

13. Pistun, Ye. P. Modeliuvannia skhem vymiriuvalnykh peretvoriuvachiv iz zastosuvanniam teoriy mnozhyn [Text] / Ye. P. Pistun, H. F. Matiko, H. B. Krykh // Metrolohiya ta prylady. – 2016. – Issue 3. – P. 53–61.
14. Domnin, L. N. Ehlementy teorii grafov [Text]: uch. pos. / L. N. Domnin. – Penza: Izd-vo Penz. gos. Un-ta, 2007. – 144 p.
15. Diestel, R. Graph Theory [Text] / R. Diestel. – 5th edition. – Springer-Verlag, Heidelberg, 2017. doi: 10.1007/978-3-662-53622-3
16. Malkin, A. Ya. Rheology: Concepts, Methods and Applications [Text] / A. Ya. Malkin, A. I. Isayev. – ChemTec Publishing, 2017. – 500 p.
17. Krykh, H. B. Matematychni modeli droselnykh elementiv hidrodinamichnykh vymiriuvalnykh peretvoriuvachiv parametriv neniutoniivskykh ridyn [Text] / H. B. Krykh // Teploenerhetyka. Inzheneriya dovkillia. Avtomatyziatsiya. – 2008. – Issue 617. – P. 122–129.
18. Steffe, J. F. Rheological methods in food process engineering [Text] / J. F. Steffe. – USA, Freeman Press, 1996. – 418 p.

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RESEARCH INTO EFFECT OF ELECTROCHEMICAL ETCHING CONDITIONS ON THE MORPHOLOGY OF POROUS GALLIUM ARSENIDE

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Проведено удосконалення способу формування поруватого арсеніду галію у розчині соляної кислоти. Досліджено основні закономірності формування поруватих просторів. Показано, що морфологічні властивості пор-GaAs залежать від умов травлення. Досліджено вплив щільності струму, часу травлення та складу електроліту на поверхневу поруватість, товщину поруватого шару та діаметр пор

Ключові слова: арсенід галію, електрохімічне травлення, морфологія, поруваті напівпровідники, умови травлення

Усовершенствован способ формирования пористого арсенида галлия в растворе соляной кислоты. Исследованы основные закономерности формирования пористых пространств. Показано, что морфологические свойства пор-GaAs зависят от условий травления. Исследовано влияние плотности тока, времени травления и состава электролита на поверхностную пористость, толщину пористого слоя и диаметр пор

Ключевые слова: арсенид галлия, электрохимическое травление, морфология, пористые полупроводники, условия травления

1. Introduction

Nanostructured materials are of considerable interest to researchers due to their unusual properties compared

with volumetric or thin-film analogs [1, 2]. Many of these properties offer prospects for the application of nanostructures of materials for electronics, photonics, power industry, etc. [3, 4].

Semiconductors, fabricated at the nanoscale, demonstrate a drastic change in optical and electron properties [5]. These changes are due, above all, to quantum-dimensional effects, associated with the quantization of charge carriers' energy, the motion of which is restricted, in one, two or three directions [6, 7]. Properties of the obtained nanostructures depend in turn on the parameters of the starting crystal and the methods of synthesis [8].

Semiconductors of group III–V have advantage over other semiconductors for microelectronic devices due to [9, 10]:

- a wide and straight band interval;
- high mobility of electrons;
- low thermal noise;
- low energy consumption.

These properties of semiconductors from groups III–V allow the use of them for manufacturing optoelectronic devices operating over wide spectral ranges [11].

However, the properties and the application of nanostructures depend on a method of synthesis [12, 13]. There are several chemical [14, 15] and physical methods that have been successfully employed for fabricating the nanostructures of various materials [16]. Plasma-based processing, such as [17, 18], remain popular:

- arc discharge;
- radiofrequency and magnetron spraying;
- pulse laser deposition;
- modified devices of dense plasma focusing (DPF), etc.

Most of these plasma methods have certain shortcomings. Some of them require heating or shifting the substrate, or ultra-high vacuum [19]. It is often impossible to achieve high density of nanocrystals on the surface with the help of these methods, however, significant etching pits are formed with defects coming out onto the surface observed [20, 21]. Most of these methods have limitations, specifically:

- low deposition rates;
- contaminants;
- large energy consumption;
- the need for super-high vacuum, etc.

The search for the optimal method to synthesize nanostructures on the surface of semiconductors is an important task.

2. Literature review and problem statement

Due to the diversity of existing methods for the synthesis of nanostructures, the formation of a wide variety of forms of nanosurfaces becomes feasible:

- quantum spots [22, 23];
- nanocrystals [24];
- nanotubes [25];
- nanothreads [26, 27];
- porous semiconductors [28, 29];
- textured surfaces [30];
- whiskers [31], etc.

Formation of porous layers on the surface of semiconductors of group A3V5 typically occurs when using chemical [32, 33] and electrochemical methods [34, 35]. These methods have the advantage over other methods due to their simplicity and possibility to control conditions of the process during experiment [36].

In paper [37], regular 3D nanoporous arrays were obtained by electrochemical etching of n-nP (100) in a solution of hydrochloric acid. The results showed that the ranges

of current density and rate of etching affect morphology of pores. It was shown that etching rate can be changed through the amplitude potential oscillation. The charge over a period and the amplitude can be adjusted by choosing appropriate electrochemical parameters. Porous layers on the surface of GaAs of the p-type were formed in a solution of hydrofluoric acid [38]. It was found that after electrochemical etching the porous layer demonstrated a significant decrease in the cathodoluminescence intensity, a change in the chemical composition and crystalline phase. It was noted that the formed layer is composed mainly of porous As_2O_3 . However, the authors of these papers confined themselves to using only one electrolyte: for InP – HCl, for GaAs – a solution of HF. Such an approach does not make it possible to assess the contribution of composition and concentration of the electrolyte to the process of formation of porous layers.

Nanoporous InP (111) was formed by the method of wet-electrochemical etching using doping [39]. Morphology of the membrane's surface was studied using a scanning electron microscope. A quasi-homogeneous and self-organizing nanoporous network that consists of semiconductor isles was detected. The preservation of basic macro dielectric properties was observed. Determining a refraction index showed optical anisotropy for the membrane, which strongly depends on the wavelength of incident light, and demonstrates an interesting inversion (positive anisotropy to negative one). The inversion of optical anisotropy was explained by a strongly decreased "metal" behavior in the membrane. However, the paper does not clarify the mechanisms of a porous layer formation on the surface of indium phosphide.

