Theses: “PLASMA-CHEMICAL SYNTHESIS OF THIN FILMS OF GALLIUM OXIDE, ZINC OXIDE and CHALCOGENIDES of the As(S,Se,Te) and As-Se-Te SYSTEMS”

GENERAL DESCRIPTION OF WORK.

The relevance of the research topic and the degree of its development. Oxide inorganic semiconductor materials, in particular oxides of group (III) of the Periodic Table (or so-called "sesquioxides", E2O3), are of great interest, and, in fact, have been rediscovered as a new class of wide-gap semiconductors. One of the most promising representatives of this class of compounds is gallium oxide (Ga2O3), which has unique electrophysical properties. Another prominent representative of modern oxide semiconductor material is zinc oxide. The possibilities of zinc oxide were fully discovered only after the first possibilities appeared for obtaining new nanoobjects based on ZnO with the most diverse morphology, such as nanoparticles and nanorods in a dispersed state. In addition, methods have been developed for forming layers of nanoparticles and nanorods on various substrates. These structures, in turn, have shown their promise for possible use in the creation of luminescent devices, solar cells, and gas sensors. Among oxygen-free materials, chalcogenide thin films are still the objects of intensive scientific research. Chalcogenide layers are highly sensitive in the spectral range from UV to far IR and are widely used as sensor elements in thermal imagers, night vision devices, in infrared optoelectronics, as well as for the manufacture of lasers and LEDs operating in the middle and far IR ranges. Their important property is also the possibility of obtaining surface reliefs both with chemical treatment after and directly in the exposure process. Recording on layers of chalcogenide glasses using the phenomenon of photocrystallization is beginning to be used in modern optical information carriers. Another direction in the use of chalcogenide structures formed by plasma-chemical deposition is their use as materials for electronic and photoresists. The first and most important stage in the preparation of semiconductor thin films is the choice of an appropriate synthesis method. It is the film synthesis technology that is the determining factor affecting the chemical and structural homogeneity of the final material, as well as its impurity composition and, as a consequence, the functional properties of microelectronics materials. The common disadvantages of existing technological approaches are the chemical and structural homogeneity of the final material, the difficulty in obtaining materials of a well-defined stoichiometry in a wide range of compositions, poor reproducibility of results, the inability to control the change in electrical or optical properties by doping within a single vacuum cycle, and the complex scalability of processes. The foregoing suggests that the development of new scientific and technological foundations for obtaining transparent inorganic semiconductor materials is a very urgent task for the development of the entire modern industry of semiconductor devices and microelectronics. The relevance of the work is determined mainly by the creation of a new plasma-chemical method for the synthesis of modern transparent inorganic oxide and chalcogenide semiconductor materials and by comprehensive studies of both the plasma-chemical processes themselves and the properties of the obtained functional materials. The performed studies fill in the gaps in information on a number of practically important properties of the obtained thin films, and also determine the conditions for obtaining functional materials based on gallium oxide, zinc oxide and chalcogenides of the As-S, As-Se, As-Te, As-Se-Te systems. in low-temperature non-equilibrium plasma, which is relevant and timely. Also relevant is the development of physical and chemical principles of plasma-chemical synthesis of thin films of functional materials, conducting comprehensive studies of their structure and properties, identifying the possibility of using the obtained materials to modify existing and create new components of microelectronics. For the first time, a technological possibility has been proposed and demonstrated to combine the use of directly high-purity elements as the only precursors of inorganic synthesis, and low-temperature non-equilibrium RF discharge plasma at reduced pressure as an initiator of chemical transformations.

