ANNOTATION

of the dissertation for the Philosophy Doctor (PhD) degree of in the program "8D07112/6D07400 - Nanomaterials and Nanotechnologies" by

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SYNTHESIS OF NANOMATERIALS BY PECVD METHOD IN A HIGH-FREQUENCY CAPACITIVE DISCHARGE

General Characteristics of the Work

The present dissertation presents the results of experiments on the synthesis of carbon nanoparticles, silicon nanoparticles, and stable silicon nanoclusters, investigations of their properties, and describes the prospects for their use and applicability in modern applied disciplines.

Relevance of the Topic

Modern scientific and technological challenges require the development of new materials with unique properties. This work is dedicated to the synthesis of nanoparticles and the creation of nanostructured materials using plasma technologies, which is an advanced field in contemporary applied science. The research and application of nanomaterials cover a wide range of industries, from medicine and pharmaceuticals to electronics and energy, highlighting their significance and the need for new materials with improved properties.

The synthesis of nanoparticles and nanomaterials by plasma-enhanced chemical vapor deposition (PECVD), widely known and well-studied in international literature, is successfully applied in various fields of science and technology. Nevertheless, the use of advanced approaches and methodologies opens up numerous opportunities for obtaining entirely new nanomaterials and improving the properties of existing ones.

One of the innovative aspects is the use of plasma discharge duty cycle modulation to control the size and properties of nanoparticles, improving the synthesis process and enhancing their application efficiency. The use of modulated plasma discharge allows precise control over the nucleation and growth processes of nanoparticles, opening new possibilities for creating materials with specified characteristics. This research contributes to a deeper understanding of the mechanisms of nano- and microparticle growth, which is crucial for developing new technological solutions. Modulation of the discharge signal duty cycle is an innovative approach that optimizes the size and properties of particles, which is critical for creating high-quality functional coatings and microstructures.

Equally interesting are the processes and methods for creating hydrophobic and superhydrophobic nanofilms on the surfaces of various materials. Materials with superhydrophobic properties are known for their high contact angles, reaching 150° or more, and low hysteresis of these angles. Superhydrophobic surfaces, by definition, have low surface energy, reducing adhesive interactions between the surface and the liquid on it. The presence of such characteristics makes the development and study of superhydrophobic surfaces particularly relevant for applied fields. This research direction is motivated by the unique properties of these materials, which allow water to form droplets that roll off the surface without wetting it, effectively carrying away contaminants. This property creates the "lotus effect," replicating the self-cleaning abilities of certain biological objects. The key factors influencing the hydrophobic properties of a surface are its chemical composition and nanostructure, which determine the adhesion of liquid droplets to the surface.

Another application of the plasma-enhanced chemical vapor deposition (PECVD) method is the synthesis of stable silicon nanoclusters in low-pressure plasma. Under certain discharge parameters, these particles can possess a permanent dipole moment. When exposed to an external constant electric field, the particles can be oriented along the field lines during deposition on the surface, allowing the electron work function of the surface to be varied within a considerable range. It should also be noted that the proposed coating with silicon superclusters not only reduces the work function but also prevents substrate material evaporation and protects it from hostile environments. This method represents a significant step towards creating low-cost, energy-efficient, and environmentally friendly electron sources.

The Aim of the Dissertation

The aim of this dissertation is to synthesize carbon and silicon nanoparticles using various methods, including high-frequency signal modulation, to obtain films with superhydrophobic properties, and to achieve controlled synthesis of ultra-stable silicon nanoclusters.

Research Objectives

1. Study the effect of high-frequency discharge modulation on the size and properties of synthesized particles in low-pressure plasma.

2. Determine the optimal parameters for obtaining stable, transparent superhydrophobic coatings resistant to atmospheric influences, moderately aggressive environments, and ultraviolet radiation.

3. Investigate silicon nanoclusters synthesized by plasma-enhanced chemical vapor deposition from the gas phase with a constant dipole moment.

Research Object

The research focuses on carbon and silicon nanoparticles synthesized by plasma-enhanced chemical vapor deposition, superhydrophobic surfaces obtained at low and atmospheric pressures, and silicon nanoclusters with a constant dipole moment.

Research Subject

The subject of the research is the properties of synthesized nanoparticles and hydrophobic coatings, focusing on the influence of the size and structure of carbon nanoclusters deposited on the surface on the electron work function.