It was shown in papers [40, 41] that there is always a minimum value for anodization voltage, at which the formation of a porous layer on the surface of semiconductors of group A3B5 becomes possible. To determine this magnitude, the authors of study [41] proposed a method, which is characterized by a gradual increase in voltage during etching. It was established that this magnitude is specific for each particular case and depends on other etching conditions. However, the unresolved problem is the influence of each factor (etching reagent's composition, ion concentration in the electrolyte solution, temperature and duration of etching) on the process of initial nucleation of pores on the surface of a semiconductor crystal.

Thus, it is possible to point to the electrochemical etching as the optimal method for pore formation on the surface of semiconductors from group A3V5. Moreover, porous spaces of silicon [42, 43], germanium [44], zinc oxide, etc. are obtained using a given method [45]. However, all these papers fail to provide a general idea about the mechanisms of formation of a porous layer during electrochemical treatment. Such a situation is explained by the fact that most research has been focused on studying the impact of a certain factor on the process of pore formation. On the contrary, it is necessary to take into account a complex of factors and to explore their correlation with morphological properties of nanostructures. Each of the parameters of a porous structure (dimensions of a pore, thickness of a porous layer, etc.) can be a result of not just a single factor but their totality. Vice versa, one factor can correlate with several parameters of a nanostructure at once. Another unresolved problem is to establish which conditions of etching affect morphological properties of the obtained porous structures. Regularities that determine dimensions of pores and surface porosity of nanostructures have not been sufficiently studied up to

now. The identified contradictions and unresolved issues are caused by:

- a large number of modifications of the method of electrochemical etching;
- a variety of semiconductors and their starting parameters that are used for the formation of a porous layer;
- a wide range of conditions that enable pore formation on the surface of a crystal;
- a lack of comprehensive approach to the evaluation of correlations between etching conditions and morphological properties of nanostructures.

Gallium arsenide has significant technological importance because it is used for manufacturing sensors [46], solar panels [47], photodetectors [48], etc. In turn, the porous gallium arsenide (por-GaAs) is also widely applied. Specifically, a porous phase can be used as a buffer layer for the fabrication of nitrides on the surface of semiconductors [49, 50]. Therefore, the optimization of the process of etching that would enable control over morphological properties of por-GaAs is an important scientific and applied task.

3. The aim and objectives of the study

The aim of present research is to establish the correlation between conditions of electrochemical etching of crystals of gallium arsenide and morphology of the obtained low-dimensional structures.

To accomplish the goal, the following tasks have been set:

- to improve the method for the formation of nanostructures on the surface of GaAs using the method of electrochemical etching;
- to examine morphological and chemical properties of the obtained nanostructures;
- to establish basic regularities in the formation of porous space on the surface of monocrystalline gallium arsenide.

4. Materials and methods applied for the formation of por-GaAs

Monocrystalline plates of gallium arsenide of the n-type with surface orientation (100) were used in the experiment. The samples were grown by the Czochralski method and alloyed with sulfur. Diameter of the samples was 5 cm, their thickness was 1 mm. The plates were polished on both sides. The basic properties of GaAs are given in Table 1.

Table 1

Physical properties of gallium arsenide

Property	Value
Length of forbidden zone at 300 K	1.424 eB
Effective mass of electrons	0.067 me
Effective mass of light holes	0.082 me
Mobility of electrons at 300 K	8,500 cm ² /(B·s)
Effective mass of heavy holes	45 me
Mobility of holes at 300 K	400 cm ² /(B·s)
Type of crystalline lattice	Cubic of sphalerite type
Melting temperature	1,240 °C
Molar mass	144.64 g/mol
State	Dark grey cubic crystals

Before the experiment, the samples were cleaned at three stages:

- stage I: immersion of the samples in a solution of sulfuric acid for 20 s and washing them in acetone for 10 min (to remove fatty pollutants from the surface);
- stage II: immersion of the samples in a 2% solution of hydrochloric acid for 2 min. and washing them with deionized water for 5 min. (to remove surface oxides);
- stage III: drying the samples in a flow of atomic nitrogen for 2 min. (to stabilize the properties).

Porous layers of gallium arsenide were formed by the method of electrolytic etching in a solution of hydrochloric acid. Device for the electrochemical treatment of crystals is shown in Fig. 1.

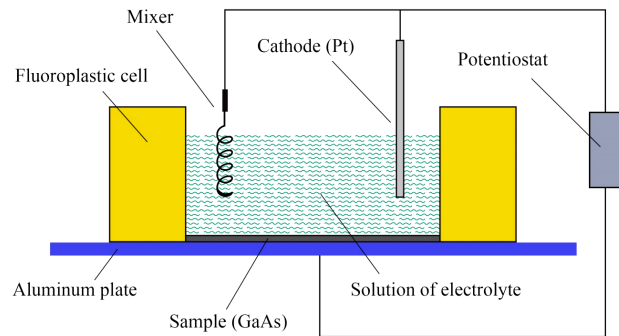


Fig. 1. Schematic of electrochemical etching of semiconductors

The experimental sample is attached by a two-sided carbon tape to the bottom of an electrolytic fluoroplastic cell. The bottom of the cell was made of aluminum plate. Platinum plate is used as the cathode. The mode of etching reagent agitation was used during etching. This procedure ensures a more uniform arrival of electrolyte ions to the surface of the samples and helps avoid bubble formation on the semiconductor plate. A mixer was used for agitation, its working part is made of Teflon.

To determine correlations between morphological properties of porous gallium arsenide and the conditions of etching, the experiment was conducted with three groups of plates.

The first group was exposed to electrochemical treatment over a fixed time of etching ($t=15$ min) and value of current density ($j=200$ mA/cm²). Different electrolyte solutions were used for this group:



For the second group, the time of etching ($t=20$ min) and the concentration of electrolyte ($12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$) were constant. Current density was selected in the range from 25 to 300 mA/cm².

To determine a dependence of morphology of por-GaAs on the duration of etching, the third group was treated in a solution of electrolyte $12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$ with the fixed value of current density ($j=250 \text{ mA/cm}^2$). The range of treatment duration was 2...30 min.

After the experiment, the samples were exposed to annealing in a stream of nitrogen. Morphology of the resulting samples was studied by using a raster electron microscope; chemical composition was determined by the EDAX method.

5. Results of research into formation of nanostructures on the surface of gallium arsenide

5.1. Correlation between the morphology of nanostructures and the concentration and composition of electrolyte

Rate of etching a crystal is determined by a number of factors:

- first, properties of the semiconductor material;
- second, properties of the etching reagent: its composition, concentration of the components, the presence of impurities in the solution, as well as temperature and agitation rate of solution.

The etching reagents that are used should [51]:

- possess selectivity, that is, the ability to actively enter reaction with the basic technological layer;
- not form reaction products (strong gas release, formation of an oxide film and clusters of complex compounds);
- allow a possibility for selecting the rate of etching, optimal for given conditions, which ensures minimum density of defects in the resulting porous layer.

