ABSTRACT

of the dissertation work on the topic:

«INVESTIGATION OF THE EFFECTS OF SELF-ORGANIZATION OF THIN LAYERS OF ZINC OXIDE ON THE SURFACE OF HIERARCHICAL POROUS SILICON FOR USE IN OPTOELECTRONICS»,

submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D071000 - "Materials Science and Technology of New Materials"

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The purpose of the work

The purpose of the dissertation work is to study the transformation of surface morphology during the formation of por-Si/ZnO structures by synthesizing light-emitting ZnO particles with an uncompensated charge.

Objectives of the study

In order to achieve the set objectives, the following tasks were set:

– Development of methods for synthesizing samples with developed surface morphology;
– Determination of mechanisms of formation of structures of different scales;
– Investigation of particles with uncompensated charge at substance formation;
– Study of luminescent properties of the obtained samples.

The object of research are:

– Zinc oxide structures of different levels formed on the surface of hierarchical porous silicon with electronic conduction;
– Zinc oxide structures of different levels formed on the surface of hierarchical porous silicon with hole conduction.

Object Modernization Methods

The structures obtained in this thesis work were characterized by combining a number of advanced research and analysis techniques:

– An electrochemical etching method was used to form porous silicon;
– A centrifugation method was used to form zinc oxide nucleated structures;
– Sol-gel method was applied to form zinc oxide base layers; Spray pyrolysis method was applied to deposit the base layers;

Methods of object investigation

– The surface structure of the obtained films was studied using an analytical scanning (scanning) electron microscope SEM, JSM-6490LA;
– The light-emitting properties were studied by photoluminescence (PL), which was measured using an Agilent Cary Eclipse spectrophotometer in the spectral range from 200 to 800 nm.
– The paramagnetic properties of the substance were investigated by electron paramagnetic resonance spectroscopy, using a JES-FA200 instrument.

– Determination of the specific surface area of the materials was realized by the BET method based on the process of thermal desorption of adsorbate gas (argon or nitrogen).
– Atomic force microscopy method, JSPM-5200, was used to determine the relief of surfaces.
– X-ray diffractometer "Burevestnik" DRON-6 was used to study the structure, texture and phase composition of mono- and polycrystalline samples.

The main provisions (proved scientific hypotheses and other conclusions, which are new knowledge), brought to defense

– Formation of porous silicon structure at removal of surface layer and reduction of anodizing current density in the process of electrochemical etching and deposition of 25 layers of zinc oxide by centrifugation and spray-pyrolysis methods allowed to form a hierarchical surface structure including macro and meso pores as well as clusters of substance of different sizes.
– Step-by-step variation of microwave power in the process of saturation of the EPR signal allowed us to effectively isolate the useful signal, and the representation of the spectrum in integral form when decomposed into components allowed us to identify paramagnetic centers with different nature.
– Application of 25 layers of zinc oxide on the surface of hierarchical porous silicon with electronic conductivity allowed to form a heterostructure with the formation of nanocrystals, the photoluminescence intensity of which is increased.
– Changing the conditions of recording EPR spectra in the process of signal saturation allowed us to reveal the formation of ZnO structures of different levels on the pore boundaries of hierarchical silicon through the mechanism of formation of F- centers.

Justification of the need for research and development

The rationale for the necessity of this research work is the relevance of research in the creation of new materials and structures for optoelectronics.

Composites based on nanomaterials embedded in matrices of different nature are promising for functional devices of new generation. They can consist of a wide range of compounds including inorganic, organic and hybrid structures [1].

The effects of self-organization of low-dimensional systems on the solid surface through the formation of periodically ordered structures are of great interest. This is due to the fact that the process is determined by quantum phenomena, which suggest new approaches to understanding the nature of matter formation.

Porous silicon (por-Si) is an attractive material due to the fact that its internal volume can be used as a nanoreactor for synthesizing various particles. The spatial separation of pores reduces the aggregation effect of nanoparticles. By controlling the shape and size of the channels, different materials with given geometric sizes and shapes can be explored. By changing the surface morphology: size, uniformity of pore outlets and surface roughness, it is possible to control the process of nucleation during the synthesis of matter on its surface. In this case, the composition of surface adsorption centers, their energy characteristics and wettability properties

play a significant role. Moreover, por-Si is a promising material due to its obvious compatibility with silicon microelectronics [2, 3].

Structures based on zinc oxide particles integrated into silicon substrates are promising as components of various semiconductor devices. The formation of ZnO nanoclusters on the surface and in the pores of the sample is an important process that can be used in gas sensors, since their sensitivity increases with increasing surface area [4-13].

