ANNOTATION

of dissertation for the Philosophy Doctor (PhD) degree at specialty «6D071000 – Materials science and technology of new materials» Nakysbekov Zhassulan on the topic **"The synthesis of copper nanoparticles by different methods and radiation modification of their structure"**

General description of work.

The dissertation work presents the results on the technology of obtaining ultradispersed particles (UDP) of copper by PVD methods in the plasma of a high-frequency capacitive discharge and electrolysis, the effect of electron irradiation on the size and structure of synthesized UDCs is investigated. For this purpose, experimental installations for electron irradiation of UDP of copper synthesized by different methods were developed, adjustment and physical start-up of the installation for irradiation were carried out. The effect of electron irradiation on the structural properties of UDP of copper was studied.

Relevance of the topic

Ultradispersed (UD) materials have attracted considerable attention over the past decades as they have the potential to be used as advanced materials with new electronic, thermal and mechanical properties for the future technology revolution. New materials include UD powders of metals, semiconductors, ceramics and polymers with sizes from 10 to 1000 nm. They can be classified into different classes based on their shape, size, or properties. UD particles can have unique physical and chemical properties due to their high specific surface area and structural features. The optical properties of metallic and semiconductor UDP significantly depend on their size, a change in which leads to coloration of optically transparent materials due to absorption of electromagnetic radiation in the visible region of the spectrum by free surface electrons of UD of metal particles (local surface plasmon resonance). Their reactivity, strength and other properties also significantly depend on their size, shape and structure. These characteristics make them suitable candidates for a variety of commercial and residential applications that include catalysis, medical applications, energy research, and environmental applications.

A huge amount of research has been devoted to the structural characteristics of UD particles, which are important both for understanding their properties, for optimizing the conditions for their manufacture and practical application. The most informative modern methods for studying the structure of UDP are such methods as transmission electron microscopy (TEM), X-ray diffraction, and photoelectron X-ray spectroscopy. It should be noted that electron and X-ray irradiation of UF particles can cause structural-phase changes in such materials, depending on parameters such as the energy and dose of the incident beam. Thus, these methods can be used not only as unique methods for studying the structure of UD materials, but also for modifying their structure and physicochemical properties for use in various industries. Although the effect of electron irradiation on solids has been the subject of intense study for a long time, systematic studies of the UD of particles are rare.

Of the large variety of UD of metal particles, a special place is given to UD of copper. Such UDCs of copper are promising in the field of ecology and biomedicine. UDP possess unique physicochemical, structural, and morphological characteristics that are important in a wide range of applications related to electronic, optoelectronic, optical, electrochemical, environmental, and biomedical fields.

At present, the synthesis of various UDP materials is an urgent task. Research in recent years has shown the possibility of obtaining ultrasonic particles of metals and their oxides, semiconductors, ceramics, polymers, etc. One of the promising methods for the synthesis of UD particles of copper is the cathode sputtering of a copper target in the plasma of a high-frequency capacitive discharge and the method of electrolysis. It has now been established that changes in the technological parameters of obtaining UDP of copper by cathode sputtering and electrolysis can be used to obtain UDP with a wide range of physicochemical properties; on the other hand, structural-phase transformations under electron irradiation with UDP of copper have not been practically studied.

The purpose of work

Obtaining UD of copper particles by methods of high-frequency cathodic sputtering and electrolysis and studying the possibility of radiation modification of their structure.

The tasks of research.

- Optimize technologies for the synthesis of ultradispersed copper particles by high-frequency cathode sputtering and electrolysis;
- To study the structure of ultradispersed copper particles obtained by methods of high-frequency cathode sputtering and electrolysis;
- Assemble the installation and develop a technique for irradiation of ultradispersed copper particles with electrons with an energy of 15 – 30 keV;
- Conduct research on the effect of electron irradiation with different energies and doses on structural changes in ultradispersed copper particles.

The subject of research is the synthesized UDP of copper and irradiated with electrons.

Research methods

The method of cathodic sputtering in the plasma of an RFC discharge and the method of electrolysis were used to synthesize UDP of copper; the main methods for studying the synthesized UDP of copper are energy dispersive analysis, X-ray diffractometry, scanning and transmission electron microscopy, optical microscopy, and small-angle X-ray scattering.

Scientific novelty of the work.

