ABSTRACT

of the dissertation on the topic

"STRUCTURE AND PHYSICAL PROPERTIES OF NEW SEMICONDUCTOR MATERIALS BASED ON COMPLEX OXIDE SYSTEMS FOR PHOTOELECTROCHEMICAL CELLS"

submitted for the degree of Doctor of Philosophy (PhD)

in the specialty

6D071000 (8D07110) – "Materials Science and Technology of New Materials"

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General characteristics of the dissertation research. The dissertation presents the results of an experimental study of the structure and photoelectrochemical properties of thin films of the complex copper-bismuth oxide system modified with metal admixtures.

Relevance of the research topic.

Photoelectrochemical cells (PECC) are devices designed to convert solar energy into electrical energy using photoelectrochemical reactions. Unlike traditional solar panels, which operate based on the photovoltaic effect in semiconductor structures, PECC function through electrochemical processes that enable the generation of electric current.

The operation of PECC is based on the ability of photosensitive materials (TiO_2, ZnO, CdSe, and others) to absorb solar radiation. This leads to the formation of electron-hole pairs, whose separation and transport within a closed electrolytic system are accompanied by redox reactions, resulting in the generation of electric current.

One of the key advantages of PECC is their environmental safety — the use of solar energy and chemical reactions without harmful emissions makes PECC a sustainable and renewable energy source. Unlike traditional silicon-based cells, PECC demonstrate high efficiency even under diffuse or low-light conditions, which broadens their range of applications, including low-light environments. An additional advantage is the simplicity of PECC manufacturing using low-cost processes, including printing and chemical deposition methods, as well as the potential for scalability and integration with various devices.

These properties determine the wide range of applications for PECC, including solar-to-electricity conversion (e.g., in TiO_2-based cells such as Grätzel cells) and hydrogen production through photoelectrochemical water splitting — one of the most promising directions in hydrogen energy. Current research focuses on developing efficient materials capable of enhancing the performance of this process.

For a considerable period, metal oxides (TiO_2, ZnO, SnO) and perovskites containing methylammonium (CH_3NH_3), a metal cation (most commonly Pb^{2+}), and a halide (I^- or Br^-) were considered the most promising compounds for PECC. However, despite their high efficiency, the practical application of these compounds is limited by two significant factors. First, their toxicity, primarily due to the presence of lead, poses a potential risk to the environment and human health. Second, their low thermodynamic and chemical stability: under the influence of

ultraviolet radiation, moisture, and temperature fluctuations, perovskite materials are prone to rapid degradation, significantly reducing their performance and reliability under practical conditions. In light of this, ongoing research aims to discover alternative compounds with a similar electronic structure but without these drawbacks.

One of the current directions in developing materials for PECC is the use of bismuth-containing compounds, which exhibit photoelectric properties comparable to traditionally used semiconductors based on tellurium, cadmium, or lead, while offering enhanced chemical stability and environmental safety. Among these, the complex oxide compound $CuBi_2O_4$ is of particular interest as a promising material for photocathodes in PECC due to its optimal band gap width (1.6–1.8 eV) for solar energy absorption in the visible spectrum, high thermal and chemical stability, non-toxicity during production and use, as well as the availability and low cost of the initial reagents.

An analysis of theoretical studies suggests that PECC with a $CuBi_2O_4$ photocathode can potentially achieve a solar energy conversion efficiency of up to ~24%. However, an examination of experimental results indicates that achieving the calculated values of photocurrent and quantum efficiency in practice remains challenging.

This is due to the fact that the diffusion length of charge carriers in $CuBi_2O_4$ (10–52 nm) is much shorter than the light penetration depth, while the values of mobility ($1.2 \cdot 10^{-3}$ cm^2 V^{-1} s^{-1}) and carrier lifetime (32–819 ns) are relatively low, while the possible presence of intrinsic defects promotes increased charge carrier recombination. One of the effective approaches to addressing this problem is the introduction of controlled admixtures into $CuBi_2O_4$ films, as well as their surface structuring. Therefore, considering the above, the development of a simple technology for producing and modifying photosensitive thin semiconductor $CuBi_2O_4$ films, along with the study of their structure and photoelectrochemical properties, is an important fundamental and applied challenge in materials science.