The rate of etching process can be managed by introducing different additives to the electrolyte. An inhibitor of the reaction is acetic acid. Acetic acid, when introduced to the etching reagent, decreases a dielectric constant of the solution, and thus inhibits the dissociation of acid into ions. In addition, it itself dissociates with a release of a large quantity of H^+ ions. As a result, cathode reactions slow down. Passivation of the surface by hydrogen takes place during etching process. The adsorbed atoms in this case may break loose from the surface of the crystal and enter the solution, however, this process occurs quite slowly and requires a longer mode. Figure 2 shows morphology of the sample, which was exposed to electrochemical treatment in a solution of hydrochloric acid with added acetic acid.

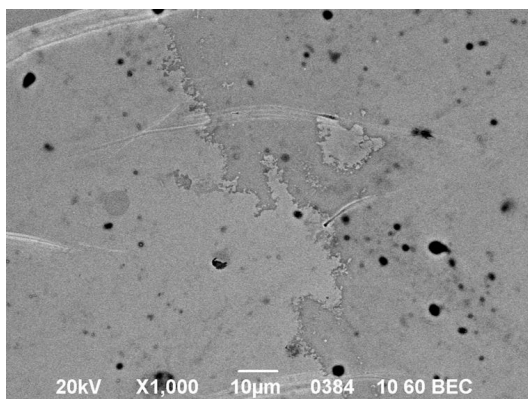


Fig. 2. Surface of gallium arsenide after treatment in the electrolyte $12\text{H}_2\text{O}+2\text{HCl}+1\text{CH}_3\text{COOH}$, etching time $t=15 \text{ min}$, current density $j=200 \text{ mA/cm}^2$

Fig. 2 shows separate etching pits. A porous layer was not formed, part of the sample was covered by an insoluble oxide film.

Bromine is a catalyst of the reaction of electrochemical dissolution of crystals. While introducing bromine to a solution of the etching reagent, it is possible to see that the reaction of etching slows down at the first moment. Then it captures an electron from the crystal and becomes a negatively charged ion of Br^- . By giving an electron to the acid (in the case of HCl) and passing into solution in the form of a neutral ion, bromine accelerates dissociation of hydrochloric acid and contributes to the cathode reactions. In this case, the number of holes in gallium arsenide increases, and the rate of etching grows.

Fig. 3 shows a lattice of pores with different diameters – from 50 to 200 nm. There can be big pits of etching with a diameter of up to 500 nm. The emergence of such pits suggests the etching of surface defects. The shape of the pores is almost round. Formation of pores along the segregation line is observed. Compositional non-homogeneity, which manifests itself in the form of substantial fluctuations in the concentration of an impurity in the bands of segregation, results in the emergence of lattice dislocations. A decrease in the level of thermoelastic stresses weakens the activity of dislocation sources and decreases uniformity of impurity distribution in the volume of the crystal.

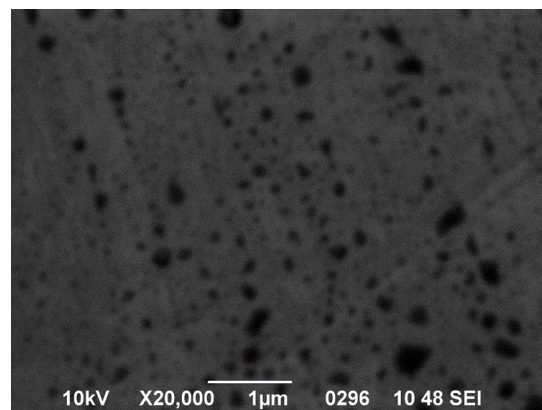


Fig. 3. Morphology of por-GaAs. Obtaining conditions: electrolyte $12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$; etching time $t=15 \text{ min}$, current density $j=200 \text{ mA/cm}^2$

Concentration of acid in the electrolyte determines the degree of porosity of the resulting structures (Table 2). Surface porosity is understood as ratio of the area of all pores on the surface to the area of the sample.

Table 2

Dependence of surface porosity of por-GaAs on the concentration of acid in electrolyte ($t=15 \text{ min}$, $j=200 \text{ mA/cm}^2$)

Electrolyte	Surface porosity, %
$12\text{H}_2\text{O}+1\text{HCl}$	12
$12\text{H}_2\text{O}+1\text{HCl}+1\text{HBr}$	25
$12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$	40
$12\text{H}_2\text{O}+3\text{HCl}+1\text{HBr}$	80
$12\text{H}_2\text{O}+5\text{HCl}+1\text{HBr}$	30

Table 2 shows that pores begin to form at minimal concentration of acid in the etching reagent ($12\text{H}_2\text{O}+1\text{HCl}$),

but there are not enough anions in the electrolyte to move the etching front to the depth of the sample. The formed pores indicate only the etching of surface defects. The most uniform porous layer was formed in the solution $12\text{H}_2\text{O} + 2\text{HCl} + 1\text{HBr}$. In this case, the formation of pores that are almost identical in size is observed (Fig. 4).

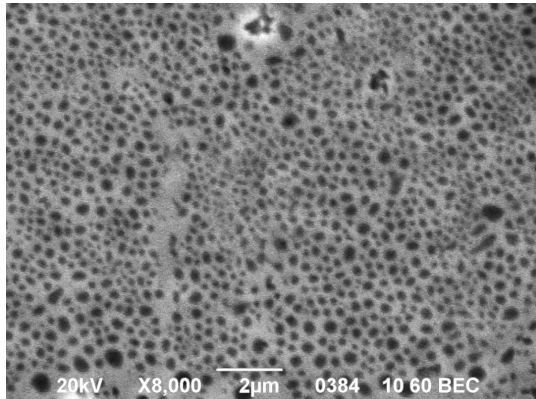


Fig. 4. Morphology of por-GaAs: $12\text{H}_2\text{O} + 3\text{HCl} + 1\text{HBr}$, electrolyte $12\text{H}_2\text{O} + 2\text{HCl} + 1\text{HBr}$; etching time $t = 15$ min, current density $j = 200$ mA/cm²

When the threshold of hydrochloric acid concentration in the solution is exceeded, the etching process slows down and the number of inlet holes of pores decreases. This may relate to the fact that the higher concentration of the electrolyte leads to an increase in the N-passivation, which gradually decreases conductivity and dielectric constant of the electrolyte. As a result, the process of etching slows down.

