характеристик и подвижности носителей заряда в твердой пленке фталоцианина меди (CuPc). Твердая пленка CuPc на подложке с токопроводящей поверхностью ITO (оксид индия-олова) была получена методом термического испарения в вакууме. Были проведены измерения спектра поглощения CuPc, в результате было установлено, что молекулы фталоцианина меди на поверхности подложки находятся в метастабильной α-фазе. Измерения вольтамперных характеристик (ВАХ) проводились при помощи потенциостата-гальваностата P20X в режиме линейной развертки. Для исследования влияния магнитного поля на фотоэлектрические характеристики образец помещался между полюсами электромагнита. В качестве имитатора солнечного света использована ксеноновая лампа с интенсивностью излучения, равной 50 мВт/см^2. В результате экспериментов было установлено, что внешнее магнитное поле оказывает влияние на значение тока короткого замыкания, в то же время подвижность носителей заряда в магнитном поле не меняется. Исследованный эффект изменения ВАХ в твердой пленке CuPc при наложении внешнего магнитного поля может быть применен в качестве быстродействующего датчика магнитного поля.

Ключевые слова: пленка фталоцианина меди, ВАХ, магнитное поле, подвижность носителей заряда.

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