ANNOTATION

to the dissertation submitted for the degree of Doctor of Philosophy (PhD) on the specialty 6D071000 – "Materials Science and Technology of New Materials"

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"SYNTHESIS OF SILICON CARBIDE NANOSTRUCTURES BY PLASMA-CHEMICAL DEPOSITION"

General description of the work.

The dissertation is devoted to the experimental investigation of the formation processes of silicon carbide nanostructures synthesized by plasma-enhanced deposition methods, namely radio-frequency reactive magnetron sputtering and microwave plasma-enhanced chemical vapor deposition.

The main focus of the work is on studying the influence of key plasma-chemical synthesis parameters, including temperature, gas composition, type of metal catalyst, as well as the crystallographic orientation and morphology of silicon substrates, on the morphological and structural characteristics of the resulting nanostructures.

A comprehensive set of experimental studies made it possible to establish correlations between the synthesis conditions and the parameters of 3C-SiC nanostructures, including their shape, size, distribution density, effective optical band gap, and structural properties.

The relevance of the dissertation theme.

Silicon carbide (SiC) nanostructures are of significant interest due to their unique combination of high thermal and chemical stability, mechanical strength, radiation resistance, and a wide range of electrophysical properties. These characteristics make nanostructured SiC a promising material for applications in nano- and microelectronics, sensor systems, high-temperature and radiation-resistant devices, and for operation under extreme external conditions.

Among the vast diversity of silicon carbide nanostructures, one-dimensional fibrous structures occupy a special place, possessing a high specific surface area, pronounced property anisotropy and efficient channels for charge and heat transfer. These features determine their potential for use as photovoltaic cells, active elements in photocatalytic systems for hydrogen production, sensors, a reinforcing phase in composite materials and functional coatings.

Despite the active development of SiC nanostructure synthesis methods, most existing approaches rely on energy-intensive high-temperature processes using organosilane precursors, which are associated with environmental risks and difficulties in morphology control. Furthermore, a significant portion of research is primarily focused on the formation of SiC film layers, while the issues of controlled growth of fibrous nanostructures—especially under low-temperature plasma-chemical conditions—remain insufficiently explored. This narrows the technological possibilities and complicates the practical implementation of these processes.

In this regard, plasma-chemical deposition methods, including radio-frequency (RF) reactive magnetron sputtering and microwave plasma-enhanced chemical vapor deposition (MW-PECVD), are of particular interest. Compared to traditional

approaches, these methods offer several advantages, such as the ability to lower the synthesis temperature, more flexible control over the reaction medium composition, the elimination of the need for organosilane precursors (in the RF magnetron method), and the potential for directed control over the morphology of the formed nanostructures.

At the same time, an analysis of scientific works dedicated to plasma-chemical synthesis of silicon carbide shows that existing results are fragmented and do not provide a holistic understanding of the patterns governing the formation of nanostructures. In particular, information remains insufficiently systematized regarding the influence of the metallic catalyst type, as well as the crystallographic orientation and morphology of silicon substrates (smooth and porous), on the formation of SiC nanostructures. The lack of comprehensive experimental studies in this direction hinders the directed control of the density, length, and structural perfection of the resulting nanostructures.

Therefore, conducting comprehensive research aimed at establishing the patterns of fibrous silicon carbide nanostructure formation under plasma-chemical conditions is a highly relevant scientific and technical task.

The purpose of the research

The objective of the dissertation is to synthesize silicon carbide micro- and nanostructures using plasma-chemical deposition methods and to establish correlation dependencies between technological synthesis parameters and material characteristics.

To achieve this goal, it is necessary to solve the following tasks:

1. To synthesize silicon carbide micro- and nanostructures using radio-frequency (RF) reactive magnetron sputtering and microwave plasma-enhanced chemical vapor deposition (MW-PECVD) methods.

2. To investigate the influence of RF reactive magnetron sputtering parameters (gas ratios, temperature, and substrate orientation) on the characteristics of the synthesized silicon carbide structures.