The aim of the dissertation was to study the structure and photoelectrochemical properties of thin films of the complex copper-bismuth oxide system $CuBi_2O_4$, modified with silver (Ag) and platinum (Pt) admixtures, for their application in photoelectrochemical cells.

Research objectives:

– To develop and optimize the technology for obtaining thin films of the complex copper-bismuth oxide system $CuBi_2O_4$ using the electrodeposition method, followed by structural modification through the introduction of silver (Ag) admixtures via electrochemical co-deposition and surface modification with platinum (Pt) nanoparticles.

– To study the structure of thin $CuBi_2O_4$ films, as well as $CuBi_2O_4$ films after composition modification with silver (Ag) admixtures and surface modification with platinum (Pt) nanoparticles, using spectroscopic and diffraction methods.

– To investigate the photoelectrochemical properties of thin films of the complex copper-bismuth oxide system before and after their modification.

– To explore the potential of using thin $CuBi_2O_4$ films, as well as $CuBi_2O_4$ films after composition modification with silver (Ag) admixtures and surface modification with platinum (Pt) nanoparticles.

Object of the research. Thin films of the complex copper-bismuth oxide system with the composition $CuBi_2O_4$, obtained by electrochemical deposition, as well as $CuBi_2O_4$ films modified with silver admixtures through co-deposition and platinum nanoparticles on the surface using the dip-coating method.

Subject of the research. The composition, structure, and photoelectrochemical properties of thin films of the complex copper-bismuth oxide system, modified with silver admixtures within the matrix and platinum nanoparticles on the surface.

Main provisions submitted for defense:

1. The fabrication of thin films based on the complex copper-bismuth oxide system ($CuBi_2O_4$) modified with silver, with a controlled structure, was achieved through a one-step process using co-electrodeposition. In $CuBi_2O_4$(Ag) films, silver partially integrates into the crystal lattice, substituting bismuth atoms, and is also present on the surface of the $CuBi_2O_4$ films in the form of a mixture of Ag_2O and Ag–O oxides.

2. Effective surface modification of $CuBi_2O_4$ films with platinum was achieved using an optimized dip-coating method with H_2PtCl_6. This process results in the formation of needle-like platinum structures on the surface of $CuBi_2O_4$ films, with lengths of approximately 100–200 nm and diameters of up to 40 nm, in a chemical state of Pt^0, without forming bonds with the matrix.

3. A significant increase in the quantum efficiency (by a factor of 4) of photocathodes based on thin films of the complex copper-bismuth oxide system $CuBi_2O_4$ is achieved by modifying the film matrix with silver at concentrations up to 1 at.%.

4. Surface modification of thin films of the complex copper-bismuth oxide system $CuBi_2O_4$ with platinum nanoparticles (up to 10 at.%) using the dip coating method significantly increases hydrogen output (by a factor of 7) in the photocatalytic process.

Experimental and theoretical research methods. The composition and structure of the films were investigated using energy-dispersive spectroscopy (EDS), electron diffraction, scanning electron microscopy (SEM), Raman spectroscopy. High-resolution X-ray photoelectron spectroscopy (HR XPS) was employed to analyze the chemical states of elements, while PEC (photoelectrochemical) methods were used to study the photoelectrochemical properties of the films.

Scientific novelty of the work lies in the following:

1. For the first time, a one-step electrochemical method for the fabrication of thin $CuBi_2O_4$ films modified with silver was developed. It was established that silver atoms partially substitute bismuth atoms within the crystal lattice and simultaneously exist on the surface in the form of oxide phases (Ag_2O and Ag–O).

2. An optimized method for surface modification of $CuBi_2O_4$ films with platinum using the dip coating technique with H_2PtCl_6 as a precursor was proposed and implemented. This method ensures the formation of needle-like nanostructures of metallic Pt^0 on the surface, which do not chemically interact with the matrix.

