SUMMARY
of the PhD Thesis on the Speciality 6D060500 - Nuclear Physics
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Synthesis and properties of nanostructured materials based on nuclear track membranes

General research characteristics. The work deals with the synthesis of metallic nanotubes in the pores of the nuclear track membranes, as well as the influence of ionizing and electronic radiation on the structural and conductive properties of the obtained nanostructures. The dependence of structural and conductive properties on the electrochemical deposition conditions (electrolyte temperature, voltage). The existence of magnetic texture with the prevailing direction of the magnetic moments of Fe atoms along the axis of the two-component iron-containing nanotubes, unlike Fe nanotubes, where there is equiprobable orientation of the magnetic moments. For the first time a controlled modification of the structural and conductive properties of Co, Cu, and Zn nanotube by electron irradiation with energy of 5 MeV has been carried out. It was shown that electronic defects annealing occurs as a result of irradiation, thereby the conductivity is increasing, while the average crystallite size is almost not changed. Also detected two-step process changes the properties of the conductive metal nanotube depending on the thermal annealing time.

High practical relevance of the experimental data is confirmed by two patents of the Republic of Kazakhstan. The researches were conducted on the basis of the L.N. Gumilev Eurasian National University, Institute of Nuclear Physics of the Republic of Kazakhstan and the Physics Department of Moscow State University named after M.V. Lomonosov.

Topicality of the reserch.

In today's world nanostructured materials are attracting more attention from the research groups, due to their unique properties and broad application range from the power converters, batteries to the media and biosensors. Progress in scientific and technological fields is primarily determined by the ability of materials and devices based on them operate under extreme conditions, including magnetic field or ionizing radiation. The use of new materials and products dictates the need not only to evaluate their resistance to various types of radiation or thermal effects, but also the possibility of using ionizing radiation with the purpose to improve the structural and electromagnetic properties of materials. The unique mechanical properties of nanotubes make these structures promising basis for a new material type combining high strength properties, thermal and chemical stability, as well as electrical conductivity and low resistance value in comparison with massive materials.

One way to change the material properties is the radiation exposure by different radiation types. Studies of the radiation exposure effect on the massive material have held for decades. It should be noted that the theory of the interaction of ionizing radiation with matter has been worked through pretty good, but the field associated with the radiation influence on the nanomaterial properties has not been studied enough. To date, there are a number of papers where the ionizing radiation effect on the structure and conductive nanomaterial properties is analyzed, at the same time the results given in these works are rather contradictory. At the moment, there is no generally accepted description of the specifics of radiation effects in nanoscale materials and their degree of influence on the structural and conductive properties, as well as the characteristics of products based on them.

Radiation effects occurring in nanomaterials under the influence of ionizing radiation have a number of features that are different from similar effects in micro- and macrodimension objects. Copper- and zinc-based nanotubes obtained by template synthesis arouse interest from view of the practical application to create new items of spacecraft equipment. During the interaction of ions with the energy comparable to the cosmic radiation energy with a nanostructure, only a small part of the incident particle energy is transmitted to it.

In this connection, a small quantity of additional charge carriers or structural defects occurs in nanostructures. Moreover, the incident particle energy growth induces the decline of generated charge carriers and defects according to reducing the linear energy transfer and the cross section of interaction with the nanostructure material atoms, while in the conventional materials the total number of charge carriers and the structural defects increases with the incident particle energy .

In turn, the electron irradiation of metallic nanostructures is an effective tool to promote the controlled modification of the material properties, such as structural, optical, electrical and magnetic ones. Under radiation with high-energy electrons, which transfer their energy to the target atoms passing through a material, there is the electronic excitation, the displacement of atoms from their original sites.

Control of radiation material modification is carried out by adjusting the energy of the particles used for irradiation and allows changing the structural and conductive properties of metal nanostructures by the defect annealing, as well as the implantation of additional charge carriers that reduces the nanostructure resistance that leads to lower power consumption during operation of microelectronic devices based on them.

Another promising direction in the nanotechnology development is a medical field of nanostructure application. Nanomedicine is a rapidly growing trend in the last decade, including methods of prevention, diagnosis and treatment of a wide range of diseases with different types of nanostructures. Control of the shape, size and chemical composition of the nanostructures on synthesis stage allows setting their physical properties and offers new opportunities for bioapplication. Pretty interesting possibility of the nanostructure application is a targeted delivery of payloads (drugs or proteins) using a magnetic field. In this method, a drug or a protein is joined to a magnetic nanostructure by functional groups, injected into the bloodstream and then transported to the subject area by the magnetic field. In the most cases, spherical magnetic nanoparticles are considered as carriers of drugs and proteins. However, small magnetic moment of these particles complicates the magnetic field focusing on them, so it cannot create enough force to resist the blood flow in the vessels. The absence of a magnetic core in nanotubes allows creating nanostructures with similar switching fields, ensuring reproducible results; a smaller specific gravity allows floatting in liquids (including biological ones) and making them suitable to use in biotechnology; a large specific surface area provides more functional relationships and thus movement of more target components at the delivery address.

