ABSTRAST

of the thesis for the degree of Doctor of Philosophy (PhD) at specialty 6D071000 - Materials science and technology of new materials Sekerbayev Kairolla Sekerbayevich on the topic: **«Optoelectronic properties of semiconductor structures based on silicon and organometal perovskites»**

General characteristics of the work. The work is devoted to the investigation of the optoelectronic properties of nanostructured silicon layers and organometal halide perovskites and heterostructures based on them.

Relevance. Currently, significant attention is given to the production and studying of various new materials based on semiconductor nanostructures including silicon which remains the main material of micro- and optoelectronics. One of the main fundamental reason for studying nanostructures is their new physical properties, which appear, for example, due to the quantum size effect for charge carriers and phonons. Porous silicon and silicon nanowires are already well-studied types of silicon nanomaterials which have shown their promise for applications in photonics, sensors, thermoelectric, photovoltaics and biomedicine.

In the last ten years and there is a high activity in studies of metal halide perovskites which are very promising for the creation of highly efficient solar cells, as well as next generation electroluminescent and laser structures produced by a low-temperature low-cost thin-film technology. In addition, metal halide perovskites have proven to be an excellent material for implementing low threshold amplification and light generation, as well as electroluminescence in light emitting diodes with efficiencies above 12%. However, despite the fast progress made over the past few years in increasing the efficiency of photovoltaic and light-emitting devices based on perovskites an understanding of the fundamental photophysical processes leading to such results is only beginning to appear. This situation is caused by the fact that photogenerated charge carriers in perovskite participate in a number of complex processes occurring on the same time scale, such as diffusion, trapping/detrapping, nonradiative recombination in deep traps in the volume, radiative recombination, nonradiative surface recombination. From a practical point of view using of metal-halide perovskites in combination with crystalline silicon-based structures to create tandem solar cells is especially relevant. Their efficiency of which exceeds that for single-layer perovskite-based elements and the best based on crystalline silicon and already reaches 32,8%.

The purpose of the work is to identify patterns in the formation of optical and photoelectric properties of anisotropic layers of silicon nanostructures and organometal perovskites on silicon substrates.

The tasks of the study. To achieve this goal, the following tasks were set:

– the optical properties theoretical and experimental studying of anisotropic nanostructured silicon layers with free charge carriers;

– obtaining films of organometal perovskite by methods of deposition from solutions and studying their optical properties;

– obtaining samples of organometal perovskite deposited on substrates of single-crystal and nanostructured silicon and studying their optoelectronic properties.

– studying the processes of nonequilibrium charge carrier's separation and recombination photogenerated in a perovskite film on dielectric and semiconductor substrates.

The objects of the study are semiconductor layers based on nanostructured silicon and organometal perovskites.

The subject of the study is the structural, optical and electrical properties of organometal perovskites, silicon nanostructures and their hybrids.

Research methods. An experimental study of the properties of the samples was carried out using electron microscopy, X-ray diffraction analysis, spectroscopic analysis of reflection coefficients, transmission and photoluminescence, analysis of photocurrent kinetics, analysis of current-voltage and spectral characteristics.

Key points to protect

1. The optical properties anisotropy in the infrared spectrum for ensembles of silicon nanostructures is determined by both the anisotropy of the shape of constituent elements and the filling factor of the analyzed effective medium, and the free charge carriers concentration, which manifests itself in a nonmonotonic frequency dependence in the range from 200 to 1000 cm^{-1} for birefringence and dichroism in silicon nanowire layers formed by chemical and electrochemical etching of crystalline silicon with free charge carriers concentration of the order of 10^{19} cm^{-3}.

2. The optical absorption edge of organometal perovskite layers based on methylammonium compounds with lead iodide-bromide is well described in the framework of the Wannier–Mott excitons where the binding energy grows from 10 to 20 meV with increasing degree of ionicity of the compound, which grows with bromine proportion.