3. To study the influence of metallic catalyst types (Ni, Cu), silicon substrate parameters (crystallographic orientation (100 and 111), morphology (smooth and porous)), and MW-PECVD technological conditions on the characteristics of the nanostructured silicon carbide.

The research methods:

The research methods include XRD (phase composition and structure), SEM (morphology and geometry), Raman spectroscopy (crystallinity and phonon properties), TEM with SAED and EDX analysis (internal structure and elemental composition), as well as spectrophotometric methods. The experiments were conducted with controlled variation of plasma-chemical synthesis parameters and catalyst types to ensure the reliability and validity of the data.

The object of the research – silicon carbide nanostructures obtained by radio-frequency reactive magnetron sputtering and microwave plasma-enhanced chemical vapor deposition.

Subject of the research — morphological and structural characteristics of SiC structures and the optimal technological parameters for their synthesis.

Scientific novelty. For the first time:

1. It has been demonstrated that 3C-SiC micro- and nanostructures can be synthesized by radio-frequency reactive magnetron sputtering at substrate temperatures of 600–700 °C without the use of organosilane precursors.

2. It was established that during microwave plasma-enhanced chemical vapor deposition, the most favorable conditions for the formation of fibrous 3C-SiC nanostructures are achieved using a nickel catalyst at temperatures of 700–800 °C, whereas the crystallographic orientation of the silicon substrate ((100) or (111)) does not significantly influence the morphology of the formed structures.

3. It was established that the use of a porous structure on Si(111) substrates during microwave plasma-enhanced chemical vapor deposition (at T ≈ 700 °C) significantly influences the growth morphology of 3C-SiC nanostructures. It was shown that under these conditions, the contribution of surface morphology and crystallographic orientation of the substrate becomes dominant, minimizing the differences between the effects of nickel and copper catalysts on fiber formation and ensuring the production of uniform nanofiber arrays with high density (~ 40 μm^{-2}).

The main provisions for the defense:

1. The formation of 3C-SiC micro- and nanostructures via radio-frequency reactive magnetron sputtering is achieved in an Ar/C_2H_2 gas environment with ratios from 1:(0.01–0.03) and substrate temperatures of 600–700 °C without the use of organosilane precursors.

2. The synthesis of dense arrays of fibrous 3C-SiC nanostructures via microwave plasma-enhanced chemical vapor deposition on smooth silicon substrates is achieved using a nickel catalyst in the temperature range of 700–800 °C in a tetramethylsilane/hydrogen gas mixture.

3. The use of (111)-oriented porous silicon substrates with a nickel or copper catalyst in microwave plasma-enhanced chemical vapor deposition promotes the growth of dense and uniform 3C-SiC nanofiber arrays at ~700 °C in a tetramethylsilane/hydrogen gas mixture.

The scientific significance of work.

The scientific significance of this dissertation lies in demonstrating the feasibility of synthesizing 3C-SiC nanostructures without the use of organosilane precursors by means of magnetron sputtering and microwave plasma-enhanced chemical vapor deposition. The study establishes the influence of synthesis temperature, catalyst type, and substrate morphology on the growth parameters of nanofibers (density, length, and alignment) as well as their structural characteristics.

The practical significance of work.

The practical significance of work is determined by the development of energy-efficient, environmentally friendly, and controllable technological regimes for the fabrication of 3C-SiC nanostructures. The obtained results demonstrate the potential application of these nanostructures as wide-bandgap absorbing layers in silicon-based tandem solar cells, as well as in photocatalytic water splitting systems and power nanoelectronic devices. The results can also be implemented in educational programs for training specialists in materials science and nanotechnology and may serve as a basis for further research.

Connection of the Dissertation with Research Programs

The dissertation research was conducted at Al-Farabi Kazakh National University. The main provisions were developed within the framework of fundamental research programs funded by the Ministry of Education and Science of the Republic of Kazakhstan under the priority "Rational use of natural resources, including water resources, geology, processing of new materials and technologies" for the project: AP05132865 "Development of plasma-chemical technology for the synthesis of silicon carbide nanostructures" (2018-2020).