One of the most promising materials for the magnetic nanostructures production is an alloy of iron with cobalt or nickel due to its higher saturation magnetization than the value for pure ferromagnetic metals Co, Ni and Fe.

The object of research are one-component metallic (Co, Cu, Zn) and two-component (FeCo, FeNi) nanostructures in the form of hollow cylinders obtained by template synthesis in nuclear track membrane pores. The research object corresponds to the thesis theme, aim and objectives.

The subject of the research is to study the basic laws of nanotubes formation in pores of track membranes based on polyethylene terephthalate, as well as the targeted modification of structural and conductive properties of metal nanotubes by irradiation with heavy ions Xe^{+22} and electrons with energies of 5 MeV. To research nanotube structure changes as a result of thermal annealing. To study dependence of structural, conductive properties, and texture of the magnetic nanotubes based on bicomponent iron triad elements (Fe, Co, Ni) on the synthesis conditions.

The scientific novelty:

- The dependence of structural and conductive properties on the geometric characteristics of template matrixes, as well as the conditions of the electrochemical deposition (electrolyte temperature, voltage) was found.
- The existence of magnetic texture with the prevailing direction of the magnetic Fe atom moments was found along the two-component iron-containing nanotube axis, unlike Fe nanotubes, where there is equiprobable orientation of the magnetic moments.
- Two-step process of conducting properties changes depending on the thermal annealing time was found: at the first stage a slight decrease in resistance caused apparently by thermal annealing of structural defects was noticed, in the second stage a sharp increase in resistance occured due to the oxide phases formation in the structure.
- The ion beam scattering simulation was conducted at the atomic structure of metallic nanotubes taking into account DC-60 accelerator features. Using Xe22 heavy ions with energies above 200 MeV allows modification of the structural properties of the entire nanotubes length.
- It is shown that electron defect annealing occurs as a result of irradiation of metallic nanostructures by electrons with energy of 5 MeV, thereby the conductivity is increasing, while crystal nanotube structure hardly varies.

Research objectives:

- To study electrochemical synthesis of one-component (Co, Cu, Zn) and bicomponent (Fe/Co, Fe/Ni) nanostructures from aqueous solutions of salts on the polymer template walls with the formation of homogeneous nanotube arrays;
- To investigate the structure and composition of the synthesized nanostructures by the modern physical and chemical methods: energy dispersive analysis, scanning

electron microscopy, X-ray diffraction, transmission electron microscopy, Mössbauer spectroscopy;

- To simulate processes of accelerated ions interaction with the synthesized nanotubes material in order to select a heavy ion for effective nanotubes modification taking into account DC-60 accelerator possibilities;
- To research the effect of ionizing radiation and thermal annealing on the structural and conductive properties of one-component nanotubes based on Co, Cu, Zn;
- To study the dependence of conductive properties and structural properties of two-component nanotubes based on iron triad elements (Fe, Co, Ni) on the synthesis conditions.

Statements for the defense:

- The research results of the influence of deposition conditions on the phase composition, structural, conductive and magnetic nanotube properties.
- It is found that the nanotube wall thickness decreases with increasing temperature of the electrolyte solution, and (or) the potential difference. At the same time a decrease of crystallite size, which is accompanied by increasing the nanotube conductivity.
- The research results of the thermal annealing effect on the properties of one-component Co, Cu, Zn nanotubes. A two-stage process of conducting properties changes is determined depending on the thermal annealing time.
- The simulation of ion beam scattering at the atomic structure of metallic nanotubes taking into account DC-60 accelerator features. Using Xe^{22} heavy ions with energies above 200 MeV allows conducting modification of the structural properties along the entire nanotubes length. The maximal Xe^{22+} ion radiation dose leading to their complete destruction was determined for Co, Cu and Zn nanotubes.

Practical significance of the research outcomes

Data about the electrochemical synthesis of metallic one- and two-component nanotubes with different aspect ratio, elemental composition, crystal structure can be used for the nanotechnology development, at the same time the used approaches in the experimental work correspond to the modern trends in the field of materials science. The heat treatment results of metallic nanostructures based on Co, Cu, Zn, as well as obtained resistance curves depending on the annealing time can be used to develop methods of targeted modification of nanostructured materials to improve their conductive properties. The data of the ionizing radiation effects on one-component nanotubes can later be used to develop a model describing the radiation effects formation in nanoscale materials and their influence degree on the structural and conductive properties, as well as the characteristics of products based on them.

