ANNOTATION

for the dissertation work

"RESEARCH AND DEVELOPMENT OF A PROMISING METHOD OF SILICON SYNTHESIS FOR LITHIUM-ION BATTERIES" submitted for the Doctor of Philosophy (PhD) degree

in the specialty "8D07101 - Nanotechnology in Engineering" done by

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The aim of the dissertation: Experimental search for new polymorphic modifications of silicon nanocrystallites for the production of thin-film anodes for lithium-ion batteries and optimization of technological parameters for their production by magnetron sputtering.

Research objectives and their place in the implementation of scientific research work

1. To study the existing problems of the identification of thin-film silicon structures and silicon nanomaterials. Chapter 1 of the dissertation considered the results of previously conducted studies in the field of analysis of thin silicon films by electron microscopy and Raman spectroscopy. A comparative analysis of these results was made, and contradictions and shortcomings were identified. Ways to resolve these contradictions were developed.;

2. Using the magnetron sputtering method, obtain thin-film silicon structures with various technological sputtering parameters. In Chapter 2 of the dissertation, the methods for conducting research were formulated, and the necessary equipment was selected to solve the tasks set.;

3. To study the features of film polymorphism using electron microscopy and Raman spectroscopy. In Chapter 3 of the dissertation work, an analysis of the surface of the silicon film of the first type (a combination of amorphous and crystalline silicon) and the film of the second type (a new type of fibrous nano-Si). In addition, deconvolution of the Raman spectra of the films of the first and second types was carried out;

4. To establish the kinetic patterns of the growth process of silicon films during magnetron sputtering and to select conditions for the greatest intensification of the process. In Chapter 4 of the dissertation, the following was studied: IneticAprocess growth of silicon films at magnetron spraying. The presence of an induction period of the process and the boundary conditions for the transition to a stationary film growth regime were revealed. The corresponding mathematical modeling was carried out.;

5. To establish the patterns of influence of technological parameters of magnetron sputtering on the ratio of various polymorphic modifications of silicon in the composition of thin films, selection of conditions for maximum increase in the proportion of nanocrystallites in the composition of films. In Chapter 4 of the dissertation, the influence of pressure in the vacuum chamber, voltage on the target, and voltage frequency on the ratio of various polymorphic modifications of silicon in the composition of the silicon film was studied. A corresponding mathematical model was created, on the basis of which the optimal parameters of the magnetron sputtering process were established.

Research methods

The dissertation is based on the following theoretical and practical principles:

- scientific approaches and theories: theory of solids and nanostructured materials;
- physicochemical and structural methods of analysis;
- statistical processing of experimental data;
- software and mathematical modeling.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense

1. A previously unknown form of fibrous silicon nanocrystallites with a diameter of 10 to 150-200 nm in a silicon film obtained by magnetron sputtering. The film structure is porous, cellular, resulting from the interweaving of silicon nanofibers. The cells have an elongated oval shape with a width and length of about 1 and 3 μm, respectively;

2. Features of the Raman spectrogram, typical for silicon films containing nanocrystallites of a new type. The peak of amorphous silicon is around 120 cm^{-1}, crystalline silicon is around 210 cm^{-1}. Both peaks have a characteristic splitting. The peak of nano-Si of a new type has a maximum at a shift of 519 cm^{-1}, which distinguishes it from spherical silicon nanocrystallites, which give a peak in the region of 514-518 cm^{-1};

3. Mathematical models describing the kinetics of growth of the thickness of silicon films obtained by magnetron sputtering at different pressures in the working chamber;

4. Dependencies of the main indicators of magnetron sputtering: the time of the induction period, the rate of film growth in the steady state and the removal of silicon from the specific power at a constant (not pulsed) voltage on the target and from the frequency of the voltage on the target at the maximum possible specific power, described by the corresponding mathematical models;

5. Mathematical model linking the proportion of nano-Si in the composition of the obtained silicon film (Y) and the main technological parameters of magnetron sputtering of silicon: Specific power on the target, W/cm2 (X1), Pressure in the working chamber, Pa (X2), Voltage frequency on the target, kHz (X3)

$$Y = -30.7846 + 62.897 \times X2 + 0.2277 \times X3 - 5.3108 \times X2^2$$

6. Practical recommendations for magnetron sputtering of silicon films based on the analysis of kinetic patterns of film thickness growth. For maximum intensification of the process without loss of the fibrous structure of silicon nanocrystallites, it is necessary to: set the specific power on the target to 60-100 W/cm2. Maintain the frequency of voltage pulses on the target at 100-500 Hz. This reduces the induction period of the process to 5-15 seconds and increases the growth rate of the silicon film to 12800 nm/min in steady-state mode. Silicon losses are up to 7-15%;

