1. Introduction

An analysis of the present state of ecological situation in Ukraine displays a trend to deterioration. The rapid pace of modern technological development has caused a significant increase in the consumption of energy resources. Energy sector is the basis for the development of all the sectors of industry. At the same time, energy sector is one of the main sources of adverse impact on the environment, such as hydro-, atmo-, and lithosphere. About half amount of anthropogenic greenhouse gas emissions and harmful substances are produced by sector of traditional energy.

On the other hand, Ukraine meets its needs in energy sector only by 70 %, that is, it is an energy dependent state. In terms of resource provision, sufficiency and reliability of electricity and heating supplies that meet the growing needs of economy and population are of paramount importance, in terms of quality of life, a crucial problem is ecologically friendly energy production. Aspects of the energy sector are a key global challenge, the nature of which directly influences not only the construction of the global economy and strategies for the development of the state, but also overcoming the environmental crisis. Hence is the relevance of finding new ways of supplying the humankind with energy.

The most promising method of alternative energy sector is the photovoltaic method of converting solar energy due to its evident advantages:

- ability to use concentrated solar radiation;
- absence of noise;
- operation simplicity;
- environmental friendliness, etc.

Shortcomings of using solar energy most often include the following: high cost of solar panels, generation of electricity only during daylight hours, dependence on climatic conditions, need for large areas for the installation of photovoltaic power plants, problems with energy accumulation; imperfection of technology and low efficiency, etc.

The imperfection of technology of creation of photovoltaic modifiers (FEM) and their low performance efficiency are major restraining factors to global replacement of traditional energy with renewable energy. Thus, there is a need for the development of innovative technologies that can improve performance efficiency and other electro-physical characteristics of solar panels.

At the modern level of production, manufacturing silicon solar elements with a total capacity of 100 GW requires not less than 1 million tons of silicon of high purity degree [1]. To achieve the expected capacity of the solar photoenergy sector by 2030 [2], it is necessary to produce pure silicon in the amount not less than 20 thousand tones annually, which is not only complicated technological and financial, but also ecological problem, because obtaining pure silicon is an environmentally harmful production. Another shortcoming of traditional silicon solar elements is relatively low energy efficiency – on average, about 11 % [1]. The use of nanostructures would allow a significant improvement of characteristics of photovoltaic modifiers.

The relevance of the research is predetermined by the necessity of solving environmental and resource problems
and lies in developing the methods of providing for environmental safety by using nanostructures for solar energy.

2. Literature review and problem statement

Paper [3] proposes the way of texturing silicon to increase effectiveness of converting solar energy. The authors of the work propose to use silicon of multi-porous structure as the front surface of the solar element. The method of “hybrid” technology based on the developed crater- and column-like morphology of silicon surface makes it possible to change the type and dimensions of the multi-porous texture in a wide range. Both chemical and electrochemical technologies do not require thermosaturation, since porous silicon is formed at room temperature.

Article [4] considers the possibility of applying two- and three-layer anti-reflecting coatings (ARC) based on porous silicon for silicon photovoltaic modifiers by means of approximation of the optical matrix. Based on this method, the spectra of displaying anti-reflecting coatings of MgF$_2$/ZnS, SiO$_2$/TiO$_2$ and MgF$_2$/CeO$_2$ were calculated, which are usually used in the photovoltaic modifiers, and the results of calculations were compared with the corresponding experimental data. It was shown that the spectra of displaying, calculated using the method of approximation of optical matrices, and the experimental data coincide. The aforementioned multilayer anti-reflectors of coating result in the improvement of characteristics of silicon solar elements, but have the following shortcomings: magnesium fluoride and zinc sulfide are relatively soft materials and have little resistance to aggressive environment, which over time leads to the degradation of parameters of solar elements. Unlike standard ARC with SiO$_2$/TiO$_2$ and other materials used in silicon photovoltaic converters, porous silicon, it is possible not only to save a small image in the visible and infrared spectrum areas, but also to expand it into the short-wave (UV) area (up to 400 nm).