5. 2. Study of the effect of anodization current density on the morphology of a porous layer of gallium arsenide

The microstructure of a por-GaAs layer correlates with the magnitude of formation current, which follows from the results of research into a cross-sectional chipping of gallium arsenide with a layer of porous GaAs on the surface. The thickness of the por-GaAs layer increases from 15 µm at formation current density 50 mA/cm² to 50 µm at 250 mA/cm² (formation time is 20 min). In this case, the morphology of por-GaAs changes from weakly-ordered to distinctly elongated (Fig. 5). Fig. 5 shows mutually parallel long channels of pores.

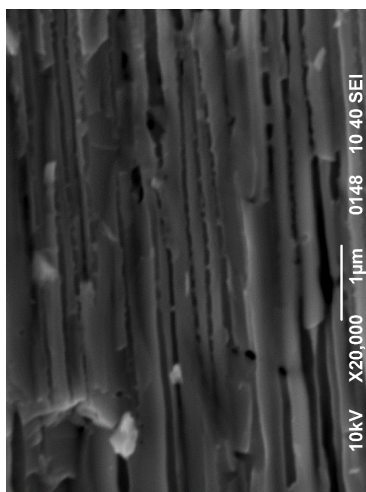


Fig. 5. REM-image of cross-section of por-GaAs: $j = 250$ mA/cm²; $t = 20$ min; electrolyte $12\text{H}_2\text{O} + 3\text{HCl} + 1\text{HBr}$

At low values of current density ($j < 25$ mA/cm²), formation of a porous layer was not observed. At current density in the range from 30 mA/cm² to 200 mA/cm², the process of electrochemical etching takes place with active formation of pores. Pores, depending on the applied anodization current, have different diameter and depth of intergrowth. However, at a certain critical value of current density (exceeding 250 mA/cm²), a porous layer is separated from the base. In this case, the surface of the GaAs plate has an uneven structure with multiple bumps and pits. Thus, we can conclude that there are minimum and maximum values of current density, at which nanostructures form on the surface of gallium arsenide. This range is determined separately for different electrolytes. Layers of porous GaAs should be formed at the maximum possible current density (the upper limit of the range). In this case, both maximum rate of growth of porous space and optimal area of the por-GaAs/ mono-GaAs are achieved.

5. 3. Effect of etching time on the morphology of porous gallium arsenide

Undisputed is the fact that morphology of porous structures depends mainly on the etching time. Proper selection of duration of electrolytic reaction plays a crucial role in obtaining nanostructures. Duration of etching reveals a clear correlation with the depth of germination of a porous layer and porosity of the resulting structures.

Fig. 6 shows a dependence chart of surface porosity of por-GaAs on etching time.

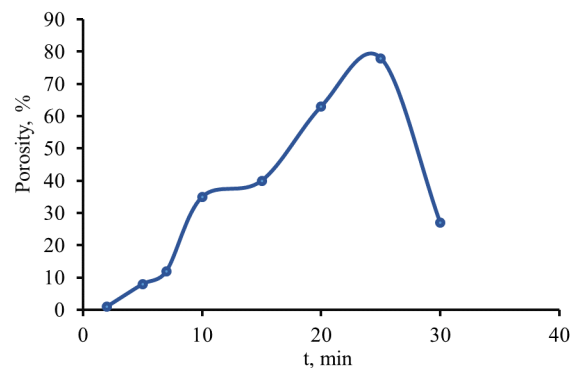


Fig. 6. Dependence of surface porosity of por-GaAs on etching duration at current density 250 mA/cm², electrolyte $12\text{H}_2\text{O} + 2\text{HCl} + 1\text{HBr}$

Fig. 6 clearly shows that porosity of por-GaAs directly correlates with etching conditions: the longer the duration of sample anodization, the greater the given magnitude.

This effect can be explained by the fact that at the beginning of etching pores are formed on favorable places of a semiconductor's surface, which include dislocation defects, microcracks, and uneven relief. At the next stage of etching, seed pore formation begins – etching pits start to emerge over the entire treated surface. Such pores are arranged randomly and branch under the surface of a sample. Next comes an increase in the diameters of the already-formed pores while nucleation of the new ones continues (Fig. 7).

When using solutions of halogens, active beginning of the process of pore formation on the surface of n-GaAs is observed after approximately five minutes following the beginning of etching. When a crystal is treated for 10...20 minutes, formation of a uniform porous layer is

observed in a wide range of current density and at various compositions of the electrolyte. When etching duration is prolonged to 30 minutes and longer, a few scenarios are likely in the course of the subsequent electrolytic process:

- termination of growth of a porous layer as a result of a passivation effect;
- formation of continuous insoluble solid films on the surface of the sample;
- depletion of etching reagent to the critical value, at which there no more anions in the electrolyte sufficient for the further nucleation of pores;
- significant etching of the surface, at which the samples obtained are characterized by severely impaired morphology;
- complete or partial dissolution of reaction products; a porous layer "crumbles" in the electrolysis process.

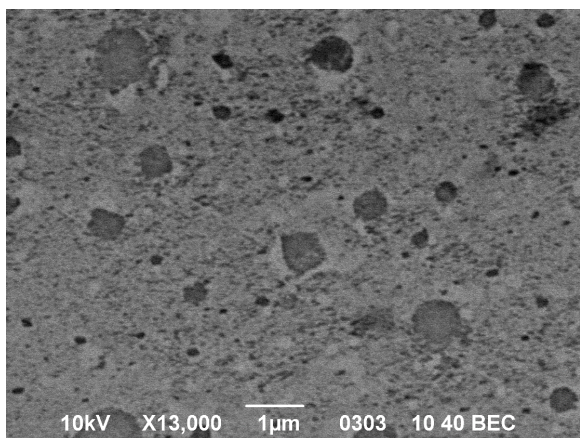


Fig. 7. REM-image of morphology of por-GaAs: $j=250 \text{ mA/cm}^2$, electrolyte $12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$; $t=10 \text{ min}$

These scenarios can be implemented simultaneously; alternatively, one of them will dominate.

The dependence of thickness of a porous layer on etching time is given in Table 3 (according to data from the microphotographic images, obtained using a scanning electron microscopy). Fig. 8 shows schematic of the process of etching a crystal over time.

Table 3

Dependence of thickness of porous layer of gallium arsenide on etching duration ($j=250 \text{ mA/cm}^2$, electrolyte $12\text{H}_2\text{O}+2\text{HCl}+1\text{HBr}$)

Etching duration, min	Thickness of porous layer, micron
2	0
5	0.8
10	3.5
15	22.6
20	44
25	45
30	38

Table 3 shows that during first 10 minutes the pores barely advance into the depth of the crystal – at this stage, a lattice of surface etching pits is formed and etching of a thin non-uniform layer occurs. The next stage (10...20 minutes) is characterized by the advancement of etching front into the

depth of the crystal. Next, we can observe a sharp slowdown in the growth of pores into the thickness of the sample due to the fact that it becomes difficult for the electrolyte to reach the bottom of a pore. In addition, the upper layer begins to etch intensively with the sample getting thinner. At this stage, the electrolyte is also being depleted of ions while the medium is alkalized. This factor also contributes to the inhibition of a pore formation process.

