ANNOTATION

for the dissertation work on the topic

«**CREATION OF NEW COMPOSITE MATERIALS BASED ON DIAMOND-LIKE CARBON FILMS MODIFIED WITH PALLADIUM NANOPARTICLES**»

submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D074000 – "Nanomaterials and Nanotechnologies"

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The aim of the thesis. Development of scientific and technological bases of the synthesis of composite amorphous diamond-like carbon materials with isolated palladium nanoparticles, to identify new properties and create new multi-purpose materials.

The following tasks were implemented to achieve the assigned aim:

1. Development of technology for the synthesis of diamond–like carbon films with various degrees of hybridization of carbon bonds, identification of optimal parameters of the magnetron ion–plasma sputtering for structural-impurity modification of films using a combined target.
2. Study of the structural features of thin nanostructured diamond-like a-C<Pd> carbon thin films, synthesized at direct current and different values of ion-plasma discharge power, depending on palladium concentration;
3. Study of the optical properties of nanocomposite diamond-like a–C<Pd> films synthesized at different values of ion-plasma discharge power, determination of the effect of palladium concentration on optical constants values and the band gap of a-C<Pd> films;
4. Study of the electrical properties of nanocomposite diamond-like a–C<Pd> films depending on palladium concentration and ion-plasma discharge power;
5. Study of the effect of the negative bias voltage on the formation of the structure and properties of thin diamond-like a-C<Pd> films.

Research methods:

- elemental analysis and determination of palladium concentration in the synthesized films was conducted using EDAX device (AMETEC Materials Analysis Division, USA) by the EDS method.
- the microstructure, size estimation of metallic nanoparticles and their size distribution in the amorphous matrix were studied by transmission electron microscopy (TEM) on a JEOL JEM-2100F (Japan) facility.
- morphology and surface structure of the synthesized films were studied by scanning electron microscopy (SEM) on a Quanta 3D 200i (FEI Company, USA) installation.
- the morphology and phase contrast of the films surface were studied by atomic force microscopy (AFM) on NTegra Therma and Solver Spectrum (NT-MDT, Russia).

- the local structure of a-C<Pd> films was studied by Raman spectroscopy (RS) method on NTegra Spectrum (NT-MDT, Russia) using excitation laser radiation at wavelengths of 473 and 633 nm.

- optical transmission spectra of the synthesized samples were measured on a Lambda 35 double-beam optical spectrophotometer (Perkin-Elmer, USA).

- electrical properties of the synthesized a-C<Pd> films were studied on a Keithley 2000 digital multimeter.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge), presented for the defense:

1. Thin diamond-like carbon a-C<Pd> films represent a new composite material consisting of a matrix with sp^2/sp^3 hybridized bonds and isolated palladium nanoparticles. The palladium nanoparticles affect the formation of carbon bonds by increasing the number of sp^2 bonds, and at Pd concentrations more than 1 at.%, the film structure changes to a graphite-like phase.

2 The increase in Pd concentration from 0 to 2.34 at.% in a-C<Pd> films leads to the decrease in light transmission from 87% to 48%, respectively, which indicates an increase in the density of π electrons of sp^2 sites forming the top of the valence band. The optical bandgap of the synthesized a-C<Pd> films changes from 1.8 eV to 0.1 eV depending on the synthesis conditions and palladium concentration.

3 The electrical properties of diamond-like carbon films can be effectively controlled by changing the palladium concentration and synthesis conditions. Charge carrier transport is characterized by a percolation conduction mechanism, which depends on the discharge power (P) during synthesis and is determined by the percolation threshold in the concentration range from 0.12 to 0.39 at.% Pd as a function of P. At the synthesis regime P=14 W, changing the palladium concentration by 1.9 at.% leads to increase of films conductivity by 10^8.

Description of the key research results:

Amorphous DLC films with isolated nanoparticles of the non-carbide-forming element palladium were obtained for the first time. Identification of the influence of magnetron sputtering parameters and palladium nanoparticles concentration on the structure and properties of a-C films was performed.

It was found that at magnetron ion-plasma sputtering of combined target, palladium does not form chemical bonds with carbon, but enters the matrix as an independent element in the form of nanoclusters. The results of AFM revealed that the structure of DLC a-C<Pd> films is formed of globules. Application of mathematical processing of AFM images allowed to estimate the size of globules, which are 15-55 nm in films with palladium nanoparticles.