In paper [5], textured pyramidal silicon layers were formed using the method of electrochemical etching. The authors demonstrated that the larger the height of pyramid clusters, the lower reflecting ability, observed in the range of short wavelengths. The feasibility of using porous silicon as material for solar elements was substantiated by researchers in article [6]. An increase in porosity of crystals causes the blue shift and an increase in photoluminescence peaks [7].

Porous silicon is widely used for optoelectronic devices due to anti-glare properties. This material has the following advantages: the expansion of the restricted zone, a wide range of absorption and a high range of optical transmission from 700–1000 nm. Paper [8] presents experimental research into electrochemically prepared porous silicon structures. It was found that with an increase in the time of etching, the thickness of por-Si also increases, and the index of refraction is reduced accordingly. A high degree of roughness of porous silicon surface implies its application as antireflecting coating, the textured surface reduces light reflection. In addition, scattering in por-Si is possible due to roughness in relation to thickness of the porous layer.

Authors of article [9] obtained solar elements based on por-Si at the efficiency of 15.5%. Porosity of the samples reached the value of 91 %, which causes blue shift of PL. Prepared samples of por-S layer with different porosity were used for manufacturing solar elements, using the following procedure. The samples were coated with photoresist. Then the mask was placed directly above the layers of porous silicon. The samples were subjected to the action of UV radiation for 40 seconds to form a patterned coating. N- and P-type of alloying were achieved by using the method of coating by placing the phosphorus and boron solution in the middle of the layers of por-Si, and then applying coating by centrifuging at the rate of 1000 rpm for 10 seconds at room temperature. Then the por-S layers were placed in a furnace at the temperature of 100 °C for 15 minutes to remove the moisture.

As we can see, world scientists actively explore the methods of creating photovoltaic modifiers based on nanostructured silicon. In addition, the nanostructures based on the semiconductor group A3V5 [10, 11] and A2V6 [12] are increasingly considered as the material for solar elements. But still there is no unified mechanism to obtain nanostructured semiconductor layers with the assigned properties. The aspects of correlation between parameters of porous layers and conditions of their obtaining are not explored enough. In addition, the problems of provision of the environmental safety (ES) by introducing nanotechnology into the alternative energy sector is not sufficiently explored either.

3. The aim and tasks of the study

The purpose of this study is to search for the methods of providing for the environmental safety by using nanostructured semiconductors as an elementary basic framework for photovoltaic modifiers of energy.

To achieve this aim, the following tasks were to be solved:

– to establish the types of negative influence of traditional energy sector on the ecological state of the environment, to compare factors of influence on the environment of traditional and non-traditional sectors of energy industry;

– to explore basic regularities of the formation of a porous layer on the surface of semiconductor of the A3V5 group and of silicon;

– to select essential technological stages of production of solar panels based on nanostructured semiconductors;

– to establish and propose methods for increasing the efficiency of photovoltaic modifiers of energy based on nanostructured materials.

4. Materials and methods of research into provision of environmental safety by using nanomaterials for solar energy sector

To solve complex technological, technical, environmental, economic and other problems, a systems analysis is widely used. This scientific approach can rationally formulate and solve complex problems, which are characterized by the capacity of structuring and selecting specific tasks, taking into account available resources. Therefore, we will accept the systems approach as methodological foundations for achieving the set purpose of providing environmental safety.

Environmental safety should be seen as a dynamic process, evolving and improving in interconnection with scientific research, design-technological and organizational-technical preparations for controlling this process. To formalize
the solution of the set problems, we used the principle of multilevel decomposition. This principle is characterized by dividing the process into hierarchical levels of functionally completed stages of solving a complex of local problems at this level.

Development of technological stages of production of solar panels was based on the principle “from the particular to the general”. In this case, attention is paid not only to the technical aspects of this process, but also to the scientific principles of obtaining and implementation of innovative technologies, in particular, obtaining materials for photo-electric modifiers of energy.