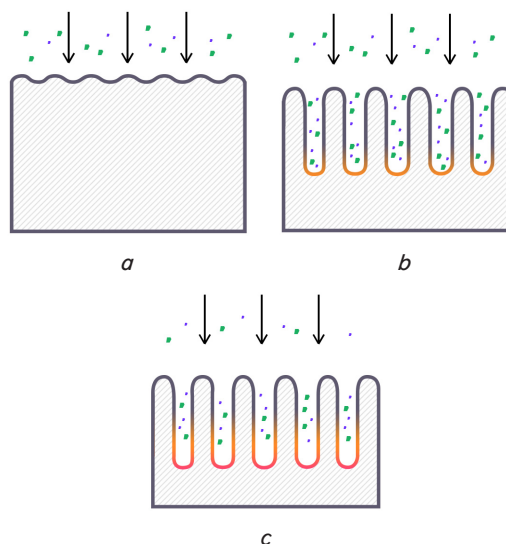


Fig. 8. Schematic of the process of pore formation during electrochemical etching of gallium arsenide: *a* – first stage (0...10 min), formation of seed pores and etching pits; *b* – second stage (10...20 min), advancing of etching front into the depth of crystal; *c* – third stage (over 20 minutes) – slowing down of etching rate

6. Discussion of results of the study of electrochemical etching of gallium arsenide

The study of the chemical composition of resulting porous samples revealed that, in the process of etching, the surface of gallium arsenide was not covered with a continuous oxide film (Fig. 9). Oxygen is present only in small concentration (up to 18 %). This indicates the formation of rare clusters of gallium oxide. Disruption in the stoichiometry of samples is observed: gallium is present in a larger concentration. This happens through a faster etching of the sublattice of arsenic atoms (Table 4). In general, for semiconductors from group A3V5, faster etching of elements of the third group is a common phenomenon. It was shown in paper [52] that a disruption in the stoichiometry during etching of indium phosphate is observed towards the excess of indium atoms.

The research conducted demonstrates the influence of etching conditions of gallium arsenide on the formation of a porous layer on the surface of a crystal. However, it should be noted that morphology of the resulting porous layers is also affected by parameters of the starting crystal:

- orientation of the surface;
- number and nature of defects;
- level of doping and elemental composition of impurities;
- conductivity type, etc.

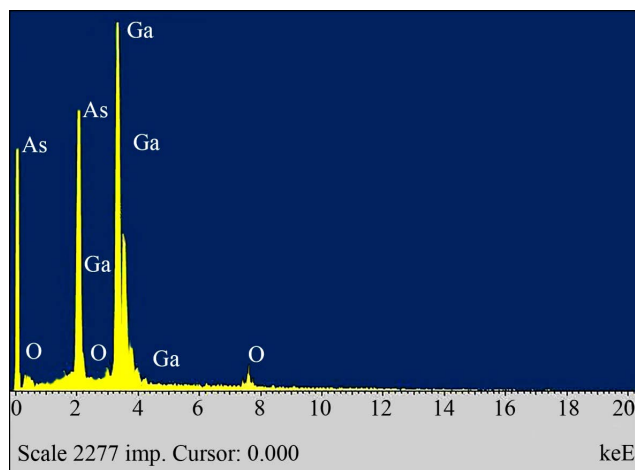


Fig. 9. Chemical composition of the surface of porous GaAs, obtained using the EDAX method

Table 4

Component composition of the surface of porous gallium arsenide (spectra taken at 3 points), obtained by the EDAX method

Spectra	Components		
	O	As	Ga
Spectrum 1	14.28	25.31	60.41
Spectrum 2	5.66	23.46	70.88
Spectrum 3	13.80	31.05	55.15

Thus, it was shown in paper [53] that orientation of the surface of a crystal determines the shape of a pore. A level of doping plays a decisive role for the configuration of nanostructures [54]. The number of etching pits on the surface of a crystal depends on the existence of point defects [55]. In addition, it is necessary to take into consideration that the self-organization processes occur during electrochemical treatment of any semiconductors. The emergence of coherence in the original chaotic medium is considered the main attribute of self-organization [56]. As a result of self-organization, the system “semiconductor/electrolyte” acquires new collective properties, not possessed by elements. These properties manifest themselves in the form of correlations, that is, relations between distant parts of the system are created and maintained. Thus, self-organization processes, on the one hand, predetermine the variety of nanostructures, on the other hand, they complicate control over processes of pore formation on the surface of semiconductors. It is due to this fact that no optimized conditions for obtaining porous semiconductors with assigned properties have been developed as yet. This results in a large number of studies and publications

on this subject and leads to the further search for ways to control the processes of pore formation. There is a need to construct a unified mathematical model that would take into consideration parameters of starting crystals, conditions for pore formation and the processes of self-organization, which take place at the interface “semiconductor–electrolyte”.

7. Conclusions

1. The improved method for obtaining nanostructures on the surface of gallium arsenide is reported. Por-GaAs layers were formed by electrochemical etching in a solution of hydrochloric and bromine acids. Stirring the electrolyte during etching makes it possible to avoid the emergence of bubbles on the surface of the crystal and contributes to the formation of a uniform porous layer.

2. Morphology of porous layers of gallium arsenide is an ensemble of round-shaped pores. The pores grow in long mutually parallel channels. The thickness of the porous layer can reach 50 μm, surface porosity – up to 80 %. Morphological properties of por-GaAs are in correlation with etching conditions. Chemical analysis of the resulting nanostructures indicates that the sublattice of arsenide is etched more efficiently than the sublattice of gallium.

3. Basic patterns in the formation of porous space on the surface of monocrystalline gallium arsenide were established. Thus, the number of pores depends on etching duration and composition of the electrolyte. Rate of etching a crystal also depends on the etching reagent. Thickness of the porous layer correlates with the duration of anodization and the current applied. Diameter of pores is a function of current density. A combination of different etching conditions determines morphology of porous samples. Understanding these processes makes it possible to control etching process and to create nanostructures with preset properties.