3. For the first time, it was demonstrated that doping thin $CuBi_2O_4$ films with silver at concentrations up to 1 at.% leads to a fourfold increase in the quantum efficiency of photocathodes. The enhancement of photoelectrochemical activity is attributed to the substitution of Bi^{3+} ions with monovalent silver Ag^+, accompanied by the formation of anion vacancies, an increase in hole concentration, and a reduction in the recombination rate of charge carriers.

4. It was established for the first time that surface modification of $CuBi_2O_4$ films with Pt nanoparticles at concentrations of up to 10 at.% provides a sevenfold increase in hydrogen output during the photocatalytic process. This enhancement is due to the increased interfacial activity and catalytic efficiency of platinum.

Relation of the dissertation to research programs. The dissertation was carried out within the framework of research work under the grant funding program for scientific research of the SC MES RK on the topics: AP05130392 "Improving the energy efficiency of photoelectrochemical solar cells through the use of new semiconductor materials" (2018–2020), AP08856338 "Photoelectrochemical solar cells based on thin-film semiconductor bismuth compounds" (2020–2022).

Approbation of the work. The results of the dissertation were presented and discussed at seminars of the DCMPTP KazNU named after al-Farabi and at 15 international scientific conferences, including: the 70th Annual Meeting of the International Society of Electrochemistry (ISE), "Electrochemistry: Linking Resources to Sustainable Development" (Durban, South Africa); the Joint Conference "Electron Beam Technologies and X-ray Optics in Microelectronics" (Chernogolovka, Russia); the III International Scientific and Practical Conference "Topical Issues of Electrochemistry, Ecology, and Corrosion Protection" (Tambov, Russia) — the presentation was awarded in the category "Exquisite Experimental Technique"; the 6th, 7th, 8th, 10th, and 12th International Conferences on Nanomaterials and Advanced Energy Storage Systems (Almaty/Nur-Sultan, Kazakhstan) — in 2020, the presentation was awarded the title of "Best Poster Presentation", and other international scientific forums.

A total of 25 publications have been produced based on the dissertation materials, including 4 publication in journals indexed in Scopus and Web of Science (2 articles (Q2-Q3) + 2 proceedings), 5 publications (including 1 patent) in editions recommended by the Committee for Quality Assurance in Education and Science; 15 publications in international conference proceedings.

The reliability and validity of the obtained results are due to the research being conducted on modern certified equipment using modern techniques. Based on the research results, a patent for utility model No. 4771 was obtained, 11.03.2020, "A method for manufacturing a composite copper-bismuth oxide electrode for photoelectrochemical applications".

Practical significance of the research.

The study demonstrated a fourfold increase in photocurrent density using the obtained $CuBi_2O_4$(Ag) thin films of the complex copper-bismuth oxide system, as well as a sevenfold increase in hydrogen yield using $CuBi_2O_4$/Pt films when employed as photoelectrodes in photocatalytic processes. Based on the developed technologies and the analysis of the obtained results regarding the structure of

$CuBi_2O_4$ thin films and their modified analogues $CuBi_2O_4$(Ag) and $CuBi_2O_4$/Pt, it can be concluded that these materials can be effectively used as photoelectrodes in photoelectrochemical and photocatalytic processes. This finding is significant for advancing both the fundamental and applied aspects of materials science and the technology of new materials.

Personal contribution of the author.

The author, as part of the research team, developed the technology for producing and the methodology for admixture and surface modification of thin films of the complex copper-bismuth oxide system ($CuBi_2O_4$). The author conducted studies of the structure, composition, and photoelectrochemical properties of $CuBi_2O_4$ thin films before and after composition and surface modification, using spectroscopic and diffraction methods. The author personally examined the structure using X-ray photoelectron spectroscopy (XPS) and performed data analysis for results obtained using SEM, electron diffraction, XPS, Raman spectroscopy, and PEC methods. The thesis statements, main results, and conclusions were formulated jointly with scientific supervisors.

Volume and structure of the dissertation.

The dissertation contains a list of designations and abbreviations, an introduction, the main body of four sections, a conclusion and a list of references. The volume of the dissertation is 138 pages of typewritten text, including 50 figures, 18 tables and 219 references.