To obtain and study the possibility of using nanomaterials for FEM, the sets of plates of semiconductors of silicon (Si), gallium arsenide (GaAs), indium phosphide (InP), gallium phosphide (GaP) were used. The plates were previously cleaned and polished. The method of photoelectrochemical etching in acid solutions was used as a method for obtaining nanostructures at the surface of semiconductors. In order to stabilize properties of the derived structures, passivation by ammonia was used. The morphology was examined with the help of a raster electronic microscope.

5. Results of studying ways of providing environmental safety based on using nanostructured semiconductors for the fabrication of solar elements

5.1. Systems approach to the problems of providing environmental safety based on nanostructures for the fabrication of solar elements

With regard to the model of providing environmental safety, a hierarchical construction of its structure and the establishment of structural links between the components mean the following subordination of its technological components: it is impossible to develop and produce technological equipment or install a range of the necessary equipment without preliminary development of technological processes of controlling the ecological safety [13].

Hierarchical levels of stages for solving a set of problems to control environmental safety, which uses innovative technologies for solar energy sector, are presented in Fig. 1. In order to construct a multilevel decomposition scheme, we used the study into the functions of components of the system of environmental safety control as an integral part of the creation of methodological base for constructing such a system [14].

In the process of building a hierarchical structure for the system of controlling the environmental safety, we adhered to the basic principles of multilevel decomposition:

- existence of vertical and horizontal links between the levels and stages;
- priority of action of the levels and stages from top to bottom;
- interrelation of the levels, variability of the selection and solution of tasks at each level.

Thus, a generalized scheme of providing environmental safety consists of four stages, each of which contains two levels. The first stage involves the identification of sources and classification of factors of environmental danger. At this level, it is necessary to study the influence of energy sector on the environment.

The task of the second stage is development of technologies and technological processes that can improve the state of environmental safety.

5.2. Identification of environmental sources and classification of factors of ecological danger in traditional and non-traditional energy sectors

Renewable energy sources are believed to be the real ways of protecting against climate changes without creating new threats for the population and future generations. Comparison of basic forms of influence of traditional and alternative energy sectors on the environment is presented in Table 1.

In this case, by preliminary technologies we should imply the methods of treatment of semiconductor plates, which will be applied to the PEP.

The third stage involves organization and implementation of technological processes that provide a specified level of environmental safety. Technological processes include the stages of production of solar panels based on semiconductor nanostructures.

At the fourth stage, it is necessary to evaluate effectiveness of the proposed technologies through examining basic physical parameters of the received structures and to explore the ways to increase efficiency of photoelectric modifiers of energy.

Fig. 1. Scheme of multilevel decomposition of the problems for providing environmental safety through the use of innovative technologies for solar energy sector

In this case, by preliminary technologies we should imply the methods of treatment of semiconductor plates, which will be applied to the PEP.

The third stage involves organization and implementation of technological processes that provide a specified level of environmental safety. Technological processes include the stages of production of solar panels based on semiconductor nanostructures.

At the fourth stage, it is necessary to evaluate effectiveness of the proposed technologies through examining basic physical parameters of the received structures and to explore the ways to increase efficiency of photoelectric modifiers of energy.

5.2. Identification of environmental sources and classification of factors of ecological danger in traditional and non-traditional energy sectors

Renewable energy sources are believed to be the real ways of protecting against climate changes without creating new threats for the population and future generations. Comparison of basic forms of influence of traditional and alternative energy sectors on the environment is presented in Table 1.

To align a constant growth in energy consumption and increasing negative effects of energy sector, taking into consideration that the humanity will feel the shortage of energy resources, may by possible using two methods: energy saving or development of environmentally friendly types of energy production, which include energy of the Sun.
5.3. Nanostructured semiconductors as the base for creating photoelectric power modifiers

Solar cells have traditionally been produced based on monocrystalline silicon. Their efficiency, as a rule, does not exceed 15–20 %. In addition, such elements are fragile and require existence of anti-reflecting coating, improvement in technologies, etc.

