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«Inverted perovskite solar cell with a NiOx/phthalocyanine-based hole transport layer»

ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D05302–«Physics»**.**

Relevance of the Research. Inverted perovskite solar cells (PSCs) have attracted significant attention due to their improved operational stability, compatibility with flexible substrates, and strong potential for application in tandem solar cells. However, their power conversion efficiency (PCE) still slightly lags behind that of conventional (n–i–p) PSCs. The main factors limiting further improvements in the efficiency and stability of inverted PSCs are the degradation of key device components, instability of photovoltaic characteristics, and non-optimized device architectures.

One of the key components of inverted PSCs is the hole-transport layer (HTL), which forms a heterojunction with the photoactive perovskite layer. The photovoltaic performance and operational stability of inverted PSCs are strongly dependent on the efficiency of charge carrier injection and transport within the HTLs.

Nickel oxide (NiO_x) is considered one of the most promising materials for the fabrication of efficient inverted p–i–n perovskite solar cells. To date, record power conversion efficiencies of approximately 23% have been achieved for NiO_x-based inverted PSCs. Such high performance is attributed to the simplicity of synthesis, wide optical bandgap, favorable alignment of the valence band maximum, and superior chemical stability compared to other inorganic hole-transport materials.

In recent years, considerable efforts have been devoted to improving the photovoltaic performance and stability of PSCs through the development of bilayer HTL materials. Such architectures enable the minimization of the energy barrier for hole extraction and the suppression of interfacial recombination. A key aspect of this approach is the precise selection of materials with appropriate work functions, ensuring optimal energy level alignment with the perovskite active layer.

One of the promising strategies for enhancing the photovoltaic characteristics and stability of PSCs is the introduction of an interfacial layer based on phthalocyanines and their metal complexes. These compounds are chemically and thermally stable, exhibit strong optical absorption in the visible spectral range, and readily form ordered thin films with high photoconductivity. The physical and chemical properties of metal phthalocyanines (MPc) can be effectively tuned by optimizing the central metal ions and molecular structure. Unlike perovskite materials, phthalocyanines do not undergo rapid light-induced degradation accompanied by the release of iodine-containing species.

Thus, a detailed investigation of charge transport and recombination mechanisms in bilayer hole-transport layers will enable the rational design of more efficient and stable solar cells, ultimately contributing to the simplification of fabrication technologies for inverted PSCs.

The aim of this dissertation is to investigate the influence of the NiO_x/MPc hole-transport layer on charge transport and recombination processes in inverted perovskite solar cells.

To achieve this aim, the following tasks were addressed during the course of the research:
– to study the effects of ambient conditions and different annealing temperatures on the morphological, optical, and photovoltaic characteristics of NiO_x films;
– to fabricate phthalocyanine nanostructures using thermal vacuum evaporation and physical gradient temperature vapor-phase deposition methods;
– to develop a fabrication technology for bilayer films based on NiO_x and phthalocyanine nanostructures;

– to investigate charge carrier transport and recombination processes in bilayer NiO_x/MPc films;

– to synthesize a perovskite layer on the surface of NiO_x/MPc nanocomposite films;

– to study the influence of phthalocyanine nanostructures on the photovoltaic and charge-transport characteristics of inverted PSCs;

– to investigate the stability of inverted perovskite solar cells based on nanostructured NiO_x/MPc films.

Objects of the research: were inverted perovskite solar cells; nanostructured nickel oxide films; nanostructures of phthalocyanine and its metal complexes; and bilayer films based on nickel oxide and phthalocyanine nanostructures.

Research Methods: Experimental studies were performed using optical spectroscopy, scanning electron microscopy, atomic force microscopy, voltammetric measurements, impedance spectroscopy, and X-ray diffraction analysis.

Scientific Novelty includes the following findings:

1. Optimal technological conditions for the synthesis of nickel oxide films were determined. A correlation between the annealing temperature and the electrophysical properties of the obtained films was established. It was shown that increasing the annealing temperature from 200 °C to 450 °C leads to an increase in the root-mean-square surface roughness (Ra) and a decrease in the NiO_x film thickness, which is associated with the formation of a denser film.

2. It was demonstrated that the resistance of the external electrodes adjacent to NiO_x increases with increasing annealing temperature, while the recombination resistance at the NiO_x/electrode interface decreases. The observed increase in the film resistance R1 with annealing temperature is attributed to film densification, whereas the decrease in resistance R2 is associated with enhanced hole recombination at the NiO_x/electrode interface. The formation of a denser NiO_x film as a result of thermal annealing contributes to a reduction in the effective hole mobility.

