ANNOTATION

of dissertation for the Philosophy Doctor (PhD) degree at specialty «6D071000 – Materials science and technology of new materials» Yermukhamed Dana on the topic

"Optical and structural properties of microstructured silicon obtained by metal-assisted chemical etching"

General description of work. The investigation of physicochemical properties and use of microstructured materials for alternative energy applications is one of the key priority areas for development of modern materials science. The present PhD thesis is devoted to the investigation of structural and optical properties correlation of the microstructured silicon for use in hydrogen energy applications. The influence of morphology and optical properties of silicon microstructures obtained by metal-assisted chemical etching on hydrogen generation efficiency during their interaction with water and water-alcohol solutions is considered. As a practical application, it has been shown that investigating structures can be successfully used for the efficient generation of hydrogen both due to chemical reaction of structures surface oxidation and due to photocatalytic reactions on the oxidizing surface.

Relevance of the topic. The presence of nanostructured materials uncharacteristic physical properties that differ from bulk materials make them promising materials for various applications. Researchers are particularly interested in semiconductor nanomaterials, since they are the main material of modern electronics, integration with which play integral part of successful application in many directions. Among the semiconductor materials, silicon micro- and nanostructures are one of the most frequently investigated materials, the application area of which extends from nanoelectronics to biomedicine. Although to date, hundreds of various reviews have published by authoritative scientific publications describing the various properties of silicon micro- and nanostructures, but questions regarding the correlation of structural features with their physical properties for the purpose of precise control in various applications remain open.

It is also worth noting that silicon micro- and nanostructures can be obtained by inexpensive and easy-to-use method of metal-assisted chemical etching, attracting more and more attention of researchers in recent years. The method of metal-assisted chemical etching is one of the methods of reducing silicon materials size, which suitable for use in industrial scale, which makes the materials obtained by this method even more attractive from practical point of view.

One of the promising applications of silicon micro- and nanostructures is hydrogen energy, based on molecular hydrogen application as a fuel. As the share of alternative energy in consumed electricity production becomes more and more every year, there is constant search for new materials to obtain available energy, as well as optimization of existing technologies. Successes in the development of number hydrogen technologies (such as fuel cells, hydrogen transport systems, metal hydride systems, and many others) indicate that hydrogen application in some cases is economically feasible now. Microstructured silicon can also serve as promising material for hydrogen energy, since this material is inexpensive, chemically active, and has number of other unique properties. Currently, photocatalytic properties of silicon micro- and nanostructures and their application for the decomposition of water and generation of molecular hydrogen investigating. Also, by using photodegradation of unsuitable water for drinking and irrigation of water into the constituent gases hydrogen and oxygen, and then reduction in liquid phase, inexpensive chemical water treatment reactors can technically be realized.

Taking into account the above mentioned, it is clear that investigating to study in detail the structural properties and their effect on other physical properties of silicon microstructures with the aim of using them for hydrogen generation is today an urgent task for both modern materials science and hydrogen energy in whole.

The purpose of work is to determine optimal conditions for silicon microstructures formation and identify patterns of structural and optical properties influence of the investigated microstructures on hydrogen generation efficiency during the reactions of their interaction with water and aqueous solutions for application in hydrogen energy.

The tasks of research. To achieve this goal, the following tasks were set:

- to investigate the formation of silicon microstructures features on silicon single crystal plate surface of p- and n-type conductivity by metal-assisted chemical etching method;

- to investigate structural properties of silicon microstructures, morphology of their surface and chemical composition of the surface layers;

- to investigate optical properties of silicon microstructures and their relationship with structural features;

- to investigate the dependence of hydrogen generation efficiency on morphology and optical properties of silicon microstructures.

Research objects are silicon microstructures.

Research subject are the regularities of morphology and optical properties influence of silicon microstructures on the hydrogen generation efficiency during their interaction with water and aqueous solutions.

Research methods. The physicochemical properties of silicon microstructures obtained by metal-assisted chemical etching were investigated using the following methods: scanning electron microscopy, spectrophotometry, IR spectroscopy, Raman spectroscopy, X-ray absorption near edge spectroscopy. The amount of generated hydrogen during interaction of investigated silicon microstructures with water and aqueous solutions was measured using gas chromatography.

The scientific novelties of work are that for the first time:

- it was experimentally shown for the first time that porous layer is formed at the base of highly doped n-type silicon microstructures, the presence of which leads to increase in the hydrogen generation efficiency by average of 2 times compared with application of low-doped n- and p-type microstructures due to increase in the specific area of active passivated surface.

- for the first time, the method of X-ray absorption near-edge spectroscopy was used to measure the absorption spectra of X-ray synchrotron radiation near the absorption edge of silicon $L_{2,3}$ and the absorption edge K oxygen of silicon microstructures obtained by metal-assisted chemical etching method of along their entire length, which made it possible at depth of up to 10 nm to more accurately determine the elemental and phase composition of the surface layers of silicon microstructures.

