ANNOTATION

of the dissertation thesis for the degree of Doctor of Philosophy (PhD) in the educational program "8D05303 - Technical Physics" by Omarova Zhansaya

"**Efficiency limits of organometallic perovskites based on $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ for photovoltaics"**

General description of work

The thesis presents the results of a study of the limits of efficiency and stability of thin perovskite films based on $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ for photovoltaic solar energy converters.

Relevance of the dissertation theme

The consumption of fossil fuels as the main source of energy creates a significant environmental burden due to emissions of combustion products into the environment. One of the possible solutions to this problem is the development and implementation of environmentally friendly energy based on the use of technologies that are alternative to the combustion of hydrocarbon energy carriers. In recent years, the fastest growing area of alternative energy is solar photovoltaics. So far, silicon solar cells have been the main growth driver in this area. Despite a number of advantages, such as an abundance of raw materials, a long service life and a high coefficient of performance (COP), silicon solar cells also have a number of disadvantages, including relatively high cost, a high degree of science-intensive manufacturing process, as well as the complexity of processing and disposal. decommissioned solar modules. This necessitates the search for new materials and semiconductor structures, among which most attention has recently been paid to perovskites based on organometallic halides of tin or lead. Perovskite solar cells are distinguished not only by their high efficiency of solar energy conversion, exceeding 25%, but also by the relative ease of manufacture, which allows them to compete in the photovoltaic market with silicon solar cells. High efficiency is achieved due to a wide range of light absorption, as well as a relatively large, compared with the film thickness, diffusion length of current carriers due to their high mobility and lifetime. In addition, the possibility of varying the band gap in perovskites makes it possible to use them in combination with silicon solar cells in tandem structures.

However, perovskite photoconverters have a number of unsolved problems. These include, first of all, structural stability and operational stability, which currently limit the widespread use of these devices. To ensure the stability of a perovskite solar cell, it is necessary to identify the causes that contribute to the destruction of its functional layers. With regard to the crystal structure of perovskite, it is relevant to study the factors that lead to intense degradation of the strength of the hydrogen bond, which leads to a strong distortion of interatomic distances, for example, due to the adsorption of atmospheric moisture. Despite significant progress in this direction, the degrading effect of the environment on the stability of organometallic perovskites in terms of the stability of molecular bonds has not been fully studied. In this regard, the study of degradation

mechanisms and the search for efficiency limits for solar cells based on organometallic halide perovskites are topical problems in modern photovoltaics.

The idea of this work is to study the structure of perovskite solar cells based on $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$, the output technical characteristics of which depend on the geometric parameters, the density of bulk and surface defects, the choice of transition layers and electrodes, through numerical simulation and optimization, as well as to study the degradation of the functional layer of a thin film solar cell under the influence of the environment.

The purpose of the research is to reveal the limit of energy conversion efficiency and stability of an organometallic perovskite element.

Research objectives.

– Develop an algorithm for numerical simulation of a thin-film perovskite solar cell based on $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ with different characteristics that affect the photoconversion efficiency limit;

– Numerically investigate the influence of volume and surface defects in the absorbing layer of $CH_3NH_3SnI_3$ on the energy conversion efficiency limit;

– To reveal the range of changes in the main characteristics of a perovskite solar cell by changing the geometric dimensions of the $CH_3NH_3SnI_3$ absorbing layer using the SCAPS 1D software package;

– Determine the optimal characteristics of the hole transport and contact layers by searching for promising materials in order to approach the efficiency limit of the perovskite solar cell;

– Investigate the effect of degradation on the atmospheric stability of the $CH_3NH_3PbI_3$ perovskite layer.

The object of the research are thin films and solar cells based on organometallic perovskites $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$.

The subject of the research is the transformation of solar energy in the field of renewable energy sources.

Research methods. To achieve the goal of the research work, the following main methods were used: a numerical method using software simulation of a SCAPS 1D solar cell; microscopy method on a scanning electron microscope "Quanta 200i 3D"; the method of vibrational spectroscopy in the mid-IR range using an FTIR spectrometer of the FSM 2203 type, the method of optical absorption in the visible range using a QEX-10 quantum efficiency measurement setup.