The formation of structures with multistage hierarchy on the surface is associated with effects at the quantum level. At the same time, nano- and microstructures contain active particles with different properties. The influence of a gradually changing magnetic field on the process of their oscillation between excited and ground energy states allowed us to identify the properties of the particles. The study by atomic force microscopy and electron paramagnetic resonance spectroscopy together allowed us to identify formations of different scales and determine their energy properties.

Description of the main results of the research

This thesis presents the methods developed in the research to synthesize the hierarchical structure of porous silicon and zinc oxide.

It is shown that a hierarchical pore structure is formed on the silicon surface by electrochemical anodic etching. Application of zinc oxide layers forms nanocrystals on the surface. The distribution of these formations over the sample surface and their size are similar.

The mechanism of formation of the structures is determined, where the important role is played by the fact that the films are deposited on a hot substrate at 400^0C.

With the increase in the number of applied layers, the EPR signal increases, several reasons for it have been identified and the main contribution is made by oxygen vacancies. The saturation study of the EPR signal shows that the sample with 25 layers contains the same characteristics of PMCs uniformly distributed in the sample volume. The localization of PMCs becomes more ordered with increasing number of layers.

The FL increases with increasing number of applied ZnO layers. The exciton luminescence is maximized when 25 ZnO layers are formed, which is related to the increase in film thickness. Moreover, the FL signal from oxygen vacancies with trapped charge on them also increases.

Thus, the deposition of 25 layers of ZnO coating on the surface of porous silicon enhances the light-emitting properties and forms energetically stable nanostructures.

The tasks set in the dissertation work have been solved in full, structural, photoluminescent and EPR properties of the synthesized structures have been investigated. Technological parameters of synthesis were determined.

Justification of novelty and importance of the obtained results

– For the first time fractal structures with three levels of hierarchy were synthesized during the preparation of hierarchical porous silicon and the formation of zinc oxide particles on it.

– For the first time, the crystallization process of the structures was revealed by the saturation method of the EPR signal based on the dependence on the relaxation time of the paramagnetic center.

– For the first time, a cyclic method of signal saturation was applied to detect a weakly intense growing EPR signal.

Correspondence to the directions of science development or state programs

The topic of the thesis corresponds to the specialized scientific direction "Energy and mechanical engineering" on the priority "Alternative energy and technologies: renewable energy sources, nuclear and hydrogen energy, other energy sources" of the National Scientific Council under the Government of the Republic of Kazakhstan.

The research presented in this dissertation was carried out within the framework of the project of grant financing of RK IRN: AP09260940 "Optimization of the structure of thin films for the manufacture of solar cells on flexible substrates" (2021-2023).

Personal contribution of the author

The personal contribution of the author consists in performing the experimental research outlined in the dissertation work, including, methods of experimental research, conducting research, analyzing and formalizing the results in the form of publications and scientific reports.

Approbation of the work

Materials of the dissertation work were reported at the following conferences and symposiums:

International level:

1. The 4th International Conference on Materials: Advanced and Emerging Materials (Barcelona, Spain) (2022).
2. IX-X международная научно – практическая конференция «Наука настоящего и будущего» (Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова) (2021), (2022)
3. II международный научный форум «Ядерная наука и технологии» (Алматы) (2019).

At the republican level:

1. IV International Scientific Forum “Nuclear science and technologies” (Almaty, 2022)

Publications

16 printed works have been published on the materials of the dissertation work, including 3 articles in international peer-reviewed scientific journals included in the Scopus/Web of Science database:

1. Abdullin, K. A., **Kemel'bekova, A. E.**, Lisitsyn, V. M., Mukhamedshina, D. M., Nemkaeva, R. R., & Tulegenova, A. T. Aerosol Synthesis of Highly Dispersed Y 3 Al 5 O 12: Ce 3+ Phosphor with Intense Photoluminescence //Physics of the Solid State. – 2019. – Т. 61. – С. 1840-1845. Percentile 27, Cites score 1.6
2. Murzalinov, D., Dmitriyeva, E., Lebedev, I., Bondar, E. A., Fedosimova, A. I., & **Kemelbekova, A**. The Effect of pH Solution in the Sol–Gel Process on the Structure and Properties of Thin SnO2 Films //Processes. – 2022. – Т. 10. – №. 6. – С. 1116. (Processes - Scopus процентиль в категории Chemical Engineering 55%, WoS квартиль Q2, IF=3.352) (SCOPUS) https://doi.org/10.3390/pr10061116
3. Murzalinov, D., **Kemelbekova, A.**, Seredavina, T., Spivak, Y., Serikkanov, A., Shongalova, A., Zhantuarov S., Moshnikov V., Mukhamedshina, D.. Self-Organization Effects of Thin ZnO Layers on the Surface of Porous Silicon by Formation of Energetically Stable Nanostructures //Materials. – 2023. – Т. 16. – №. 2. – С. 838. Q2, Percentile 63, IF=3.7, https://doi.org/10.3390/ma16020838