Overcoming a number of problems becomes possible under condition of nanostructuring of semiconductors, namely the formation of a porous layer on the surface of the plates [15]. Such technology can largely improve the electrical and physical properties of solar elements due to the multifold increase in the working area of the plate (due to the existence of a huge number of pores at the surface). In addition, a significant increase in the efficiency of solar elements is expected, as well as the intensity of their absorption of light, the possibility of accumulation of large amount of energy, a longer operation term (increasing life cycle of the device), etc.

As it was mentioned above, porous surfaces are formed by the method of photoelectrochemical etching. Using various modes of processing, one can control parameters of the obtained structures (Table 2, Fig. 2). The plates of semiconductors of Si, InP, GaAs, GaP with the n-type of conductivity with the orientation of the surface were selected (111). The period of etching for all samples was the same – 10 min, density of current was 150 mA/cm².

Table 1

<table>
<thead>
<tr>
<th>Influence</th>
<th>Traditional energy sector</th>
<th>Solar energy sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resources</td>
<td>use of non-renewable resources</td>
<td>the energy source is completely renewable</td>
</tr>
<tr>
<td>Hydrosphere</td>
<td>thermal pollution of water bodies, exhausts of polluting substances</td>
<td>does not influence the state of hydrosphere</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>thermal effect, gases and dust emission into the atmosphere</td>
<td>ecologically friendly kind of energy</td>
</tr>
<tr>
<td>Lithosphere</td>
<td>pollution during energy carriers transportation and burying wastes and during energy production</td>
<td>does not pollute lithosphere, however requires considerable areas for locating PES</td>
</tr>
<tr>
<td>Radioactivity</td>
<td>contamination with radioactive and toxic wastes</td>
<td>radioactive elements are not used</td>
</tr>
<tr>
<td>Temperature of atmosphere</td>
<td>temperature rise</td>
<td>there is an opinion that the use of solar energy is able to increase considerably temperature near the surface of Earth, but this theory has not been proved</td>
</tr>
<tr>
<td>Hydrological mode of rivers</td>
<td>change in the mode under the influence of hydroelectric power plants as, as a result, pollution on the territory of a water body</td>
<td>does not influence</td>
</tr>
<tr>
<td>Electromagnetic fields</td>
<td>creation of electromagnetic fields around the electric power lines</td>
<td>are not created</td>
</tr>
<tr>
<td>Technogenic catastrophes</td>
<td>there is a risk (supported by many examples) of emergencies at power plants</td>
<td>this kind of risk is reduced to minimum. When one panel fails, the others continue operation without any changes</td>
</tr>
</tbody>
</table>

5.4. Influence of different types of energy sector on the environment

Table 2

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Electrolyte</th>
<th>Dimensions of pores, μm</th>
<th>Specific features of pores formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (Fig. 2, a)</td>
<td>HF: H₂O=1:1</td>
<td>0.2–0.4</td>
<td>Cylindrical pores, surface is covered with passivating layer</td>
</tr>
<tr>
<td>InP (Fig. 2, b)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.4–0.8</td>
<td>Cylindrical pores, the length of a pore is 100 μm</td>
</tr>
<tr>
<td>GaAs (Fig. 2, c)</td>
<td>HF: H₂O=1:1</td>
<td>0.05–0.1</td>
<td>Densely packed cylindrical pores</td>
</tr>
<tr>
<td>GaP (Fig. 2, d)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.1–0.4</td>
<td>Densely packed cylindrical pores first grow in crystallographic directions, then are leveled along the lines of current, the length of a pore is up to 100 μm</td>
</tr>
<tr>
<td>Si (Fig. 2, a)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.1–0.4</td>
<td>Cylindrical pores, the length of a pore is 100 μm</td>
</tr>
<tr>
<td>InP (Fig. 2, b)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.6–0.9</td>
<td>Uneven pored layer with low porosity (up to 20 %), the surface is covered with an oxide layer</td>
</tr>
<tr>
<td>GaAs (Fig. 2, c)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.4–0.8</td>
<td>Porosity amounts to 30 %, the length of a pore may amount up to 20 μm</td>
</tr>
<tr>
<td>GaP (Fig. 2, d)</td>
<td>HF₂O₂C₂H₂OH=2:1:1</td>
<td>0.5–0.8</td>
<td>Pores have a “cra- ter” construction, are located on the surface unevenly, the length of a pore is 10–20 μm</td>
</tr>
</tbody>
</table>

The received structures are characterized by stability of chemical and electrical properties. Porosity of samples is in a wide range from 20 to 80 %, the most common is the value of 40–60 %. According to results of the study, we can conclude that the smaller the size of pores, the more orderly the pores are arranged and the larger the value of porosity is.