7. Magnetron sputtering parameters, based on the developed mathematical model, at which the maximum concentration of fiber-type silicon nanocrystallites in the film composition is achieved. The calculated maximum share of nano-Si in the film of 75.06% is achieved at a voltage frequency on the target of 100 Hz and a pressure in the working chamber of 1.9 Pa.

Description of the main results of the study

During the scientific research the following scientific results were obtained:

1) The analysis of methods for identifying thin silicon films was carried out. It was found that the current situation does not provide a single reliable way to analyze such materials. It was found that the most successful in this regard is the method of Raman spectroscopy and electron microscopy. However, these methods require further clarification when identifying film nanostructures. The main direction of improving silicon anodes is the creation of film structures, since they accelerate the charging process and increase the stability of lithium-ion batteries to cycling. The most suitable method for creating such structures is physical spraying. Analysis of commercial offers of silicon anodes shows that existing film developments are not yet ready for commercialization, since most silicon anodes are made on the basis of nanopowders, not films. This does not allow revealing the potential of nanotechnology in these applications. It was necessary to radically increase the productivity of existing spraying processes. This will allow scaling the experimental results to the industrial level. It was necessary to find out how, at the technological level, it would be possible to achieve the optimal morphology of film structures and the polymorphism of silicon in the composition of the films;

2) A previously unknown form of fibrous silicon nanocrystallites with a diameter of 10 to 150 nm has been identified in a silicon film obtained by magnetron sputtering. The film structure is porous and cellular, resulting from the interweaving of silicon nanofibers. The cells have an elongated oval shape with a width and length of about 1 and 3 μm, respectively;

3) The Raman spectrogram features characteristic of silicon films containing new-type nanocrystallites were established. The peak of amorphous silicon is in the region of 120 cm-1, and that of crystalline silicon is in the region of 210 cm-1. Both peaks have a characteristic splitting. The peak of the new-type nanosilicon has a maximum at a shift of 519 cm-1, which distinguishes it from spherical silicon nanocrystallites, which give a peak in the region of 514-518 cm-1;

4) Mathematical models have been developed that describe the kinetics of growth of the thickness of silicon films obtained by magnetron sputtering at different pressures in the working chamber;

5) The dependences of the main indicators of magnetron sputtering have been established: the time of the induction period, the rate of film growth in a steady state and the removal of silicon on the specific power at a constant (not pulsed) voltage on the target and on the frequency of the voltage on the target at the maximum possible specific power, described by the corresponding mathematical models;

6) A mathematical model has been created that links the proportion of nano-Si in the composition of the obtained silicon film (Y) and the main technological parameters of magnetron sputtering of silicon: Specific power on the target, W/cm2 (X1), Pressure in the working chamber, Pa (X2), Voltage frequency on the target, kHz (X3)

$$Y = -30{,}7846 + 62{,}897 \times X2 + 0{,}2277 \times X3 - 5{,}3108 \times X2^2$$

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8) NAyden pparametersmagnetron sputtering, based on the developed mathematical model, in which the maximum concentration of fiber-type silicon nanocrystallites in the film composition is achieved. The calculated maximum proportion of nano-Si in the film of 75.06% was achievedetsyaat a voltage frequency on the target of 100 Hz and a pressure in the working chamber of 1.9 Pa;

9) The efficiency of using new silicon nanofilms with an increased content of nanocrystalline silicon nC and new fibrous silicon nanocrystallites with a diameter of 10 to 150-200 nm in the silicon film composition has been proven experimentally and by electrochemical testing. The advantage of the new silicon material over existing analogues has been substantiated.

Justification of the novelty and importance of the obtained results

The rationale for this dissertation is related to the increasingscientific and practical need to develop more efficient lithium-ion batteries. One promising direction is to replace the traditional graphite anode with anodes formed from nanosized silicon films. This approach allows for increased stability and predictability of the operational characteristics of batteries. As part of the research, new thin-film silicon materials are being developed that contain fibrous silicon nanocrystallites with a diameter of 10 to 150-200 nm in the film, which opens up opportunities for creating anodes with improved mechanical and electrochemical properties.