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References

1. Langa, S. Uniform and Nonuniform Nucleation of Pores during the Anodization of Si, Ge, and III-V Semiconductors [Text] / S. Langa, J. Carstensen, M. Christophersen, K. Steen, S. Frey, I. M. Tiginyanu, H. Föll // Journal of The Electrochemical Society. – 2005. – Vol. 152, Issue 8. – P. C525. doi: 10.1149/1.1940847
2. Naddaf, M. Nanostructuring-induced modification of optical properties of p-GaAs (100) [Text] / M. Naddaf, S. Saloum // Physica E: Low-dimensional Systems and Nanostructures. – 2009. – Vol. 41, Issue 10. – P. 1784–1788. doi: 10.1016/j.physe.2009.06.086
3. Naddaf, M. Novel optical and structural properties of porous GaAs formed by anodic etching of n+-GaAs in a HF:C₂H₅OH:HCl:H₂O₂:H₂O electrolyte: effect of etching time [Text] / M. Naddaf, M. Saad // Journal of Materials Science: Materials in Electronics. – 2013. – Vol. 24, Issue 7. – P. 2254–2263. doi: 10.1007/s10854-013-1087-4

4. Khrypunov, G. Increasing the efficiency of film solar cells based on cadmium telluride [Text] / G. Khrypunov, S. Vambol, N. Deyneko, Y. Sychikova // *Eastern-European Journal of Enterprise Technologies*. – 2016. – Vol. 6, Issue 5 (84). – P. 12–18. doi: 10.15587/1729-4061.2016.85617
5. Mangla, O. A study on aberrations in energy band gap of quantum confined gallium arsenide spherical nanoparticles [Text] / O. Mangla, S. Roy // *Materials Letters*. – 2015. – Vol. 143. – P. 48–50. doi: 10.1016/j.matlet.2014.12.083
6. Lebib, A. Structural and luminescent characteristics of porous GaAs [Text] / A. Lebib, E. Ben Amara, L. Beji // *Journal of Luminescence*. – 2017. – Vol. 188. – P. 337–341. doi: 10.1016/j.jlumin.2017.04.023
7. Suchikova, Y. Provision of environmental safety through the use of porous semiconductors for solar energy sector [Text] / Y. Suchikova // *Eastern-European Journal of Enterprise Technologies*. – 2016. – Vol. 6, Issue 5 (84). – P. 26–33. doi: 10.15587/1729-4061.2016.85848
8. Dubey, R. S. Electrochemical Fabrication of Porous Silicon Structures for Solar Cells [Text] / R. S. Dubey // *Nanoscience and Nanoengineering*. – 2013. – Vol. 1, Issue 1. – P. 36–40.
9. Suchikova, Y. A. Blue shift of photoluminescence spectrum of porous InP [Text] / Y. A. Suchikova, V. V. Kidalov, A. A. Konovalenko, G. A. Sukach // *ECS Transactions*. – 2010. – Vol. 25, Issue 24. – P. 59–64. doi: 10.1149/1.3316113
10. Beckemper, S. Generation of Periodic Micro- and Nano-structures by Parameter-Controlled Three-beam Laser Interference Technique [Text] / S. Beckemper // *Journal of Laser Micro/Nanoengineering*. – 2011. – Vol. 6, Issue 1. – P. 49–53. doi: 10.2961/jlmn.2011.01.0011
11. Md Taib, M. I. Improvement of Porous GaAs (100) Structure through Electrochemical Etching Based on DMF Solution [Text] / M. I. Md Taib, N. Zainal, Z. Hassan // *Journal of Nanomaterials*. – 2014. – Vol. 2014. – P. 1–7. doi: 10.1155/2014/294385
12. Tiginyanu, I. Metallized Porous GaP Templates for Electronic and Photonic Applications [Text] / I. Tiginyanu, E. Monaico, V. Sergentu, A. Tiron, V. Ursaki // *ECS Journal of Solid State Science and Technology*. – 2014. – Vol. 4, Issue 3. – P. P57–P62. doi: 10.1149/2.0011503jss
13. Suchikova, Y. A. Influence of the Carrier Concentration of Indium Phosphide on the Porous Layer Formation [Text] / Y. A. Suchikova, V. V. Kidalov, G. A. Sukach // *Journal of Nano- and Electronic Physics*. – 2010. – Vol. 2, Issue 4. – P. 142–147.
14. Rajendran, V. Development of Nanomaterials from Natural Resources for Various Industrial Applications [Text] / V. Rajendran // *Advanced Materials Research*. – 2009. – Vol. 67. – P. 71–76. doi: 10.4028/www.scientific.net/amr.67.71
15. Efros, A. L. Origin and control of blinking in quantum dots [Text] / A. L. Efros, D. J. Nesbitt // *Nature Nanotechnology*. – 2016. – Vol. 11, Issue 8. – P. 661–671. doi: 10.1038/nnano.2016.140
16. Suchikova, Y. A. Influence of type anion of electrolyte on morphology porous inp obtained by electrochemical etching [Text] / Y. A. Suchikova, V. V. Kidalov, G. A. Sukach // *Journal of Nano- and Electronic Physics*. – 2009. – Vol. 1, Issue 4. – P. 111–118.
17. Mangla, O. GaN nanostructures by hot dense and extremely non-equilibrium plasma and their characterizations [Text] / O. Mangla, M. P. Srivastava // *Journal of Materials Science*. – 2012. – Vol. 48, Issue 1. – P. 304–310. doi: 10.1007/s10853-012-6746-y
18. Malhotra, Y. Extremely non-equilibrium synthesis of luminescent zinc oxide nanoparticles through energetic ion condensation in a dense plasma focus device [Text] / Y. Malhotra, S. Roy, M. P. Srivastava, C. R. Kant, K. Ostrikov // *Journal of Physics D: Applied Physics*. – 2009. – Vol. 42, Issue 15. – P. 155202. doi: 10.1088/0022-3727/42/15/155202
19. Srivastava, A. Study of hafnium oxide deposited using Dense Plasma Focus machine for film structure and electrical properties as a MOS device [Text] / A. Srivastava, R. K. Nahar, C. K. Sarkar, W. P. Singh, Y. Malhotra // *Microelectronics Reliability*. – 2011. – Vol. 51, Issue 4. – P. 751–755. doi: 10.1016/j.microrel.2010.12.002
20. Mangla, O. Lanthanum oxide nanostructured films synthesized using hot dense and extremely non-equilibrium plasma for nanoelectronic device applications [Text] / O. Mangla, A. Srivastava, Y. Malhotra, K. Ostrikov // *Journal of Materials Science*. – 2013. – Vol. 49, Issue 4. – P. 1594–1605. doi: 10.1007/s10853-013-7842-3
21. Suchikova, Y. A. Influence of dislocations on the process of pore formation in n-InP (111) single crystals [Text] / Y. A. Suchikova, V. V. Kidalov, G. A. Sukach // *Semiconductors*. – 2011. – Vol. 45, Issue 1. – P. 121–124. doi: 10.1134/s1063782611010192
22. Lodahl, P. Interfacing single photons and single quantum dots with photonic nanostructures [Text] / P. Lodahl, S. Mahmoodian, S. Stobbe // *Reviews of Modern Physics*. – 2015. – Vol. 87, Issue 2. – P. 347–400. doi: 10.1109/piers.2016.7735045
23. Beattie, N. S. Analysis of InAs/GaAs quantum dot solar cells using Suns- V oc measurements [Text] / N. S. Beattie, G. Zoppi, P. See, I. Farrer, M. Duchamp, D. J. Morrison et. al. // *Solar Energy Materials and Solar Cells*. – 2014. – Vol. 130. – P. 241–245. doi: 10.1016/j.solmat.2014.07.022
24. Mei, L. Gas Sensing of SnO₂ Nanocrystals Revisited: Developing Ultra-Sensitive Sensors for Detecting the H₂S Leakage of Biogas [Text] / L. Mei, Y. Chen, J. Ma // *Scientific Reports*. – 2014. – Vol. 4, Issue 1. doi: 10.1038/srep06028
25. Shukla, S. Dye removal using electrochemistry and semiconductor oxide nanotubes [Text] / S. Shukla, M. A. Oturan // *Environmental Chemistry Letters*. – 2015. – Vol. 13, Issue 2. – P. 157–172. doi: 10.1007/s10311-015-0501-y
26. Monaico, E. Formation of InP nanomembranes and nanowires under fast anodic etching of bulk substrates [Text] / E. Monaico, I. Tiginyanu, O. Volciuc, T. Mehrtens, A. Rosenauer, J. Gutowski, K. Nielsch // *Electrochemistry Communications*. – 2014. – Vol. 47. – P. 29–32. doi: 10.1016/j.elecom.2014.07.015
27. Gerngross, M.-D. Electrochemical growth of Co nanowires in ultra-high aspect ratio InP membranes: FFT-impedance spectroscopy of the growth process and magnetic properties [Text] / M.-D. Gerngross, J. Carstensen, H. Föll // *Nanoscale Research Letters*. – 2014. – Vol. 9, Issue 1. – P. 316. doi: 10.1186/1556-276x-9-316