Connection of the work with the plan of public research programs.

This work has been done in connection with scientific-research programs:

Joint project with the Brookhaven national laboratory and the Institute of Nuclear Physics of Ministry of Energetics of the Republic of Kazakhstan «Development of scientific principles of track-etched membranes application in modern materials science» according to the financing program of the International Scientific - Technical Center (Project K-2051).

Targeted funding program of the Ministry of Education and Science of the Republic of Kazakhstan «Development of new functional materials based on polyethylene terephthalate and polycarbonate track membranes, performance of fundamental, experimental and design researches on the use of new membrane types» № 561 from 07.04. 2015

055 «Scientific and/or scientific and technical activities», the routine 101 «Grant funding for research» according to the priority Sustainable use of natural resources, raw materials and production processing on the theme «Obtainment of magnetic nanomaterials based on polymer track membranes» under the contract №45 from «12» February 2015

Personal contribution of the PhD student. Preparation of template matrixes based PET membranes by chemical etching, as well as the selection of the optimal parameters of obtaining templates with cylindrical and asymmetrical (conical) pore geometry, electrochemical deposition of metal nanostructures under different deposition conditions, conducting researches of structural and conductive characteristics of the obtained nanostructures by scanning electron microscopy and energy-dispersive X-ray analysis are carried out by the author together with the staff of the Laboratory of Solid State Physics in the Astana subsidiary of the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. Theoretical mean free path calculations of the accelerated ions in metallic nanotubes and selection of the optimal parameters of ionizing radiation and heat treatment for the targeted modification of the structural characteristics were carried out by the author. At the same time every intermediate and final research result was discussed with the thesis supervisor, professor, K.K.Kadyrzhanov, co-supervisor, professor of the Physics Department of Moscow State University named after M.V.Lomonosov, doctor of physical and mathematical sciences V.S. Rusakov, Director of the the Astana subsidiary INP ME AF RK, associate professor M.V. Zdorovets, senior researcher at Scientific and Practical Materials Research Centre in Belarus, candidate of physical and mathematical sciences E.Y. Kanyukov.

Approbation of the thesis outcomes. The thesis results were presented at the 9th International Conference of Nuclear and Radiation Physics "INPC 2013" (Almaty, Kazakhstan, 2013), at the IX International scientific conference of students and young scientists "Science and Education - 2014" (Astana, Kazakhstan, 2014), at the 10th international conference «Ion implantation and other applications of ions and electrons» (city of Kazimierz Dolny, Poland), at the 19th International Conference «Ion Beam Modification of Materials», (Leuven, Belgium, 2014), at the XII International Conference «Advanced technologies, equipment and analytical systems for materials and nanomaterials», at VKTGU (Ust-Kamenogorsk, Kazakhstan, 2015), at the X International Scientific Conference of students and young scientists «Science and Education – 2015» (Astana, Kazakhstan, 2015), at the 11th International Conference «The interaction of radiation with solids» (WITT - 2015), (Minsk, Belarus, 2015), at the 9th international meeting «APCTP - BLTP JINR Joint Workshop Modern Problems of Nuclear and Elementary Particle Physics», (Almaty, Kazakhstan, 2015), at the 9th international symposium «Swift Heavy Ions in Matter», (Darmshadt, Germany, 2015), at the international conference "Physics of St. Petersburg - 2015" (Saint - Petersburg, Russian Federation, 2015), at the X International scientific conference "Youth in Science -2015" (Minsk, Belarus, 2015), at the 50th School PNPI on condensed matter physics "FCS - 2016" (Gatchina, St. Petersburg, Russian Federation, 2016), at the XI International scientific conference of students and young scientists "Science and education - 2016" (Astana, Kazakhstan, 2016), at the XIII International scientific conference "Solid State Physics" (Astana, Kazakhstan, 2016).

Publications. The main research results are published in 36 printed works which are full compliance with the dissertation theme: including 6 articles in peer-reviewed journals with non-zero impact - factor included in the Scopus and Web of Science databases, 2 patents, 11 articles in journals from the list approved by the Committee for education and science control of the MES, 17 abstracts and papers to the reports at international and national conferences.

Volume and structure of the thesis. The thesis consists of an introduction, five chapters, conclusion and list of references. In the concluding paragraphs of each chapter a brief summary is formulated. The thesis volume is 141 typewritten pages, including 75 figures, 23 tables and bibliography of 171 titles.