- the relationship between structural and optical properties of vertically oriented arrays of silicon wire-like microstructures detailed investigation was made, the dependence of total reflection coefficient from geometric parameters of silicon microstructures layers obtained by metal-assisted chemical etching in a wide spectral range of 250-2200 nm was studied and explained.

- the mechanisms of hydrogen generation during the interaction of vertically oriented silicon microstructures with water under illumination with white LED source are considered for the first time. It has been experimentally established that the hydrogen generation occurs as result of complex process consisting mainly of silicon microstructures surface oxidation and parallel photoinduced decomposition of water molecules on suboxide groups SiO_x (where $1.3 < x < 1.7$).

Main provisions to be protected

1. In the process of metal-assisted chemical etching of high-alloyed ($n \geq 10^{20}$ cm^{-3}) silicon monocrystalline n-type wafers in a solution of 5M HF: H_2O_2 (30%) at volume ratio (10:1) within 10 minutes additional layer is formed porous silicon with thickness of 2.8 ± 0.1 μm between the synthesized layer of vertically oriented silicon microstructures and initial substrate, the presence of which leads to two time increase in the efficiency of hydrogen generation in comparison with low-alloyed microstructures, where additional porous layer does not form.

2. For the first time, the structure and phase composition of vertically oriented silicon microstructures obtained by metal-assisted chemical etching along their entire length was investigated by X-ray absorption near-edge spectroscopy, which made it possible to determine the presence of active suboxide groups $SiO_{1.3}$ and $SiO_{1.7}$, the presence of which leads to increase in the efficiency of photoinduced hydrogen generation in the interaction of these structures with water.

3. Silicon microstructures obtained by metal-assisted chemical etching are characterized by low values of total light reflectance (R) 1-6% in the UV region of spectrum (250-400 nm), which is due to the effect of multiple reflections from the walls of vertically oriented SMs and further absorption in structure, and high values of R (80-90%) in the IR region (900-2000 nm) due to the contribution of Mie scattering.

4. The generation of molecular hydrogen during the interaction of highly doped n-type silicon microstructures with water under illumination with 20 mW/cm^2 LED white light source occurs due to complex of reactions: oxidation of the microstructures surface and photoinduced decomposition of water molecules, catalyzed by silicon suboxide layer SiO_x (where $1.3 < x < 1.7$).

Theoretical and practical significance of the work lies in the fact that investigations results of silicon microstructures structural and optical properties presented in this work are important contribution to the development of ideas about physical processes in microstructured semiconductor materials. The practical significance of research lies in the possibility of using microstructured silicon in hydrogen generation processes for application in hydrogen energy, as well as for cleaning dirty water.

Personal contribution of the author. Author took part in all main stages of research work: do experiments on obtaining silicon microstructures by metal-assisted chemical etching method, spectroscopic measurements, experiments on measuring and determining the amount of hydrogen released during chemical reactions between investigated structures and aqueous solutions, analysis and data processing. The measurements were carried out at the Faculty of Physics and Technology of al-Farabi KazNU, as well as during internships at the Leibniz Institute of Photon Technologies (Jena, Germany).

Approbation of work. The research results presented in this paper were reported at International conferences: “Modern advances in physics and fundamental physical education” (Almaty, Kazakhstan, 2016), 17th International multidisciplinary scientific geoconference SGEM-2017 “Nano, bio, green and space-technologies for a sustainable future. ” (Albena, Bulgaria 2017), X International Student Conference “Modern Global Trends: Challenges and Risks for Central Asia” (Almaty, 2018), V International Scientific Conference “Modern Problems of Condensed Matter Physics, Nanotechnology and Nanomaterials” (Almaty, 2018), 19th International multidisciplinary scientific geoconference SGEM-2019 "Nano, bio, green and space-technologies for a sustainable future" (Albena, Bulgaria 2019).

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.

Publications. The main results of work are presented in 13 scientific publications, of which 3 articles are published in international peer-reviewed journals (Scientific reports IF-4.011; Materials Research Express IF-1.449; Brief Communications on Physics, LPI IF-0.325.); 3 articles in journals recommended by Committee for Control in the field of Education and Science of Ministry of Education and Science of the Republic of Kazakhstan - “Bulletin of the NAS RK”, “physical and mathematical” series, “chemistry and technology” series and “Journal of evolution problems of the open systems”; 7 works in the proceedings of international conferences.

Relationship of the thesis topic with the plans of scientific works. The dissertation was partially done in accordance with the plans of research grant funded by the Ministry of Education and Science of Republic of Kazakhstan for 2018-2020 yy.: “Development of optimization methods focused on wide class of applied nanotechnology problems”, IRN No. AP05133366.