3. In hybrid structures based on layers of organometal perovskites deposited from solutions on crystalline silicon and silicon nanowires substrates the electric field formed in the perovskite layer influences its photoluminescent properties leading to the maximum of the exciton band shift and on the transfer of photoexcited charge carriers in the structure which manifests itself in the dependence of the intensity and lifetimes of the photocurrent and photoluminescence on the applied bias voltage.

4. Kinetics of the decay of photoluminescence intensity after pulsed laser excitation of organometal perovskite layers obtained by vacuum deposition depend on the ambipolar diffusion coefficient of photoexcited charge carriers as well as on the defects concentration on the layer surface and on the interface between the perovskite layer and the substrate, which is well described by the theoretical model based on kinetic equations for diffusion and recombination of nonequilibrium charge carriers.

Research novelty

1. For the first time, it has been theoretically and experimentally established that the dichroism of nanostructured silicon layers with free charge carriers can have a nonmonotonic spectral dependence in the infrared spectrum.

2. Theoretical analysis absorption spectra edge of organometal perovskites based on methylammonium compounds with lead iodide-bromide for the first time allowed to estimate to estimate the excitons binding energy in these compounds.

3. A phenomenological model is proposed for describing the kinetics of the decay of the photoluminescence intensity and the magnitude of the photocurrent in perovskite layers on a semiconductor substrate.

4. It was shown on the basis of a quantitative analysis of experimental data on the kinetics of photoluminescence decay in the layers of organometal perovskites based on methylammonium compounds with lead iodide obtained by vacuum deposition that the ambipolar diffusion coefficient of charge carriers can reach values of at least 1 cm^2/s which makes their promising for use in photovoltaics.

The theoretical and practical significance of the study consists in the fact that the results presented in the paper contribute both to the development of theoretical concepts of the physical properties of semiconductor nanostructures and help to find their optimal parameters for applications in photonics and photovoltaics. Layers and multilayer structures based on nanostructured silicon and organometal perovskites are especially promising for use in solar energy devices. The practical use of the developed methods of theoretical analysis of the optical properties of such structures also makes a significant contribution to the development of technology for creating new generation solar cells.

Personal contribution of the author. Author took part in all the main stages of research from experiments on obtaining samples, measuring optical and electrical characteristics as well as building theoretical models. Research was conducted in the al-Farabi KazNU and during two foreign training in Moscow, Russia (Lomonosov MSU, 2018) and in Valencia, Spain (Institute of Materials Science of the University of Valencia, 2018).

Approbation of work. Results of studies shown in this work were reported and discussed:

– at the International Conference «Recent Advances in Photovoltaics: Novel materials and device concepts for flexible and thin – film solar cells» (Bukhara, Uzbekistan 2016, 28 September –1 October);

– at the International Conference and Exhibition on «Renewable Energy Technologies» (Islamabad, Pakistan 2016);

– at the VI International Symposium on Coherent Optical Radiation of Semiconductor Compounds and Structures (Moscow, Russia 2017).

The reliability and validity of the results are confirmed by publications in journals recommended by the Committee for Control of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan and in the proceedings of international scientific conferences near and far abroad.

Publications The main results are presented in 10 scientific publications of which 4 articles in rating journals with non-zero impact factor: «The journal of Physical chemistry letters» (impact-factor 7.329), «Semiconductors», «Contents Technical Physics Letters», «JETP Letters», 1 in journals recommended by the Committee for Control of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 5 papers in proceedings of international conferences.

Relationship between the topic of the dissertation and the plans of scientific works. The dissertation was carried out in accordance with the plans of a research grant funded by the Ministry of Education and Science of the Republic of Kazakhstan: «Formation and stabilization of effective thin-layer perovskite solar cells with a heterojunction invert structure» (code AP05130083/GF5, 2018-2020) and «Creation and research of new highly efficient solar cells based on organometal perovskites» (code 3079/GF4, for 2016-2018).

Volume and structure of the dissertation. The dissertation is written on 115 pages of typewritten text and consists of an introduction, 3 sections, conclusion and a list of used sources, contains 76 figures and 5 tables. The list of used sources includes 140 items.