Main Research Findings:

1. Modulating the frequency of the high-frequency capacitive discharge of an argon/methane mixture from 1 Hz to 10 kHz increases the average size of synthesized nanoparticles from 26 nm to 61 nm while maintaining other plasma parameters.
2. Superhydrophobic films synthesized in atmospheric pressure high-frequency capacitive discharge plasma with a power of 200 W, an Ar/HMDSO gas flow (40 sccm/12 sccm), have a light transmittance of at least 90% and a contact angle of at least 160°.
3. The PECVD synthesis of silicon nanoclusters in an argon/silane (98%/2%) gas mixture plasma with a power of 10 W, pressure of 63 Pa, gas flow of 20 sccm, plasma on-time from 25 ms to 50 ms, and 1000 cycles produces ultra-stable silicon nanoclusters with a constant electric dipole moment in the size range of 40 nm to 67 nm, significantly reducing the electron work function when deposited on surfaces.

The main research results obtained and established in the course of the thesis work:

1. Nanoparticles were synthesized in a high-frequency discharge plasma by chemical vapor deposition from the gas phase at various buffer and reactive gas flows, as well as at various modulations of the high-frequency signal duty cycle. For instance, at a discharge power of 100 W, pressure of 1 torr, and modulation frequency of 100 Hz, the average size of the synthesized particles was 47 nm. Increasing the modulation frequency to 1 kHz resulted in an average particle size of 60 nm. Optimal parameters (gas concentrations, modulation frequency) were also determined for obtaining nanofilms with various surface morphologies. The influence of these conditions on the hydrophobic properties of the obtained surfaces was identified.

2. Extensive series of experiments were conducted on the synthesis of carbon and silicon nanoparticles at low and atmospheric pressures. Films with hydrophobic properties were obtained. It was proven that during PECVD synthesis at low pressure in a gas mixture of argon/methane and argon/acetylene, the morphology of the resulting surface depends on the concentration of the reactive gas. For instance, at a methane concentration of 7%, the synthesized nanofilm has a wetting angle of not less than 150°, classifying it as superhydrophobic.

   To synthesize hydrophobic surfaces on various materials at atmospheric pressure, an experimental setup based on a plasma jet was assembled, using HMDSO vapor as a precursor and argon as the plasma-forming gas. To automate the process of applying the nanofilm and obtaining a uniform layer, a small CNC machine was used as a plotter. The synthesized surfaces had contact angles of not less than 160°. They were also resistant to moderately aggressive chemicals, ultraviolet radiation, high temperatures, weather conditions, and mechanical impact. It was demonstrated that the surfaces retained their properties when heated up to 300°C, and maintained hydrophobicity for at least 18 months when exposed to outdoor conditions. With a single application of the particle layer, the light transmittance was not less than 90%, which, combined with the self-cleaning property, opens up prospects for using such coatings to protect the surface of solar elements from dust. Experiments showed that these types of nanofilms can be applied to various materials such as plastics, fabrics, paper, glass, metals, and others.
3. For the synthesis of silicon nanoclusters in a plasma environment at low pressure, the experimental setup was modified and improved. A system for automation with control of the number of cycles, the duration of plasma pulses (exposure time), and the time required for particle deposition was developed and successfully applied. An external constant voltage source was integrated into the automation system via galvanic isolation.

   Silicon nanoclusters were synthesized in a high-frequency capacitive discharge in a gas mixture of silane (SiH_4) and argon (Ar) with exposure times ranging from 25 ms to 50 ms on various types of substrates (quartz, glass, silicon, aluminum, copper). Samples obtained on silicon substrates showed a decrease in the electron work function from the surface. This is attributed to the presence of a constant dipole moment in the silicon nanoclusters. The lowest work function was measured for the sample with an exposure time of 40 ms. XPS analysis showed the absence of a crystalline structure in the nanofilm samples with exposure times of 25 ms, 30 ms, and 40 ms. However, at an exposure time of 50 ms, nanocrystals begin to nucleate, and they, as known, do not have a dipole moment. This is likely related to the increase in the electron work function.

Experimental and theoretical methods

To characterize the medium, the following were performed:

- calculation of the concentration and temperature of electrons in the plasma from emission spectral lines

- electrical diagnostics of plasma by obtaining the voltammetric characteristic, determining the self-bias voltage at different experimental parameters

- measurements using the microwave cavity method to analyze plasma composition and monitor changes in its structure.