The scientific novelty and originality of the dissertation work lies in the fact that for the first time in it:

- it was experimentally established that the synthesis of ultradispersed copper particles with a developed surface occurs in a narrow range of variation of technological parameters (argon pressure 40 – 53 Pa, argon flow $1 – 1.5 \cdot 10^{-6}$ m^3/s and ion-plasma discharge power 150 – 200 W);

- it was shown for the first time that when ultradispersed particles of copper oxide are irradiated with electrons with an energy of 18 keV and a current density of 50 μA/cm^2, a chemical reaction occurs in which copper oxide (CuO) → copper oxide (Cu2O) at a dose of 0.8 MGy and copper oxide (Cu_2O) → metallic copper at a dose of 3.2 MGy, which is associated with the restructuring of the electronic shells leading to a change in the types of chemical bonds;
- it was shown for the first time that when ultradispersed copper particles are irradiated by a pulsed electron beam with an energy of 0.5 MeV and a current density of 60 A/cm^2 at a dose of 2.5 kGy, an increase in the lattice parameter is observed, in the dose range from 12 to 50 kGy the lattice parameter decreases;
- it was established for the first time that irradiation of ultradispersed copper particles with an electron beam with an accelerating voltage of 20 kV and a current density of 0.6 μA/cm^2 in the dose range of 40 – 60 kGy leads to a halving of the average crystallite size.

The practical significance of the study.

The results of the study can be directly applied to crushing the average size of crystallites in UDP of copper by the method of electron irradiation, which is confirmed by the received patent No. 34284 RK MPK B22F 9/04 (2006.01). The technological parameters of the method of cathode sputtering in an RF discharge plasma proposed in this work can be used to synthesize UDP of copper with a developed surface. Also, the experimental results on the irradiation of UDP of copper with electrons can be used to effectively control the size of the fcc lattice parameter of copper. In addition, the paper proposes a diagram of a device for irradiation with electrons and the irradiation parameters at which the phase composition of the UDP of copper oxide can be effectively controlled.

Main provisions to be protected:

I. At cathodic sputtering of a copper target in a high-frequency capacitive plasma discharge in a narrow range of technological parameters: argon pressure 40 – 53 Pa, argon flow 1 - $1.5 \cdot 10^{-6}$ m^3/s and plasma discharge power 150 – 200 W, ultradispersed copper particles with a developed surface.

II. Electron irradiation of ultradispersed copper oxide particles with electrons with an energy of 18 keV and a current density of 50 μA/cm^2 leads to chemical reactions: copper oxide (CuO) transforms into copper oxide (Cu_2O), and then into metallic copper (bypassing additional processes to reduce ultradispersed particles copper).

III. Efficient control of the size of the lattice parameter of ultradispersed copper particles is achieved by varying the dose of pulsed electron irradiation (pulse duration 100 ns, 1 pulse per 2 seconds) and a fixed electron energy of 0.5 MeV, current density 60 A/cm^2. At an irradiation dose D = 2.5 kGy, the lattice parameter a_0 increases by 0.04 %, in the dose range D = 12 – 50 kGy, the lattice parameter a_0 decreases to 0.13 %.

IV. When ultradispersed copper particles are irradiated with an electron beam with an energy of 20 keV and a current density of 0.6 μA/cm^2 in the dose range from 40 to 60 kGy, the crystallite size decreases from 55 to 25 nm.

The personal contribution of the author lies in the fact that the entire volume of the dissertation work, the choice of the research method, problem solving, and the modernization of the experimental setup were carried out by the author independently. The setting of tasks and discussion of the results were carried out jointly with the scientific advisers. The synthesis of UD copper particles and their irradiation with electrons, the study and analysis of structural changes were completely carried out by the author.

The reliability of results are confirmed by publications in editions recommended by the Committee for Control in the field of Education and Science of Ministry of Education and Science of the Republic of Kazakhstan and in the proceedings of international scientific conferences near and far abroad.

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

– Nakysbekov Z. et al. The change in the lattice parameter of Cu nanopowders under the action of a pulsed electron beam //International Journal of Nanotechnology. – 2019. – Т. 16. – №. 1-3. – С. 115-121.