In this work the optical and photoelectric properties of silicon nanostructures and organometal perovskites were theoretically and experimentally studied, and the following main results were obtained:

1. Theoretical analysis within the framework of approximating the effective medium of the optical properties of layers of anisotropic silicon nanocrystals revealed a strong dependence of their birefringence, reflection anisotropy and dichroism on the concentration of free charge carriers in nanocrystals in the range from 10^{18} to 10^{20} cm^{-3} as well as on the filling factor of the medium with nanocrystals. A nonmonotonic dependence of the IR spectra of the difference transmission of anisotropic layers of porous silicon obtained on substrates of heavily doped crystalline silicon was experimentally discovered and theoretically substantiated. The results obtained indicate new possibilities for using anisotropic silicon nanostructures in photonics and terahertz optics as active media for controlling optical radiation.

2. The optical properties of organometal halide perovskites films obtained by the two-step deposition from solutions with different composition of iodine and bromine are studied. The obtained data indicate an increase in the contribution of excitons to the light absorption near the edge of the band gap in perovskite bromides as compared with iodine-containing ones. The absorption edge of organometal perovskites based on methylammonium compounds with lead iodide bromide can be described in terms of the Wannier-Mott excitons model with binding energies about 10 and 20 meV for $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$, respectively, which can be explained by enhanced excitons coupling in a material with a higher ion bonds.

3. A quantitative phenomenological model of recombination and charge separation in layers of organometal perovskites deposited on various substrates is

proposed and allows to calculate the transient distribution profiles of nonequilibrium charge carriers taking into account the built-in electric field in the perovskite layer, thickness, diffusion coefficients and lifetimes of nonequilibrium charge carriers, as well as the rate of surface nonradiative recombination at the layer surface and at the interface with the substrate. This allows to model experimentally measured photoluminescence intensity decay kinetics and photocurrent under pulsed photoexcitation with varying intensity.

4. The photoluminescence (PL) kinetics of the methylammonium lead-iodide perovskites layers obtained by vacuum evaporation on dielectric substrates was studied. It was demonstrated that at a concentration of photoexcited charge carriers of 10^{15}–10^{16} cm^{-3}, at which the contribution of interband recombination can be neglected, short PL kinetics lifetimes is explained by the relatively fast diffusion of charge carriers which leads to nonradiative recombination on the surface. Using the numerical solution of the one-dimensional diffusion equation the PL kinetics was simulated and the coefficients of ambipolar diffusion, D, and surface recombination, S, in such layers were determined. It was found that the diffusion coefficient, D, exceeds 1 cm^2/s which is an order of magnitude greater than usually observed in layers of a similar perovskite obtained from solutions. At the same time simulations showed high values of the surface recombination rate $S \sim 10^4$ cm/s in perovskite layers obtained by vacuum evaporation. Higher values of D in the latter are explained by the absence of electronic traps specific to analogous metal halide perovskites obtained from solutions. The obtained results are applicable for express diagnostics of optoelectronic quality of organometal perovskites layers for use in highly efficient solar cells.

5. A shift in the photoluminescence spectrum of organometal perovskites to higher photon energies and a shortening of the photoluminescence lifetime as compared to layers deposited on a glass substrate coated with conductive metal oxides was detected. It is explained by the influence of an electric field with a strength of the order of 10 kV/cm in the formed heterostructure on silicon substrate leading to field ionization and decay of excitons in the perovskite layer. The experimental and theoretical study of photoluminescence and photocurrent in heterostructures based on organometal perovskites layers deposited on crystalline silicon substrates and silicon nanowires layers revealed the possibility of efficient separation and photoexcited charge carriers transport which manifests itself in the dependence of the intensity and lifetimes of the photocurrent and photoluminescence on the applied bias voltage. The results obtained indicate the possibility of using organometal perovskites layers in light-emitting optoelectronic devices compatible with silicon control elements.