Practical significance of the work

The dissertation work contains elements of applied research related to optimization of the technological process of magnetron sputtering, but the scientific significance and subsequent economic effect of the work will be associated with the creation of a fundamentally new polymorphic modification of nanosilicon in the composition of film structures - fibrous silicon. This material has no analogues yet.

In the dissertation work, experiments were conducted using modern research methods that were as close as possible to production conditions, which determines a sufficient degree of reliability of the results of scientific work. The results of scientific research presented in the dissertation work, methods and techniques for the manufacture of thin film silicon anodes are accepted for implementation in Ansa Silicon LLP when the company moves to this stage of its development through the organization of vertically integrated silicon production, which is currently in the stage of formation of metallurgical silicon MG-Si.

Compliance with scientific development directions or state programs

The research and development of a promising method for synthesizing silicon for lithium-ion batteries corresponds to the priority areas of scientific development in the Republic of Kazakhstan, outlined in the Concept for the Development of Higher Education and Science for 2023-2029 (Resolution of the Government of the Republic of Kazakhstan dated March 28, 2023 No. 248). The document focuses on the development of new materials, energy accumulation and storage technologies, which is directly related to the topic of lithium-ion batteries and the use of innovative silicon-based materials.

In addition, this study is consistent with the objectives of the State Program for Industrial and Innovative Development of the Republic of Kazakhstan for 2020–2025 (Resolution of the Government of the Republic of Kazakhstan dated December 31, 2019 No. 1050), within the framework of which the priority is the development of high-tech industries, including the production of components for electronics and energy saving. The results obtained can contribute to technological independence and increased competitiveness of the domestic industry.

Contribution of the doctoral student to the preparation of each publication

The personal participation of a doctoral student in obtaining scientific results consists of planning and conducting experiments, performing theoretical and experimental research, discussing and summarizing the results.

On the topic of the dissertation, 4 scientific works have been published, including: 1 (one) article in a peer-reviewed scientific publication on the scientific direction of the dissertation topic, indexed in the Science Citation Index Expanded of the Web of Science (Clarivate Analytics) database and by CiteScore in the Scopus (Elsevier) database IF = 1.9 Quartile (Web of Science) - Q3, SCOPUS-40 Percentile, 3 (three) articles in domestic publications in the field of physics, nanomaterials and nanotechnology, recommended by the COCSON MES RK.

Information on the main publications indexed in the Science Citation Index Expanded of the Web of Science database (Clarivate Analytics), in a peer-reviewed scientific publication with a CiteScore percentile in the Scopus database (Elsevier) on the topic of the dissertation:

KS Tolubayev, BA Zhautikov, NN Zobnin, GS Dairbekova, SK Kabiyeva Kinetics of Thickness Growth of Silicon Films During Pulsed Magnetron Sputtering Using the Caroline D12C System // Condens. Matter 2025, 10, 19,https://doi.org/10.3390/condmat10010019

Information on publications in editions recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan for the publication of the main results of scientific activity:

1. KS Tolubayev, BA Zhautikov, NN Zobnin, GS Dairbekova, SK Kabiyeva, RT Al-Kasasbeh Modeling the influence of technological parameters of the magnetron sputtering process using the Caroline D12C system on the proportion of nanocrystallites in the structure of thin silicon films // Integrated Use of Mineral Raw Materials. No. 3 (334), 2025, DOI: 10.31643/2025/6445.27

2. KS Tolubayev, BA Zhautikov, NN Zobnin, GS Dairbekova, SK Kabiyeva Identification and quantification of silicon polymorphism in magnetron sputtered thin films // “ShKTU Khabarshysy” No. 3, 2024, pp. 85-94, DOI 10.51885/1561-4212_2024_3_85

3. KS Tolubayev, BA Zhautikov, NN Zobnin, GS Dairbekova, SK Kabiyeva Kinetics of Thickness Growth of Silicon Films During Pulsed Magnetron Sputtering Using the Caroline D12C System // Condens. Matter 2025, 10, 19, https://doi.org/10.3390/condmat10010019.