The aim of the work is to develop the scientific and technological foundations of the plasma-chemical method for the synthesis of modern inorganic semiconductor materials using the example of gallium oxide, zinc oxide and chalcogenides of the As-S, As-Se, As-Te, As-Se-Te systems in a low-temperature nonequilibrium RF discharge plasma at reduced pressure and the study of their physico-chemical properties**.**

Research objectives:

1. Development of technology for plasma-chemical synthesis of thin films of gallium oxide in complex reaction gas mixtures (Ga-O2-Ar), (Ga-I2-O2-Ar), (Ga-O2-H2-Ar), analysis and optimization of process conditions with with the aim of obtaining β-Ga2O3 films by heteroepitaxial growth that are close to epitaxial in their parameters,

2. Development of technology for plasma-chemical synthesis of thin films of gallium oxide doped with gallium nitride, zinc and aluminum directly in the process of plasma-chemical deposition in a wide range of compositions,

3. Development of a method for the plasma-chemical synthesis of nanostructured and epitaxial thin films of zinc oxide, study of process parameters and determination of the mechanisms of interaction of precursors in plasma,

4. Development of technology for plasma-chemical synthesis of thin films of chalcogenide systems As-S, As-Se, As-Te and As-Se-Te, establishing the influence of process parameters on their physical and chemical properties, in order to obtain final thin films of a certain stoichiometry of a high degree of chemical and structural homogeneity to create elements of integrated optics.

5. Development of a technology for the synthesis of thin films of the As-S system doped with ytterbium in a wide range of compositions under conditions of low-temperature nonequilibrium plasma using arsenic monosulfide, elemental ytterbium and high-purity sulfur as precursors in order to reveal the features of the structural and optical properties of the obtained samples**.**

Scientific novelty of the obtained results:

1. Plasma-chemical synthesis of thin films of gallium oxide in reaction gas mixtures (Ga-O2-Ar), (Ga-O2-H2-Ar) and (Ga-I2-O2-H2) was carried out for the first time. Possible mechanisms of reactions are proposed depending on the ratios of the initial substances in the gas phase and the power supplied to the plasma discharge. The possibility of obtaining both nanostructured polycrystalline and close to single-crystalline thin films of β-Ga2O3 in one stage, i.e. without subsequent annealing, under conditions of heteroepistecal growth. The β-Ga2O3 films, which are similar in structure to single-crystal films, have a roughness of about 0.64 nm and a full width of the rocking curve at half maximum of 6.5º.

2. For the first time, samples of thin nanostructured β-Ga2O3 films doped with nitrogen were obtained by plasma-chemical vapor deposition on c-sapphire substrates, with the GaN content varied from 0 to 10 wt %. %, zinc, in which the zinc content varied from 0 to 10 at.% and aluminum, where the aluminum content varied from 0 to 8 at.%.

3. For the first time, nanostructured and close to single-crystal thin films of zinc oxide were obtained using high-purity zinc as a source of zinc in a plasma-forming mixture (O2-H2) under conditions of low-temperature nonequilibrium RF discharge plasma. It is shown that within the framework of the proposed method of synthesis, it is possible to obtain various structures of zinc oxide - nanocolumns, nanoflakes, nanoflower beds, etc. by varying the settling conditions. For the first time, under conditions of heteroepitaxial growth, thin films of zinc oxide close to single-crystal with a full width of the rocking curve at half maximum - 1.0º were obtained by plasma-chemical deposition.

4. For the first time, chalcogenide films of the As-S, As-Se, As-Te and As-Se-Te systems were obtained by plasma-chemical vapor deposition under conditions of non-equilibrium low-temperature RF discharge plasma at reduced pressure by direct synthesis from the corresponding high-purity elements in a wide range of compositions. Their physico-chemical properties - surface morphology, structure, as well as transmission in different ranges of the spectrum - are determined. It is shown that the obtained materials have surface roughness at the level of 1-3 nm.

5. For the first time, chalcogenide films of the As-S system of various chemical compositions were obtained by the conversion of arsenic monosulfide in plasma, followed by doping with ytterbium at a level of 1-7 at.% directly in the process of plasma-chemical synthesis. It is shown that under conditions of plasma-chemical deposition, the formation of a structure from structural units (As2S2) is possible, which leads to a significant expansion of the transmission range of thin films of the As-S system from 1–12 microns to 1–20 microns due to the absence of intrinsic absorption lines of the As2S3 structural fragment.