The author's personal contribution. The author personally formulated the research objectives, planned the experiments, and carried out the modernization of the magnetron sputtering setup. The author independently synthesized samples using the magnetron sputtering method. In the MW-PECVD method, the author played a key role in selecting the deposition regimes and analyzing the obtained data. The entire set of structural and morphological studies (XRD, SEM, Raman spectroscopy, spectrophotometry) was performed and interpreted by the author personally. The scientific statements, conclusions, and publications in peer-reviewed journals were prepared independently by the applicant.

Approbation of the dissertation. The results obtained in the dissertation work were published, reported and discussed:

1. **Suyundykova, G. S.,** Mansurov, B. Z., Partizan, G., Kenzhegulov, A. K., Medyanova, B. S., Aliev, B. A., Zhumadilov, B. E. X-ray Investigation of SiC Nanostructure on Cu Films. // Journal of Nano- and Electronic Physics. 2019. Vol. 11. No. 2. (https://doi.org/10.21272/jnep.11(2).02002). (Scopus percentile 31% Q3)
2. Mansurov B.Z., Kenzhegulov A.K., Medyanova B.S., Partizan G., **Suyundykova G.S.,** Zhumadilov B., Mansurova M.E., Koztayeva U.P., Aliyev B.A. Investigation of SiC and C nanostructures obtained by MWCVD // Eurasian Chemico-Technological Journal. 2017. Vol. 19. No. 2. P. 165–175. (https://doi.org/10.18321/ectj648). (WoS: IF 1.2, Q3. Scopus percentile 14%)
3. Zhumadilov B., **Suyundykova, G. S.,** Partizan G., Medyanova B., Kenzhegulov A., Aliyev B. Structure and morphology of SiC nanostructures synthesized on Cu films // Materials Today. 2020. Vol. 31. P. 417–420. (https://doi.org/10.1016/j.matpr.2020.01.385). (Scopus percentile 38%, Q3)
4. **Суюндыкова Г.С.,** Мансуров Б.З., Кенжегулов А.К., Медянова Б.С., Партизан Г., Жумадилов Б.Р., Алиев Б.А. Синтез наноструктур SiC и C на буферном слое Ni методом плазмохимического осаждения // Вестник Казахстанско-Британского технического университета. 2018. Т. 16. Вып. 2. С. 28–37.
5. **Суюндыкова Г.С.,** Кенжегулов А.К., Мансуров Б.З., Медянова Б.С., Партизан Г. Исследование наноструктур SiC и C, полученных на поверхности буферного слоя меди // Современные проблемы физики конденсированного состояния, нанотехнологии и наноматериалов: материалы V Междунар. науч. конф. Алматы, 2018. С. 287.
6. **Суюндыкова Г.С.,** Кенжегулов А.К., Оспанали А.Т., Медянова Б.С.,

Партизан Г., Алиев Б.А. СЭМ-исследование наноструктур SiC, полученных методом высокочастотного магнетронного распыления // Вестник КазНИТУ. Технические науки. 2020. № 3 (139). С. 268–273.

7. Kenzhegulov A.K., **Suyundykova, G. S.,** Mansurov B.Z., Medyanova B.S. Synthesis of SiC nanostructures on the surface of copper films // The Physics and Chemistry of Carbon and Nanoenergetic Materials: proceedings of the X International Symposium. Almaty, 2018. Ch. 7. P. 1.

8. **Суюндыкова Г.С.,** Мансуров Б.З., Кенжегулов А.К., Медянова Б.С. Синтез наноструктур SiC и C на Ni-пленках методом МТ-ПХГФТ // Химическая физика и наноматериалы: материалы III конференции студентов и молодых ученых, посвященной памяти Мансурова Батыра Зулхаировича. Алматы, 2018. С. 32.

The volume and structure of the dissertation.

The dissertation consists of a list of symbols and abbreviations, an introduction, a main part comprising four sections, a conclusion, and a list of references. The total volume of the dissertation is 121 pages of typewritten text, including 89 figures, 7 tables, 5 formulas, and 179 bibliographic references.