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*as a manuscript*

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# Determination of quantum efficiency of photogeneration of charge carriers in films of new polymer composites by electrographic discharge method

Dissertation summary
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**Topicality of the research**.

Organic photovoltaics is a dynamically developing field of science with enormous potential. The development of thin-film electronics is driven by the creation of polymer and composite materials, which enable the formation of thin films using solution-based coating methods (e.g., inkjet printing) and exhibit photoconductivity. Solution-processed film formation techniques offer advantages over technologies for growing crystalline wafers or amorphous layers from inorganic semiconductors due to simpler technological requirements, which reduces the cost of manufacturing photodetectors, photomatrices, and devices for converting sunlight into electricity.

Advantages of organic photoconductors:

Low production cost: Synthesis and processing of organic materials are typically cheaper than their inorganic counterparts.

Mechanical flexibility: Many organic photoconductors are flexible, opening up possibilities for creating flexible and wearable electronics.

Tunable physicochemical properties: The properties of organic photoconductors can be varied by chemical modification, allowing them to be optimized for specific applications.

In this regard, the search for new polymer composites and the study of their photoelectric properties is an urgent task of modern thin-film and microelectronics.

The main parameter characterizing the efficiency of organic polymer films is the external quantum yield (quantum efficiency) of photogeneration. It can be determined by measuring the photocurrent at a constant applied field, provided that the photocurrent does not change due to the trapping of charge carriers, i.e., all generated charge carriers reach the electrodes. This indicator reflects what proportion of absorbed photons leads to the formation of electron-hole pairs capable of participating in charge transfer. High photogeneration efficiency is achieved in materials with a wide absorption band and efficient separation of excited states into free charge carriers. EQE plays a key role in the development of promising structures for organic photovoltaic cells.

In turn, the development of organic polymer sample structures requires a change in the existing approaches and methods for studying their characteristics. Various methods, such as the time-of-flight method, the space-charge-limited current method, and the field-effect transistor method, allow one to study the transport of charge carriers and determine their mobility in newly fabricated polymer films. However, these methods have a number of limitations and cannot be used, for example, under conditions of charging samples with high fields, where a high field can lead to damage to the sample under study.

Therefore, the issue of improving the methods used to analyze the characteristics of organic polymer films is also becoming relevant.

Polymer materials lack long-range order. The transport of free charge carriers between molecules occurs by a hopping mechanism with overcoming similar barriers. Charge carriers can fall into a deep energy well (trap) and cease to contribute to the photocurrent. For this reason, the photocurrent measurement after excitation by a given number of photons will decrease. This pattern is observed when conducting a time-of-flight experiment, so its use

In this regard, the development of integrated approaches that combine various experimental techniques is becoming the main direction for achieving success in the field of organic optoelectronics.

Considering all the requirements, features, and limitations, the electrophotographic method is the preferred method for measuring the quantum efficiency of photogeneration. However, in the original version or its variations, it is impossible to obtain reliable data on the basis of which the quantum efficiency of photogeneration will be calculated. The dissertation research presents a new modified setup for measuring EQE by the electrophotographic method.

**Degree of elaboration of the topic**

The study of the photoelectric properties of new organic polymers is a relevant area in the development of efficient optoelectronic devices. To study photosensitivity, the quantum yield of photogeneration, and the influence of additives, the electrophotographic method (EG), the time-of-flight method (TOF)

for measuring charge carrier mobility, and the MIS-CELIV method for selective study of electron and hole mobility in thin-film structures, described in the literature, are used.

Changes in the chemical composition of the samples are also being investigated. For example, the introduction of silicon atoms, magnetic nanoparticles, and dyes into layers leads to a change in photosensitivity, an expansion of the spectral sensitivity region, and an increase in photoconductivity. Efficiency significantly depends on the type and structure of the additives, as well as on the structure of the matrix itself. Crystallization and the formation of mixed microcrystals with dyes enhances the photoelectric properties due to more efficient charge transfer. Photoinduced electron transfer between neighboring molecules is the limiting step in most organic photoconductors. The external electric field, the activation energy, the lifetime of the electron-hole pair, and the band gap have a significant impact on the efficiency of pair separation and the generation of free charge carriers. An important area is the development of bipolar photoconductive composites based on a combination of p- and n-type materials, which makes it possible to achieve simultaneous and balanced transport of holes and electrons and increase the efficiency of photovoltaic devices.