The influence of palladium nanoparticles on the formation of the local structure of DLC films was studied. Palladium nanoparticles act as a catalyst in the formation of carbon bonds and increase the number of sp^2 sites, and at Pd concentrations of more than 1 at.% the film structure changes to graphite-like

phase. In addition, the influence of the substrate on the formation of the structure of diamond-like a-C<Pd> films is revealed.

It is found that the optical bandgap of the synthesized diamond-like a-C<Pd> films decreases with increasing palladium concentration. This is explaind by the increase in the concentration of sp^2 sites and as a consequence of π electrons.

The study of the dark conductivity of DLC a-C<Pd> films revealed that an increase in the Pd concentration leads to a decrease in the distance between the conducting regions, which lowers the potential barrier of charge flow and significantly increases the conductivity.

Justification of the novelty and importance of the results obtained:

Composite amorphous DLC films with isolated palladium nanoparticles have been synthesized for the first time.

It has been established that controlling the modes and parameters of synthesis and impurity modification makes it possible to obtain amorphous DLC films with varying degree of hybridization of carbon bonds.

It has been shown that modification of DLC films with palladium leads to a significant change in the band gap. The percolation mechanism of conductivity in a-C<Pd> films was revealed.

Research in this direction is important for the development of nanotechnology of new materials and nanoelectronics. The established modes and parameters of magnetron ion-plasma sputtering make it possible to control the structural characteristics and electronic properties of diamond-like carbon films within a wide range.

Modified DLC a-C<Pd> films are nanocomposites with new properties and can be used as transparent matrices for photonic and plasmonic structures. The change in a wide range of optical properties of nanocomposite DLC a-C<Pd> films makes them a promising multifunctional material for the development of new sensor devices, devices for the reception and processing of optical signals.

Compliance with directions of science development or government programs.

The wide application of diamond-like carbon films in various fields is conditioned by such characteristics as high mechanical strength, high hardness, low friction coefficient, high resistivity, chemical inertness, associated with the peculiarities of the structure determined by the ratio of sp^2/sp^3 hybridized bonds.

Impurity modification of DLC films with atoms of non-carbide-forming elements can lead to the manifestation of new properties in the carbon matrix. The structure and electronic properties of composite films with impurities of non-carbide-forming metals can significantly differ from the properties of pure DLC films. Modification with palladium nanoparticles will reveal new physicochemical properties and phenomena that can be manifested by the isolated nanoparticles in DLC nanofilms and expand the field of their application.

The study in this direction is important for the creation of new nanocomposite materials that are used in opto- and nanoelectronics devices.

Dissertation work was carried out on the priority direction of science development: Geology, extraction and processing of mineral and hydrocarbon raw materials, technologies, safe products and structures and in the specialized scientific direction: Nanomaterials and nanotechnology new materials. Also the work was carried out in the framework of Grant financing projects AP05131495 "Creation of new composite materials based on carbon media with platinum group nanoparticles", 2018 – 2021, AP08855745 "Development of nanostructured composite materials based on silicon–containing amorphous diamond-like carbon films" 2020 - 2022.

The author's personal contribution

The statement of the aim and tasks of the dissertation work was carried out jointly with the scientific supervisor, Ph.D., Ryaguzov A.P. All experimental work on obtaining nanocomposite films was carried out by the author personally. The author personally measured optical and electrical properties. Experimental studies of the surface morphology and measurement of the Raman spectra of synthesized samples were carried out jointly with a research group of employees of the NNLOT al–Farabi Kazakh National University. The analysis of all the results obtained and presented in the thesis was discussed with the supervisor. The author jointly by the supervisor participated in the writing of scientific articles and testing research results during her participation in major-specific scientific events (conferences, seminars, round tables, etc.).

Description of the contribution of the doctoral student to the preparation of each publication.

The results of the dissertation are published in 16 articles, among them 4 – in international scientific journals (Q1, Q2 and Q3 quartile according to Journal Citation Reports of Clarivate Analytics and/or available in the database Scopus, percentile indicator according to CiteScore) 12 articles are in the proceedings of international research and practical conferences. The dissertator is the corresponding author of the main scientific articles written based on the results of conducted scientific research.

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3) Assembayeva A., Ryaguzov A.P., Nemkayeva R.R., Guseinov N.R., Myrzabekova M.M. Research of the structure of a-C<Pd> films by the Raman spectroscopy method// Materials Today: Proceedings 25 (2020) 58–63.

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