The novelty and originality of the dissertation work lies in the fact that for the first time in it:

1) A generalized model of an effective perovskite solar cell has been developed, which differs from existing models by taking into account the influence of the density of bulk and surface defects in order to approximate the experimental results.

2) The dependence of the efficiency of a perovskite solar cell on the thickness of the absorbing layer, the type of the hole-transport layer and the contact

layer was numerically established using a numerical experiment to select the optimal characteristics;

3) It has been experimentally revealed that an increase in the concentration of bulk defects in the $CH_3NH_3PbI_3$ perovskite layer, caused by the process of hydration of the perovskite material, from values not exceeding 10^{12} cm^{-3} to values above 10^{16} cm^{-3}, leads to hydration and deterioration in efficiency from 30% to 15 %.

The theoretical and practical significance of the research lies in the fact that the results presented in the work contribute to the development of theoretical ideas about the efficiency of a perovskite solar cell and help to find their optimal parameters for use in photovoltaics. The results of the best structure of the $TiO_2/CH_3NH_3SnI_3/Cu_2O$ perovskite solar cell, obtained in this dissertation work, allow us to approach the maximum theoretical limit of Shockley-Quaisser efficiency, which brings us closer to widespread commercial implementation.

The significance of the results obtained is confirmed by publications in international peer-reviewed publications and participation in regular international conferences, as well as by the patent of the Republic of Kazakhstan No. 7458, copyright certificate No. 33477.

The main provisions submitted for defense

1. The developed generalized model of a perovskite solar cell based on $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$, taking into account the influence of volumetric defects in the light-absorbing layer in the range from 10^{10} cm^{-3} to 10^{17} cm^{-3} and surface defects in the range from 10^{10} to 10^{17} cm^{-2}, accounting for which allows you to vary the efficiency from 30% to 6%.

2. An optimal sequence of electrically conductive and semiconductor layers $FTO/TiO_2/CH_3NH_3SnI_3/Cu_2O/Pt$ with a light-absorbing layer thickness equal to 700 nm, at which the efficiency limit of a perovskite solar cell based on $CH_3NH_3SnI_3$ with an efficiency = 28% and a fill factor FF = 84% is reached.

3. The influence of the environment leads to an increase in the concentration of volumetric defects in $CH_3NH_3PbI_3$ caused by the hydration process of perovskite material from values not exceeding 10^{12} cm^{-3} to values over 10^{16} cm^{-3}, and the prevention of hydration allows to achieve a twofold increase in the efficiency of the solar cell from 15% to 30%.

Connection of the topic of the dissertation work with the plans of scientific work

The dissertation work was partially implemented in accordance with the research plans for 2018-2022: "AP05133651 - Production and research of promising renewable sources based on flexible organic semiconductor materials" and "AP08855738 - Glass-forming organic molecules in thin films of cryovacuum structural-phase transformations of condensates and relaxation processes".

The author's personal contribution lies in the fact that he completed the entire volume of dissertation work, including experimental work, computer modeling and quantitative evaluation of experience, analysis of scientific materials and preparation for publication. The setting of tasks, the choice of research

methods and the discussion of the results were carried out jointly with scientific consultants.

The reliability and validity of the results obtained is confirmed by the presence of publications in journals of the far abroad with a non-zero impact factor and in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, as well as in the proceedings of international scientific conferences of the near and far abroad.

Publications

Based on the materials of the dissertation work, 15 printed works were published: 9 works in the materials of International scientific conferences, 4 in journals from the list of CQASESMES RK for the publication of the main results of the dissertation for the PhD degree and 2 articles in a journal of foreign countries with a high impact factor included in international information resources Web of Science (Clarivate Analytics, USA) and Scopus (Elsevier, the Netherlands).

Volume and structure thesis

The dissertation work consists of an introduction, four sections, a conclusion and a list of sources used. The work is presented on 143 pages of printed text, contains 52 figures, 8 tables and a list of references from 223 titles.