The measurement technique is also developing. In particular, the proposed modified version of the electrophotographic method has several advantages in the study of photoelectric properties, such as high sensitivity, no need for ohmic contacts, and the ability to measure at early stages, before trapping charge carriers. The results obtained indicate the prospects for using organic polymers to create efficient optoelectronic devices. Doping, morphology control, and understanding of photogeneration mechanisms open possibilities for fine-tuning the photoelectric properties of materials and optimizing the operation of devices based on them.

As part of the dissertation research, data were obtained for new polymer samples in composites with thieno[3,2-b]indole derivatives ISC3 (3%) and ISC4 (1.6%). It was revealed that when sensitizing a polymer with low molecular weight compounds, one should take into account not only the spectral absorption band, but

also the position of the energy levels of the compounds relative to the levels of electronic states in the adjacent functional layer.

In the newly created setup for measuring EG by the method using an electrometer on a field-effect transistor, presented in the dissertation research, it is possible to do without connecting contacts to the sample, which would become an obstacle to obtaining a correct EQE picture. To measure the surface potential, an electrometer based on a field-effect transistor is used, which simplifies the measuring setup without degrading its sensitivity. The use of the proposed version of the method for determining the efficiency of photogeneration of charge carriers will improve the search for and development of new materials for photovoltaic devices. Limitations of use have been identified; Not applicable at low fields (the picture of the surface potential decay is unstable). Also, the method is not applicable at too high fields - in some polymer films, a high field can lead to its destruction. The created installation was delivered to the educational and research laboratory of functional safety of space systems and devices of MIEM HSE in addition to the time-of-flight stand, which will allow for a comprehensive approach to the research and development of new materials, as well as the use of the installation in educational laboratory work.

**The purpose** of this dissertation is to study the photogeneration of free charge carriers in films of new polymer composites by the method of electrophotographic discharge.

The following **tasks were solved**:

- The processes of photogeneration of charge carriers in films of polymer composites and methods for determining the quantum yield of photogeneration were analyzed.
- Possible options for measuring circuits of the electrophotographic method were analyzed, their advantages and disadvantages were clarified.
- A measuring circuit by the electrophotographic method is proposed.
- An experimental setup of the electrophotographic method was manufactured and debugged.

- Testing of the installation was carried out: measurements of the kinetics of photoinduced conductivity on a known polymer composite were carried out.
- The necessary conditions for film samples for the correct measurement of the quantum yield in polymer photoconductors have been established.
- The efficiency of photogeneration of charge carriers in films of new polymer composites has been determined.

Prospects for further development of the topic are:

- Revision of the experimental setup. The installation was set up in such a way as to carry out measurements on the linear section of the I–V characteristic of the transistor. To "get" to this area, it is possible to use operational amplifiers with different switching circuits. When using op-amps, no additional adjustment within the framework of reaching the linear section will be required.
- Further synthesis and research of new polymer samples with various options for physicochemical properties. Identification of dependencies affecting the efficiency of polymer films, formation of recommendations for improving their characteristics.

**The object** of the study is new organic polymer samples.

**The subject** of the study is the improvement of the quantum efficiency of photogeneration when changing the structure of samples and its measurement on a newly created setup using a modified electrophotographic method.

**The scientific novelty** of the work:

- For the first time, the quantum efficiency of photogeneration in polymer composites based on poly-N-vinylcarbazole with the addition of a thieno[3,2-b]indole derivative ISC3 and ISC4 was investigated. The following were established: the influence of the composition of the inactive substituent R in molecules on the quantum efficiency of photogeneration (EQE) and the reason for the reduced EQE value in the composite associated with the energy barrier at the photoconductor-hole transport layer interface.

- A variant of the electrophotographic method for measuring the kinetics of the surface potential decay of film polymer samples on a setup using an electrometer on a field-effect transistor is presented. The “coronator – sample – field effect transistor electrometer – ADC” link was used for the first time. In previously known circuits, the blocks of the measuring installation could be used separately. The proposed measuring circuit simplifies and reduces the cost of the installation itself without compromising the quality of measurements.

The work is of **theoretical significance** for identifying the patterns of increasing the quantum efficiency of photogeneration during the synthesis of new organic polymer films

- A modified method for measuring the surface potential of electrified semiconductor films is presented
- Various methods for measuring the characteristics of films were studied, and their disadvantages in comparison with the proposed method were identified.
- Options for improving the photoelectric properties of polymer samples are considered.
- Recommendations are given on the preparation of polymer samples taking into account the identified characteristics.