– Nakysbekov Zh. T. et al. Synthesis of Copper Nanoparticles by Cathode Sputtering in Radio-frequency Plasma //Journal of Nano-& Electronic Physics. – 2018. – Т. 10. – №. 3;

– Накысбеков Ж.Т., Буранбаев М.Ж., Габдуллин М.Т., Айтжанов М.Б., Суюндыкова Г.С., Досеке У. Рентгеноструктурный анализ нанопорошка меди // Вестник КазНИТУ. – 2018. – №. 2. – С. 503;

– Накысбеков Ж.Т., Буранбаев М.Ж., Айтжанов М.Б., Суюндыкова Г.С., Шаймуханова А.Т., Габдуллин М.Т.. Влияния электронного пучка малой мощности на структуру нанопорошков меди // Вестник КазНИТУ. – 2017. – №. 4. – С. 246;

– Накысбеков Ж.Т., Мухамадиев Д.К., Бибатырова Л.К., Даму А., Нұрғали Е.Е. Особенности различий синтеза медных порошков и покрытий электрохимическом методом // Вестник КазНИТУ. – 2016. – №. 5. – С.586;

– Накысбеков Ж.Т., Буранбаев М.Ж., Айтжанов М.Б., Габдуллин М.Т. Изменение параметра решетки нанопорошка меди под действием импульсного электронного пучка большой энергии // Сборник тезисов IX ежегодной конференции НОР. –М. Россия, 2018. – С. 29;

– Buranbaev M., Yar-Mukhamedova G., Bozheyev F., Nakysbekov Zh., Aitzhanov M. Phase transition of hexagonal Be nanocrystal into cubic superlattice under X-ray radiation // 18th International Multidisciplinary Scientific GeoConference SGEM2018. – Albena, Bulgaria, 2018. –P. 393;

– Nakysbekov Zh.T., Buranbaev M.Zh., Gabdullin M.T., Aitzhanov M.B., Suyundykova G.S. Influence of low power electron irradiation on the structure of copper nanopowder // 9th International conference on Advanced Nanomaterials, Aveiru, Portugal, 2017;

– Buranbaev M.Zh., Embergenova K.R., Nakysbekov Zh. The radiographik analysis of the copper nanopowder irradiated by fast electrons // International scientific and practical conference World Science, - Dubai, 2015. – P.62;

– Накысбеков Ж.Т., Айтжанов М.Б., Тоганбаева А.К., Бегманов С.М., Мәді Д.Ө., Получение нанопорошков меди катодным распылением // Международная научная конференция студентов и молодых ученых «Фараби Әлемі".– Алматы, 2018;

– Накысбеков Ж.Т., Буранбаев М.Ж., Айтжанов М.Б., Мухамадиев Д.К., Габдуллин М.Т. Синтез наночастицы меди методом электролиза // IV Международная Научная Конференция «Современные проблемы физики конденсированного состояния, нанотехнологий и наноматериалов» (Сарсембиновские чтения)", Алматы, 10-12 сентября 2016.– С. 171-174;

– Накысбеков Ж.Т., Буранбаев М.Ж., Айтжанов М.Б., Мухамадиев Д.К., Габдуллин М.Т. Особенности формирования электролитических порошков меди и влияние электронного облучения на их размеры // IV Международная Научная Конференция «Современные проблемы физики конденсированного состояния, нанотехнологий и наноматериалов» (Сарсембиновские чтения)", Алматы, 10-12 сентября 2016. – С. 167-171.

– Способ радиационного дробления нанопорошков меди электронным пучком: пат. №34284 РК МПК B22F 9/04 (2006.01), B22F 1/00 (2006.01), B02C 19/18 (2006.01)/ Накысбеков Ж.Т., Буранбаев М.Ж., Габдуллин М.Т. и др. Патентообладатель КазНУ; заявл. 2018/0705.1; бюл. № 16-24.04.2020

Publications.

Based on the materials of the dissertation work, 18 printed works were published: 3 in journals from the CCFES List of the Ministry of Education and Science of the Republic of Kazakhstan to publish the main results of the dissertation for a PhD degree and 2 articles in journals with an impact factor included in the international information resource Scopus (Elsevier, Netherlands) 13 works in the materials of International scientific conferences and 1 innovative patent of the Republic of Kazakhstan.

The volume and structure of the thesis. The dissertation work consists of an introduction, 3 chapters, a conclusion and a list of used sources of 240 titles, contains 109 pages of basic computer text, including 73 figures and 7 tables.

The first chapter of the dissertation is devoted to a review of the literature and the formulation of the main scientific problem. Data on the general characteristics of methods for obtaining UD copper particles are presented here. It also describes the current state of research on the effect of radiation on the structure of UD materials.

In the second chapter of the thesis, experiments on the synthesis of copper particles by methods of cathode sputtering and electrolysis are presented, as well as recommendations for choosing the optimal technological parameters for obtaining ultradispersed copper particles.

The third chapter is devoted to experiments on irradiation of synthesized UD copper particles and a discussion of the main experimental results obtained and their analysis.