Theoretical and practical significance of the research. This work creates the scientific basis for the creation of industrial technologies for the synthesis of thin films of gallium oxide, including nanostructured doped with gallium nitride, zinc and aluminum, nanostructured films of zinc oxide, chalcogenides of the systems As-S, As-Se, As-Te and As-Se- Te and, in general, is aimed at solving the problems of developing new methods for the synthesis of functional inorganic materials with desired properties. The obtained information about the properties of functional materials is in demand in scientific and technological processes in modeling, designing and creating new elements of microelectronics and IR optics.

1. A technology has been developed for direct single-stage plasma-chemical synthesis of polycrystalline nanostructured β-Ga2O3 films in Ga-O2-Ar and Ga-O2-H2-Ar reaction gas mixtures and β-Ga2O3 epitaxial films in a Ga-I2-O2-H2-Ar mixture under conditions heteroepitaxial growth.

2. A technology has been developed for the plasma-chemical synthesis of thin gallium oxide films nanostructured and doped with gallium nitride, zinc, and aluminum directly in the process of plasma-chemical deposition in a wide range of compositions.

3. A universal plasma-chemical method for the synthesis of nanostructured and epitaxial zinc oxide films has been developed, in which various structures can be obtained by changing the deposition conditions.

4. A plasma-chemical technology has been developed for the synthesis of chalcogenide thin films of the As-S, As-Se, As-Te and As-Se-Te systems under conditions of non-equilibrium low-temperature plasma of an RF discharge from high-purity elements in a wide range of compositions, which makes it possible to obtain materials of high chemical and structural homogeneity and roughness up to 3 nm.

5. A technology has been developed by doping As-S thin films with ytterbium at a level of 1-7 at.% directly in the process of plasma-chemical synthesis.

Methodology and research methods. To study the regularities and features of the physicochemical principles of the formation of functional thin films based on gallium oxide, zinc oxide and As-S, As-Se, As-Te and As-Se-Te chalcogenide systems, to study their structure and properties, the following methods were used research: optical emission spectroscopy, probe diagnostics, scanning electron microscopy; mass spectrometry; atomic force microscopy; Raman spectroscopy; IR spectroscopy; energy dispersive X-ray spectroscopy; x-ray phase analysis; differential scanning calorimetry; quantum chemical calculations**.**

The object of research was the plasma-chemical synthesis of inorganic semiconductor thin films based on gallium oxide, ZnO and chalcogenide systems As-S, As-Se, As-Te and As-Se-Te with different stoichiometry and morphology:

- thin polycrystalline and epitaxial films of gallium oxide obtained with different composition of plasma-forming mixtures, including alloyed with gallium nitride, zinc and aluminum;

- nanostructured and epitaxial zinc oxide films deposited at various parameters of the plasma-chemical process;

- thin amorphous films of the As-S system, synthesized from elemental arsenic and sulfur, as well as by conversion of As4S4, in plasma, including those doped with ytterbium;

- amorphous thin films of chalcogenide systems As-Se, As-Te, and As-Se-Te obtained from the corresponding elements**.**

The key scientific problem, which the dissertation is aimed at solving, is the creation of scientific and technological foundations for a new method for the synthesis of inorganic semiconductor materials based on a combination of plasma initiation of chemical transformations under conditions of a non-equilibrium low-temperature inductive RF discharge at reduced pressure and the use of high-purity elements as starting materials, to create the element base of domestic microelectronics, IR optics and photonics based on thin films of gallium oxide, ZnO and chalcogenides of the As-S, As-Se, As-Te and As-Se-Te systems**.**

The main results and provisions submitted for defense:

1. Experimental data and theoretical provisions, which together form the physicochemical foundations of the plasma-chemical technology for the synthesis of thin films of gallium oxide, zinc oxide and As-S, As-Se, As-Te and As-Se-Te chalcogenides,

2. The results of the study of the physicochemical properties of thin films of gallium oxide, zinc oxide, as well as chalcogenides of the As-S, As-Se, As-Te and As-Se-Te system.