**The practical significance of the work**:

- A new experimental setup has been created for measuring the quantum efficiency of photogeneration in new polymer samples.
- New organic semiconductor samples with identified options for improving their characteristics have been manufactured. Theoretical assumptions regarding the possibilities of sensitization with various compounds have been experimentally confirmed.
- A measuring installation for recording the potential by a modified method was delivered to the Educational and Research Laboratory of Functional Safety of Space Systems and Devices of MIEM HSE in addition to the

existing station for a time-of-flight experiment. Using the installation, it is possible to measure the quantum efficiency of photogeneration in organic polymer samples and search for new highly efficient organic compounds. It is also possible to use the installation for educational and laboratory purposes within the framework of laboratory courses.

The **research methods** used in the work are physical experiment, physical modeling method.

**The following is submitted for defense**:

- The advantage of the electrophotographic method is that the installation can do without connecting contacts to the sample, which would become an obstacle to obtaining a correct EQE picture. To measure the surface potential, an electrometer based on a field-effect transistor is used, which simplifies the measuring setup without degrading its sensitivity. The use of the proposed version of the method for determining the efficiency of photogeneration of charge carriers will improve the search for and development of new materials for photovoltaic devices. At fields less than 103 V/cm, the use of the EG method is limited due to the instability of the surface potential decay picture. Also, the method is not applicable at too high fields - in some polymer films, a high field can lead to a change in surface morphology.
- Using the example of PVC film samples with various types of dye, the influence of the hole transport layer on the rate of charge carrier transfer from the photoactive layer to the electrode is shown. The addition of a PEDOT layer between the photoactive layer and the electrode improved hole transport, and the introduction of silicon nanoparticles into PEDOT further increased the rate of hole transfer to the electrode and, thereby, brought the measured EQE closer to the value of the quantum yield of photogeneration of charge carriers.
- In the process of sensitizing polymeric materials with low molecular weight compounds, in addition to analyzing the spectral absorption band of the

sensitizer, it is necessary to take into account the energy correspondence of the frontier molecular orbitals (HOMO and LUMO) of the sensitizer and electronic states in the adjacent functional layer responsible for charge carrier transfer to the electrodes of the optoelectronic device.

- Introduction of the thieno[3,2-b]indole fragment into the structure of the dye improves the charge-transport characteristics of photovoltaic devices.

**Personal contribution** of the author is presented at all stages of the dissertation research. Measurements of the properties of films and interpretation of the results obtained were carried out personally by the author of the dissertation or with his direct active participation.

The dissertation **consists** of an introduction, 5 chapters, a conclusion and a bibliography.

The introduction substantiates the relevance of the research topic; the degree of its elaboration is indicated; the purpose, objectives, scientific novelty of the research are formulated; the provisions submitted for defense are presented.

The first chapter provides a literature review on the topic of the dissertation research, the characteristics of organic substances, the main physical and chemical principles and phenomena inherent in organic structures are indicated. The principles of electrography, the history of its origin, the features of electrophotographic discharge, and the distribution of the electric field are described.

The second chapter describes the known principles of polymer sample research, the features of charge transfer in polymer films.

The third chapter describes the electrogaphic method. Its essence, physics of the process, options for assembling measuring installations, their features, disadvantages. The measurement scheme by the modified EG method is given, the created new experimental setup is described.

The fourth chapter describes an experimental study of polymer films of new materials. The discussion of the obtained results revealed patterns, recommendations for the sensitization of polymer samples are given.

The conclusion formulates the main results obtained in the dissertation work.

The work meets the requirements of clauses 3.1, 3.3, 3.4 - 3.8, 3.10 Regulations on the Award of Academic Degrees at the National Research University Higher School of Economics, as well as : "Engineering Sciences and Applied Mathematics" in terms of clauses: "Research of new processes and phenomena that increase the efficiency of radio engineering, electronic and telecommunication devices and systems, Physicochemical studies of technological processes for obtaining new and improving existing materials for various industries, development and improvement of methods for studying the structure and determining the physical and technological characteristics of materials", as well as specialties in accordance with the nomenclature of specialties of scientific workers approved by the Ministry of Science and Higher Education of the Russian Federation 2.2.2. "Electronic component base of micro- and nanoelectronics".

As part of the work on the dissertation research, the following articles were published:

1. Astafev A.V. The photoconductivity of a composite of poly-N-vinylcarbazole with carbocyanine dye improved by silicon nanoparticles/ Astafev A.V., Tameev A.R., Ilin A., Sayarov I. R., Tedoradze M. G. // Nanobiotechnology Reports. 2023. V.18. Suppl.1. P.S1-S5.

2. Астафьев А.В. Эффективность фотогенерации носителей заряда в композите поли-N-винилкарбазола с производными тиено[3,2-b]индола/ Астафьев А.В., Тедорадзе М.Г., Тамеев А.Р. // Материаловедение (перевод). 2024. №5. С. 17-22.