4 articles in publications recommended by the Committee for Quality Assurance in the Sphere of Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan:

1. **Кемелбекова А.Е.**, Мухамедшина Д.М. Синтез высокодисперсных форм оксида цинка легированных редкоземельными элементами (обзор), Комплексное Использование Минерального Сырья. №4.2019, Алматы, стр. 12-18, ISSN 2224-5243
2. **Кемелбекова А.Е.**, МухамедшинаД.М., Мить К.А., Мошников В.А.// Обзор современных методов получения тонких пленок ZnO:Eu /Вестник КазНИТУ №6.2019, Алматы, стр. 824-829, ISSN 1680-9211 (химико-металлургические науки)
3. **A. Kemelbekova**, E. A. Dmitrieva, I. A. Lebedev, E. A. Grushevskaya, D. O. Murzalinov, A. I. Fedosimova, Zh., A. T. Temiraliyev The effect of deposition technique on formation of transparent conductive coatings of SnO2 // Physical Sciences and Technology (KazNU). – 2022. – Vol. 9. No (КОКСНВО) https://doi.org/10.26577/phst.2022.v9.i1.05
4. **А.Е.Кемелбекова**, А.Қ.Шонғалова, С.Қ. Шегебай, М. Карибаев, Ж.Сайлау, А.С. Серикканов / Проведение скрининговых расчетов кристаллической структуры ZnO и изучение применения в перовскитных солнечных элементах, «Вестник НАН РК», № 2, 2022 г. Стр. 122-133

9 Proceedings of international scientific and practical conferences:

1. Мухамедшина Д.М., **Кемелбекова А.Е**. Получение пленок оксида цинка легированных оксидом европия методом золь-геля, РДРЗ-19, V- всероссийская

конференция с международным участием, «V-российский день редких земель», 2019 г, стр.78.

2. **Кемелбекова А.Е.** ZnO:Eu құрылымдық ерекшеліктерін зерттеу, Ғылымының өзекті мәселелері-Халықаралық практикалық конференция материалдары, 22 қараша, 2018ж, https://doi.org/10.31643/2018.061

3. **Кемелбекова А.Е.,** Мухамедшина Д.М., Мить К.А., Мошников В. А., Синтез и исследование антиотражающих пленок ZnO:Eu для увеличения КПД солнечных фотоэлементов. Печатное II международный научный форум «Ядерная наука и технологии», 24-27 июня 2019 г. Алматы: РГП ИЯФ. стр. 126

4. **Кемелбекова А.Е.,** Мухамедшина Д.М., Мить К.А., Синтез, строение и люминсцентные свойства комплекса оксида цинка легированные РЗМ, «Нанофизика и Наноматериалы», Сборник научных трудов международного симпозиума, 27-28 ноября, 2019. Санкт-Петербург. стр. 116-121.

5. **Кемелбекова А.Е.,** Обзор синтеза наностержней ZnO, выращенных химическим путем на пористой кремниевой подложке, IX Научно – практическая конференция с международным участием «Наука настоящего и будущего», (Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова). ННБ IX, Санкт-Петербург, 13 – 15 мая 2021, стр.80-83

6. **А.Е.Кемелбекова**, Д.М.Мухамедшина, Д.О.Мурзалинов, Н.В. Идрисов Эффекты самоорганизации тонких слоев zno на поверхности пористого кремния //X международная научно- практическая конференция «Наука настоящего и будущего» (Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова). – 2022 https://nnb.etu.ru/assets/files/rezultaty/mag/2022/nnb-x_2022_tom-1.pdf

7. Murzalinov D, **Kemelbekova A** Formation of light-emitting particles with different parameters by coating ZnO on a silicon surface with several porosity levels / The 4th International Conference on Materials: Advanced and Emerging Materials (Barcelona,Spain).–P.33 https://icm2022.sciforum.net/events_files/642/customs/fba04cb7bfb982480fdb838031250a49.pdf

8. М.А. Бегунов, Е.А. Дмитриева, **А.Е. Кемелбекова**, Д.О. Мурзалинов Дефектообразование светоизлучающих частиц при формировании иерархической пористой поверхности $ZnO/SiO_2/Si$ структур / XI международная научно- практическая конференция «Наука настоящего и будущего» (Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова). – 2023

9. Т.А. Середавина, Д.О. Мурзалинов, Р.М. Жапаков, **А.Е. Кемелбекова**, Е.А. Дмитриева, С.Р. Жантуаров Формирование сверхтонких светоизлучающих структур ZnO путем захвата вещества на границах пор иерархического кремния / XIII Международная конференция «Аморфные и микрокристаллические полупроводники», 3-5 июля, Москва. – 2023.