3. The relationship between the structural features of metal phthalocyanine nanostructures and the efficiency of charge carrier generation and transport was established. It was found that a reduction in the density of grain boundaries decreases the number of defects, thereby enhancing charge transport efficiency and improving the performance of PSCs.

4. It was established that the MPc interlayer functions as a photoactive layer, expanding the spectral sensitivity and leading to an increase in the efficiency of inverted PSCs. It was shown that the introduction of cobalt phthalocyanine as an interfacial hole-transport layer results in a significant improvement in photovoltaic characteristics and enhanced stability of perovskite solar cells.

5. It was found that in nanoribbons, phthalocyanine molecules are aligned along the molecular axis and form a lamellar structure, which increases the charge carrier mean free path. This leads to an enhancement of the electrical conductivity of the MPc interlayer. It was shown that the charge carrier mobility increases when transitioning from H_2Pc to CoPc. As a result, PSCs with NiO_x/CoPc-based HTLs exhibited the highest power conversion efficiency of 20.7%, which is higher than that of PSCs based on NiO_x alone (18.1%).

Key Provisions Submitted for Defense:

1. Thermal annealing of NiO_x films from 200 °C to 450 °C results in the formation of thin, dense layers with low interfacial resistance at the NiO_x/Al boundary.

2.The bilayer NiO_x/MPc hole-transport layer enhances light absorption and improves hole transport, leading to an increase in the power conversion efficiency of inverted perovskite solar cells up to 18.9%.

3.The lamellar structure of the CoPc nanoribbon interlayer between the perovskite and NiO_x increases the charge carrier density under light absorption and enhances hole mobility by 3.7 times, resulting in a power conversion efficiency of 20.7% for the perovskite solar cells.

Author's Personal Contribution: The author carried out the fabrication of phthalocyanine nanostructures and prepared bilayer hole-transport films based on NiO_x and phthalocyanine and its metal complexes. The surface morphology of the obtained nanostructures and bilayer films was investigated using atomic force microscopy and scanning electron microscopy. Absorption spectra, X-ray diffraction patterns, current–voltage characteristics, impedance spectra, and the operational stability of solar cells were measured. Computer-based processing of the experimental data was performed. The analysis of the obtained results and the overall conclusions of the dissertation were carried out jointly with the scientific advisors.

Relationship of the dissertation with research programs. The dissertation was carried out in accordance with the research plans of the Fundamental Research Programs coordinated by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, within the framework of the following projects: AP19576784 *"Application of phthalocyanine and its metal complexes to enhance the efficiency and stability of perovskite solar cells"* (2023–2025), and AP19679938 *"Development of perovskite solar cells based on bilayer nanostructured composite NiO_x/MPc films"* (2023–2025).

Approbation of the research and publications. The main results of the dissertation were presented and discussed at the following conferences: the XIV International Conference on Photonics and Information Optics, Proceedings, National Research Nuclear University MEPhI, Moscow, 2025, pp. 307–308; Proceedings of the International Scientific Conference dedicated to the 100th anniversary of Academician E. A. Buketov, Karaganda, 2025, pp. 24–27; Proceedings of the International Scientific Conference "Innovative Development of Modern Physical Science: New Approaches and Current Research", Karaganda, 2025, pp. 29–33.

Publications.

Based on the results of the dissertation, a total of 7 publications have been produced: 3 articles in journals indexed in Thomson Reuters and Scopus (1 article in *Optical Materials*, 2024, IF 3.9, Q2, percentile 72; 1 article in *Small*, 2025, IF 12.1, Q1, percentile 92; 1 article in *Materials Letters*, 2025, IF 2.7, Q3, percentile 73); 1 article in journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan; and 3 publications in the proceedings of international and national conferences.

Practical significance of the research

1. The studied electrophysical properties of nanostructures based on nickel oxide and phthalocyanine determine their potential for practical applications in optoelectronic devices as well as components of inverted solar cells.
2. The high chemical and thermal stability of phthalocyanines enables the blocking of perovskite degradation pathways by preventing direct contact between the perovskite layer and nickel oxide. This leads to improved photovoltaic performance and enhanced stability of inverted PSCs.
3. Optimization of deposition methods and appropriate surface modification of the HTLs allows for the fabrication of highly efficient and stable solar cells, thereby reducing the production cost of inverted PSCs.

Structure and Volume of the Dissertation:

The structure of the dissertation is determined by the research objectives and consists of an introduction, four chapters, a conclusion, a bibliography, and an appendix. The dissertation is presented on 99 pages of typed text, illustrated with 49 figures and 17 tables, and includes a list of 199 references.