28. Suchikova, Y. A. Preparation of nanoporous n-InP(100) layers by electrochemical etching in HCl solution [Text] / Y. A. Suchikova, V. V. Kidalov, G. A. Sukach // *Functional Materials*. – 2010. – Vol. 17, Issue 1. – P. 131–134.
29. Vambol, S. Research into regularities of pore formation on the surface of semiconductors [Text] / S. Vambol, I. Bogdanov, V. Vambol, Y. Suchikova, O. Kondratenko, O. Hurenko, S. Onishchenko // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 3, Issue 5 (87). – P. 37–44. doi: 10.15587/1729-4061.2017.104039
30. Suchikova, Y. A. Texturation of the Phosphide Indium Surface [Text] / Y. A. Suchikova, V. V. Kidalov, O. S. Balan, G. A. Sukach // *Journal of Nano- and Electronic Physics*. – 2010. – Vol. 2, Issue 1. – P. 50–53.
31. Lazarenko, A. S. Model of Formation of Nano-Sized Whiskers Out of Channels of the Triple Junctions of Grain Boundaries of Polycrystal [Text] / A. S. Lazarenko // *Journal of Nano- and Electronic Physics*. – 2011. – Vol. 3, Issue 4. – P. 59–64.
32. Koshevoi, V. L. Study of producing sensors based on porous layers of GaP: Te semiconductors with the use of electrodiffusion contacts [Text] / V. L. Koshevoi, A. O. Belorus // 2017 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus). – 2017. doi: 10.1109/eiconrus.2017.7910833
33. Makhnij, V. P. Optical properties of microporous n-GaAs [Text] / V. P. Makhnij, I. I. German, V. M. Sklarchuk // *Telecommunications and Radio Engineering*. – 2015. – Vol. 74, Issue 16. – P. 1467–1472. doi: 10.1615/telecomradeng.v74.i16.60
34. Monaico, E. Porosification of III–V and II–VI Semiconductor Compounds [Text] / E. Monaico, G. Colibaba, D. Nedeoglo, K. Nielsch // *Journal of Nanoelectronics and Optoelectronics*. – 2014. – Vol. 9, Issue 2. – P. 307–311. doi: 10.1166/jno.2014.1581
35. Vambol, S. Analysis of the ways to provide ecological safety for the products of nanotechnologies throughout their life cycle [Text] / S. Vambol, V. Vambol, Y. Sychikova, N. Deyneko // *Eastern-European Journal of Enterprise Technologies*. – 2017. – Vol. 1, Issue 10 (85). – P. 27–36. doi: 10.15587/1729-4061.2017.85847
36. Wloka, J. Pore Morphology and Self-Organization Effects during Etching of n-Type GaP(100) in Bromide Solutions [Text] / J. Wloka, K. Mueller, P. Schmuki // *Electrochemical and Solid-State Letters*. – 2005. – Vol. 8, Issue 12. – P. B72. doi: 10.1149/1.2103507
37. Chai, X. Tunable Electrochemical Oscillation and Regular 3D Nanopore Arrays of InP [Text] / X. Chai, Z. Weng, L. Xu, Z. Wang // *Journal of the Electrochemical Society*. – 2015. – Vol. 162, Issue 9. – P. E129–E133. doi: 10.1149/2.0341509jes
38. Bioud, Y. A. Chemical Composition of Nanoporous Layer Formed by Electrochemical Etching of p-Type GaAs [Text] / Y. A. Bioud, A. Boucherif, A. Belarouci, E. Paradis, D. Drouin, R. Arès // *Nanoscale Research Letters*. – 2016. – Vol. 11, Issue 1. doi: 10.1186/s11671-016-1642-z
39. Steele, J. A. Optical reflectance studies of highly specular anisotropic nanoporous (111) InP membrane [Text] / J. A. Steele, R. A. Lewis, L. Sirbu, M. Enachi, I. M. Tiginyanu, V. A. Skuratov // *Semiconductor Science and Technology*. – 2015. – Vol. 30, Issue 4. – P. 044003. doi: 10.1088/0268-1242/30/4/044003
40. Ulin, V. P. Electrochemical pore formation mechanism in III–V crystals (Part I) [Text] / V. P. Ulin, S. G. Konnikov // *Semiconductors*. – 2007. – Vol. 41, Issue 7. – P. 832–844. doi: 10.1134/s1063782607070111
41. Sychikova, Ya. A. Dependence of the threshold voltage in indium-phosphide pore formation on the electrolyte composition [Text] / Ya. A. Sychikova, V. V. Kidalov, G. A. Sukach // *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*. – 2013. – Vol. 7, Issue 4. – P. 626–630. doi: 10.1134/s1027451013030130
42. Dzhafarov, T. Silicon Solar Cells with Nanoporous Silicon Layer [Text] / T. Dzhafarov; A. Morales-Acevedo (Ed.) // *Solar Cells – Research and Application Perspectives*. – 2013. doi: 10.5772/51593
43. Heidari, M. Ultraprecision surface flattening of porous silicon by diamond turning [Text] / M. Heidari, J. Yan // *Precision Engineering*. – 2017. – Vol. 49. – P. 262–277. doi: 10.1016/j.precisioneng.2017.02.015
44. Hooda, S. Nanopores formation and shape evolution in Ge during intense ionizing irradiation [Text] / S. Hooda, S. A. Khan, B. Satpati, A. Uedono, S. Sellaiyan, K. Asokan et. al. // *Microporous and Mesoporous Materials*. – 2016. – Vol. 225. – P. 323–330. doi: 10.1016/j.micromeso.2016.01.006
45. Ching, C. G. Fabrication of porous ZnO via electrochemical etching using 10wt% potassium hydroxide solution [Text] / C. G. Ching, P. K. Ooi, S. S. Ng, M. A. Ahmad, Z. Hassan, H. Abu Hassan, M. J. Abdullah // *Materials Science in Semiconductor Processing*. – 2013. – Vol. 16, Issue 1. – P. 70–76. doi: 10.1016/j.mssp.2012.06.017
46. Hamann, E. Performance of a Medipix3RX Spectroscopic Pixel Detector With a High Resistivity Gallium Arsenide Sensor [Text] / E. Hamann, T. Koenig, M. Zuber, A. Cecilia, A. Tyazhev, O. Tolbanov et. al. // *IEEE Transactions on Medical Imaging*. – 2015. – Vol. 34, Issue 3. – P. 707–715. doi: 10.1109/tmi.2014.2317314
47. Takamoto, T. Application of InGaP/GaAs/InGaAs triple junction solar cells to space use and concentrator photovoltaic [Text] / T. Takamoto, H. Washio, H. Juso // 2014 IEEE 40th Photovoltaic Specialist Conference (PVSC). – 2014. doi: 10.1109/pvsc.2014.6924936
48. Dai, X. GaAs/AlGaAs Nanowire Photodetector [Text] / X. Dai, S. Zhang, Z. Wang, G. Adamo, H. Liu, Y. Huang et. al. // *Nano Letters*. – 2014. – Vol. 14, Issue 5. – P. 2688–2693. doi: 10.1021/nl5006004
49. Jin, Z. Epitaxial growth of GaN on porous Si (111) substrate [Text] / Z. Jin, L. Guo, L. Xiao, R. Liang, J. Wang // 2016 5th International Symposium on Next-Generation Electronics (ISNE). – 2016. doi: 10.1109/isne.2016.7543306
50. Suchikova, Y. A. Synthesis of indium nitride epitaxial layers on a substrate of porous indium phosphide [Text] / Y. A. Suchikova // *Journal of Nano- and Electronic Physics*. – 2015. – Vol. 7, Issue 3. – P. 03017-1–03017-3.
51. Trindade, T. Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives [Text] / T. Trindade, P. O'Brien, N. L. Pickett // *Chemistry of Materials*. – 2001. – Vol. 13, Issue 11. – P. 3843–3858. doi: 10.1021/cm000843p