Analyzing data in Table 3, it can be argued that the addition of electrolyte ethanol to the solution leads to increased permeability of the solvent into the pores. This creates a better germination of pores into the crystal thickness and creation of massive pores.
The non-uniformity of porosity and thickness of porous layers can be explained by the existence of bubbles that are formed in the electrolyte and stick to the surface of the crystal. To avoid this non-uniformity, the concentration of HF must be locally constant at the surface of the treated sample. Removal of bubbles from the surface of the plate, and therefore obtaining homogeneous layers of porous layer is achieved by mixing the electrolyte. Distance between the plate and the platinum cathode also affects the uniformity, while the shape of the platinum cathode virtually has no impact on uniformity.

It is necessary to note that the most common regularities in the formation of porous layers at the surface of semiconductors were presented above. The processes of pores formation differ for different crystals. At present, there is no single model for the formation of nanostructures. However, in all cases, it is possible to conduct certain generalizations:

- thickness of a porous layer correlates with the duration of crystal etching. In this case, there is critical duration of time, within which the pores formation is terminated and alternative processes take place (removal of porous layer from the surface, polishing etc.). For each semiconductor, this period is an individual indicator;
- density of current, at which processes of the pores formation are observed, is in the range from 20 to 200 mA/cm². At lower density of current, only a local etching of the deformed areas of plate takes place, whereas at an excessively large index of this parameter, the plate polishing is observed;
- hydrofluoric acid is not only a single available etcher for semiconductors of the group A3V5 and silicon. Pores may be formed using bromide, nitric and hydrochloric acids. In this case, the morphology of porous plates will be significantly different depending on the chosen type of etcher and its concentration in electrolyte;
- the shape of the pores and density of porous layer are also strongly influenced by parameters of the crystal itself – the type of conductivity, surface orientation, degree of alloying of plates, the number of point defects and dislocations, etc.

By varying the conditions of etching for different crystals, it is possible to obtain a significant diversity of morphology of porous layers. The main task is the possibility to control the processes of self-organization of nanostructures with the view to forming porous layers with the assigned properties. In more detail the processes of pores formation at the surface of semiconductors are considered in papers [16, 17]. Studies [18–20] present mechanisms for the formation of nanostructures on other semiconductors. Summarizing the obtained experimental data, we concluded that during the formation of low-dimensional structures, the processes of self-organization appear, however, it becomes possible to predict morphological and, as a consequence, electro-physical properties of the obtained structures changing conditions of the experiment.

5. Development of technological stages of the fabrication of solar panels

Technological route determines the sequence of operations and composition of technological equipment. Quality of the device and effectiveness of its production largely depend on the way the technological route is built. Development of the route includes:

1) selection of technological bases and the sequence of producing the elements;
2) determination of the workpiece modules and technological transitions;
3) development of the sequence of workpiece treatment;
4) formation of operations. The basic most important stages are presented in Fig. 3.

It should be noted that, in reality, different variants of the sequence of production of the same construction are possible. This multi-variability is the resulting effect of a large number of factors: size of the series, availability of production equipment, a variety of tools, the ease of installation, organizational factors, etc.

5. Assessment of feasibility of using nanostructures for photoelectric modifiers

The formation of porous layers at the surface of semiconductors results, first of all, in an increase in the effective area by thousands and tens of thousands times (depending on the degree of porosity). Obviously, this fact leads to the increased efficiency (20 % and higher) of solar modules under condition of using nanostructures. Photoluminescence of porous structures demonstrates a shift in the visible portion of light. Due to this, the target range of electromagnetic radiation extends throughout the entire visible region, including its long-wave part. The high degree of roughness of the porous layer surface implies the possibility of its use as antireflection coating, since the textured surface reduces
the light reflection. In addition, scattering is possible due to roughness in relation to thickness of the porous layer.