Structure and volume of the thesis. The dissertation is written on 101 pages of typewritten text and consists of an introduction, three sections, conclusion and list of used sources, contains 57 figures and 1 table. The list of used sources includes 123 items.

The first chapter of dissertation is devoted to literature review and main scientific task formulation. It provides data on general characteristics of silicon micro- and nanostructures, on their physical properties, obtaining methods by "top-down" and "bottom-up" approach, as well as on their use as materials for hydrogen energy. Also describes the current state and problems of hydrogen energy, gives description of the basic principles of hydrogen operation systems.

Obtaining method of investigated silicon microstructures samples, as well as the measuring techniques used in research described in the second chapter of dissertation. The silicon microstructures formation technology by metal-assisted chemical etching of monocrystalline silicon is described. Also, the second chapter described measuring techniques for investigating transmission, reflection, Raman spectra and methods of scanning electron microscopy, X-ray absorption near edge spectroscopy and gas chromatography.

The third chapter is devoted to discussion of the main obtained experimental results and their analysis.

In the dissertation work, optimal conditions for the formation of silicon microstructures were experimentally determined and regularities of the influence of investigated microstructures structural and optical properties on the efficiency of hydrogen generation in the reactions of their interaction with water and aqueous solutions for use in hydrogen energy were determined and following main results were obtained:

1. The influence of metal-assisted chemical etching formation conditions on the structure of resulting silicon microstructures and morphology of their surface has been investigated in detail. It has been found that the growth rate of SMs on n-type substrate is 3.5 times higher than the etching rate of p-type silicon single-crystal substrate. It varies in the range of 0.8-0.9 ± 0.01 μm/min and 1.1-1.4 μm/min ± 0.01 for SMs obtained by silver deposition for 15 and 30 seconds, respectively.

2. It was determined that the volume ratio of 10:1 for 5M HF and H_2O_2 (30%) is the optimal composition of electrolyte for MACE, in which etching occurs more intense dissolution of silicon and formed vertical oriented microstructures.

3. It was found that for SMs obtained on n-type silicon, increase in porosity is observed with increase in etching time. The porosity of SM samples increases from 40±4% at MACE time of 5 minutes to 50±5% at etching time of 10 minutes. The optimal time for silver nanoparticles deposition for obtaining SMs on n-type silicon is 15 seconds.

4. It is shown that the total reflection coefficient of light in UV region of spectrum in SMs obtained by MACE method for all samples remains low in the range of 5-7%, and in the visible region observed coefficient increasing due to increase in diffuse reflection component. This is due to light localization effect of caused by

multiple reflections from the walls of vertically oriented SMs and further absorption in the structure. The increase in reflection in IR region is explained by the contribution of Mie scattering.

5. From Raman spectra analysis of the SMs, it was found that with increase in SM length, increasing of the main silicon peak shift to the low-frequency region, from 520 cm^{-1} to 500 cm^{-1}, is observed, which indicates the presence of new chemical bonds on the structures surface due to surface passivation. Also, increase in the main Raman peak half-width with increase in the SM layer thickness indicates the formation of less ordered phase in the SM structure. The observation of quasi-amorphous phase in Raman spectra is associated with the processes of oxidation SM surface to silicon dioxide. On average, this process occurs at approximately the same rate for all investigated experimental samples.

6. It has been shown experimentally that during SMs growth on the surface of highly doped n-type substrates, porous silicon layer is additionally formed between SM array and silicon substrate. Thus, the specific area of active surface of the silicon microstructure increases. The presence of such developed surface in highly doped silicon microstructures leads to increase in the amount of generated hydrogen upon the interaction of SM with water ~ 2 times in comparison with SM on the surface of low-doped n-type silicon. The large yield of hydrogen occurs presumably due to passivating Si-H bonds rupture on the SM surface.

7. According to the XANES investigation results of SM surface the local arrangement of silicon and oxygen atoms indicates the presence of uniform silicon suboxide (SiO_x) film with thickness of no more than 10 nm on the surface of SM upper layer and in the lower part of structures close to the substrate. This confirms assumption that the hydrogen generation during interaction of SM with water is also carried out due to the reaction of photoinduced decomposition of water on the SiO_x surface. The contribution of the photocatalytic decomposition of water due to the presence of silicon suboxide SiO_x to the hydrogen generation process is lower than surface oxidation process, since silicon suboxide is unstable and nowadays takes on stable stoichiometric form of SiO_2.

8. It is shown that silver mirror reaction can be successfully used to maximize the coverage of developed surface of silicon microstructures obtained by metal-assisted chemical etching.

9. It was found that after MACE, residual silver particles are present in the silicon microstructures arrays, their presence increases hydrogen generation for ~ 10% during white light illumination. In this case, silver nanoparticles act as additional scattering centers. It has been shown experimentally that the hydrogen generation upon SM interaction with water in the dark occurs due to the SM surface oxidation, and under illumination not only due to oxidation, but due to the charge transfer process.