52. Suchikova, Y. O. Sulfide Passivation of Indium Phosphide Porous Surfaces [Text] / Y. O. Suchikova // Journal of Nano- and Electronic Physics. – 2017. – Vol. 9, Issue 1. – P. 01006-1–01006-4. doi: 10.21272/jnep.9(1).01006
53. Yana, S. Porous Indium Phosphide: Preparation and Properties [Text] / S. Yana // Handbook of Nanoelectrochemistry. – 2015. – P. 283–305. doi: 10.1007/978-3-319-15266-0_28
54. Bechambi, O. Photocatalytic activity of ZnO doped with Ag on the degradation of endocrine disrupting under UV irradiation and the investigation of its antibacterial activity [Text] / O. Bechambi, M. Chalbi, W. Najjar, S. Sayadi // Applied Surface Science. – 2015. – Vol. 347. – P. 414–420. doi: 10.1016/j.apsusc.2015.03.049
55. Wu, X. S. Surface Spot Defects Inspection of Multi-Crystalline Silicon Wafers Based on HALCON [Text] / X. S. Wu, R. Miao, Y. D. Si, C. M. Lou, D. X. Xu, X. N. Chu // Advanced Materials Research. – 2014. – Vol. 1081. – P. 241–245. doi: 10.4028/www.scientific.net/amr.1081.241
56. Vikhrov, S. P. Growth processes of noncrystalline semiconductors from positions of the self-organizing theory [Text] / S. P. Vikhrov, N. V. Bodyagin, T. G. Larina, S. M. Mursalov // Semiconductors. – 2005. – Vol. 39, Issue 8. – P. 953–959.

Для дослідження процесу нестационарної теплопередачі через плоску стінку був розроблений наближений аналітичний метод рішення задачі в зосередженій постановці. Працездатність методу продемонстрована на прикладі рішення задач, що послідовно ускладнюються, для плоскої пластини: симетричного, несиметричного нагріву і нестационарної теплопередачі. Показана адекватність отриманих рішень в рамках точності інженерних розрахунків

Ключові слова: нестационарна теплопередача, акумуляція енергії, плоска стінка, аналітичний розрахунок, наближене рішення

Для исследования процесса нестационарной теплопередачи через плоскую стенку разработан приближенный аналитический метод решения задачи в сосредоточенной постановке. Работоспособность метода продемонстрирована на примере решения последовательно усложняющихся задач для плоской пластины: симметричного, несимметричного нагрева и нестационарной теплопередачи. Показана адекватность полученных решений в рамках точности инженерных расчетов

Ключевые слова: нестационарная теплопередача, аккумуляция энергии, плоская стенка, аналитический расчет, приближенное решение

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DEVELOPMENT OF THE METHOD OF APPROXIMATE SOLUTION TO THE NONSTATIONARY PROBLEM ON HEAT TRANSFER THROUGH A FLAT WALL

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1. Introduction

The inertiality of change in the thermophysical parameters during operation process of heat power equipment is one of the reasons for the instability of its functioning and its deviations from the optimal state. The magnitude of

delay in changing controlled magnitudes following external disturbances and controlling impacts depends on the accumulating properties of equipment under operation. This effect manifests itself in various parts of the equipment by changing the flow of energy compared with the flow that arrives with fuel. Energy flows are predetermined by the