The represented above advantages of using nanostructured semiconductors over the monocrystalline ones make them unquestioned candidates as the basic material for PEP.

6. Discussion of results of research into provision of environmental safety by using nanostructures for solar energy sector

As a result of the study, we completed all four stages of the multi-level decomposition of the problems for providing environmental safety through the use of innovative technologies for solar energy sector (Fig. 1). Thus, at the first two levels, the main sources of threats arising from the use of traditional energy sources were analyzed and comparative analysis of the impact of traditional and alternative energy sectors was conducted. The third and the fourth levels were completed through development of the technology for obtaining nanostructures and identification of the basic regularities of the formation of porous layers at the surface of semiconductors. In the course of completing the fifth and the sixth levels, technological stages of the production of solar panels based on nanostructures were developed. The latter two levels involved studying the feasibility of using nanostructures for solar cells as an effective tool to provide environmental safety.

However, in this case it would be incorrect to talk about the possibility of using obtained generalizing results for the formation of a unified system to control the environmental safety. To design the system to control the environmental safety, which uses innovative technologies for solar energy sector, it is necessary to conduct a series of comprehensive studies, namely [21]:

- development of database of initial data for creating SCES;
- further improvement of technologies for obtaining materials for photoelectric modifiers and development of technological regulations for PEP;
- research into the processes that provide control of the environmental safety, etc.

A system for control of the environmental safety through the use of innovative technologies for solar energy sector requires a detailed step-by-step analysis of all components of the process of manufacturing solar elements based on the nanostructured porous materials, which becomes the basis for further research.

A special feature of the presented study is the systems approach to the solution of problems of environmental safety. This approach is based on the identification of local
problems and their stage-by-stage solution. Such studies are of interdisciplinary and multidisciplinary nature and allow a comprehensive approach to the issues of provision of environmental safety.

7. Conclusions

1. A scheme of provision of the environmental safety through the use of innovative technologies for solar energy sector was developed. This scheme is a multilevel decomposition of the problems that includes the following levels: initial data for creating SCES, improved technologies for the provision of ES, organization and implementation of technological processes that ensure the assigned level of ES and results of using innovative technologies. A split into levels allows comprehensive and efficient solution to the problem of providing the assigned level of environmental safety and obtaining functional products.

2. It was found that traditional energy sector causes significantly more damage to the environment than alternative energy sources. In particular, it leads to the thermal effect, dust and gases emission, creates electromagnetic fields, etc. Reducing this effect is possible through gradual replacement of traditional energy with the alternative one.

3. Basic regularities of the formation of porous layer at the surface of semiconductor of the A3V5 group and silicon were explored. To obtain nanostructures, it is expedient to use the method of electrochemical etching in the solution of hydrofluoric acid. Technical conditions are selected individually for each semiconductor.

4. A generalized scheme for the technological process of producing solar elements based on nanostructured semiconductors was presented. The scheme contains a three-stage technology, which includes obtaining nanostructures, manufacturing photoelectric modifiers and direct production of solar elements.

5. It was demonstrated that the use of nanostructures for solar elements might increase their efficiency (20% and higher) due to the increase in effective area of the receiving surface. The passivating layer that is formed during etching of semiconductor provides for the stabilization of properties and reduces sensitivity to the surface contamination.

Acknowledgements

The work was conducted within the framework of the scientific state-funded study “Nanostructured semiconductors for the energy efficient environmentally friendly technologies that increase the level of energy saving and environmental safety of the urban system (State registration number 0116U006961).

References


1. Introduction

The problem of improving the durability and corrosion resistance of machine parts is topical for the equipment functioning at high speeds and loads. Ceramic composite materials of high wear resistance are very promising in such working conditions. These materials are also resistant to effects of aggressive environments. Such requirements are met by ceramic composites based on silicon carbide and aluminum oxide, which have high physical and mechanical properties and are inexpensive and non-scarse materials.