The obtained results were analyzed using analytical equipment such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) for high-resolution imaging, atomic force microscopy (AFM), Raman spectroscopy, ultraviolet-visible (UV-VIS) spectroscopy to study the optical properties of the obtained nanomaterials and determine their electronic structure and interaction with light, and X-ray photoelectron spectroscopy (XPS) for surface analysis of the obtained nanomaterials and to obtain information about the chemical composition, including the study of the elemental composition on the surface of the obtained silicon nanocluster samples.

The author's personal contribution consists of conducting all the research, selecting the methodology for the studies, solving problems, and upgrading the experimental setup independently. The formulation of tasks and the discussion of the experimental results were carried out jointly with scientific consultants.

The reliability and validity of the obtained results are confirmed by publications in high-impact factor journals in distant foreign countries and in publications recommended by the Committee for Control 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 in both near and distant foreign countries.

Presentation and Publication of the Work

The results obtained in the dissertation were presented and discussed at the following international conferences and seminars:

- International Conference on Strongly Correlated Coulomb Systems "SCCS-2017" (2017, Kiel, Germany)

- International Conference on Advanced Nanomaterials "ANM-2017" (2017, Aveiro, Portugal)

- International Dusty Plasma Workshop Seminar (2018, Baltimore, USA)

- International Conference on Applied Nanotechnology and Nanoscience "ANNIC 2017" (2017, Rome, Italy)

- International Conference on Nanomaterials and Advanced Energy Storage Systems "INESS-2017" (2017, Astana, Kazakhstan)

- International Seminar on Nanotechnologies for Young Scientists "IWYS-2016" (2016, Putrajaya, Malaysia)

- International Conference "JSAP-2017" (2017, Japan).

Publications

Based on the materials of the dissertation, 17 printed works have been published: 2 in journals from the List of the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan for the publication of the main results of the dissertation for the degree of PhD, and 7 articles in journals from distant foreign countries with a non-zero impact factor, included in the Web of Science and Scopus international information resources databases; 8 works in the materials of international scientific conferences.

List of publications

1. Ussenkhan S.S., Kyrykbay B. A., Yerlanuly Y., Orazbayev S.A., Gabdullin M.T., Ramazanov T.S., **Zhunisbekov, A.T.,** Utegenov A.U., Fabricating durable and stable superhydrophobic coatings by the atmospheric pressure plasma polymerisation of hexamethyldisiloxane // Helion – 2024 – Vol. 10, P. E23844 (Q1, Percentile 86%)
2. Orazbayev S.A., Zhumadilov R.E., **Zhunisbekov, A.T.**, Yerlanuly Y., Gabdullin M.T., Utegenov A.U., Ramazanov, Super hydrophobic carbonous surfaces production by PECVD methods // Applied Surface Science – 2020 – Vol. 515, P. 146050 (Q1, Percentile 94%)
3. Orazbayev, S.A., Zhumadylov, R.E., **Zhunisbekov, A.T.**, Ramazanov, T.S., Gabdullin, M. T Yerlanuly Y., Obtaining of copper nanoparticles in combined RF+DC discharge plasma // Materials Today: Proceedings. – 2020. – Vol. 20. – P. 329 - 334.
4. Zhumadilov, R., Orazbayev, S., **Zhunisbekov, A.T.**, Ramazanov, T., Raiymkhanov, Z. Synthesis of silicon nanoparticles for hydrogen gas production // Materials Today: Proceedings. – 2019. – Vol. 31. – P. 444 - 448.
5. Orazbayev, S.A., Utegenov A.U., **Zhunisbekov, A.T.**, Slamyiya M., Dosbolayev M.K., Ramazanov T.S. Synthesis of carbon and copper nanoparticles in radio frequency plasma with additional electrostatic field // Contributions to Plasma Physics. – 2018. – Vol. 58. – P. 961-966. (Q3, Percentile 39%)
6. Orazbayev, S., Gabdullin, M., Ramazanov, T., Dosbolayev, M.K., **Zhunisbekov, A.T.**, Omirbekov, D., Otarbay, Z. The method of synthesizing of

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8. Жумадилов Р.Е., Жунисбеков А.Т., Оразбаев С.А., Габдуллин М. Т. Получение наночастиц меди в плазме комбинированного ВЧ+DC разряда // Вестник КазНИТУ – 2021 – No 4 – с. 76-81

9. Жунисбеков А.Т., Жумадилов Р.Е., Оразбаев С.А., Әлішеров Н., Габдуллин М. Т., Ибрашев К.Н., Үсенхан С.С. Получение гидрофобной поверхности в плазме атмосферного давления // КазНИТУ – 2020 – No 1 (137) – с. 584-589