

Investigation of the porous GaP layers' chemical composition and the quality of the tests carried out

S. Vambol ^a, V. Vambol ^{a,*}, Y. Suchikova ^b, I. Bogdanov ^c, O. Kondratenko ^a

^a Technogenic and Ecological Safety Faculty, National University of Civil Protection of Ukraine, 61023, Chernyshevskaya str., 94, Kharkiv, Ukraine

^b Vocational Education Department, Berdyansk State Pedagogical University, 71100, Berdyansk, Shmidt str., 4, Ukraine

^c Rector, Berdyansk State Pedagogical University, 71100, Berdyansk, Shmidt str., 4, Ukraine

* Corresponding e-mail address: violavambol@gmail.com

ABSTRACT

Purpose: The purpose of this study is to establish the quality of tests for determining the chemical composition of the porous surface obtained by the method of electrochemical etching, based on the indicators of convergence and reproducibility of the results.

Design/methodology/approach: The method of electrochemical etching was used to obtain layers of porous gallium phosphide, which can be used as buffer layers for nitrides formation on their basis. Por-GaP was formed in a solution of hydrofluoric acid at a current density of $j = 100 \text{ mA/cm}^2$, etching was carried out for 20 minutes. The resulting structures sulfide passivation was carried out, thus avoiding the formation of an oxide film on the samples surfaces. For this purpose, porous gallium phosphide samples were kept in a sulfide solution for 10 minutes and dried in a stream of nitrogen. The chemical composition of the porous GaP surface layers has been investigated. To do this, the method of electron-probe INCA Energy microanalysis was used. The research was carried out on the entire surface of the sample in order to calculate the total spectrum of the elemental composition of the sample under study.

Findings: It was established that during anodizing, the stoichiometry of the crystals investigated did not shift significantly towards the excess of gallium atoms. Oxygen is present at an insignificant concentration of 0.3%. This indicates the effectiveness of conducting the sulfide passivation of the sample surface following the electrochemical treatment. The presence of fluorine atoms that appeared on the surface as a result of the reaction with the electrolyte during etching, is observed in extremely low concentration. Experimental studies have shown that the sample chosen can be used as a standard enterprise sample when analyzing the chemical composition of the surface of porous gallium phosphide due to its convergence, reproducibility, homogeneity. In addition, the given method for determining the standard sample can be applied to other porous semiconductors. Conducting such studies is an important technological task that will allow us to create a series of standard samples of porous semiconductors of A3B5 group.

Research limitations/implications: The research was carried out for porous gallium phosphide samples synthesized in the solution of hydrofluoric acid, though, carrying out of similar experiments for por-GaP obtained in other conditions, is necessary.

Practical implications: The studies of the reproducibility and convergence of the experiment have an important practical significance, since it is the reproducibility of the experiment results that is the main problem to modern material science, all the more to nanoengineering. Therefore, the technique proposed, will allow the synthesis of por-GaP layers with adjustable properties, will facilitate their widespread implementation in the real sectors of industry. The obtained porous layers can be used as standard samples.

Originality/value: The main problem in the nanostructures synthesis is the adjustability of properties. The technique presented allows to form stable layers of the porous gallium phosphide with the surface chemical composition known in advance. In addition, carrying out the sulfide passivation allows to stabilize por-GaP properties, which is an important process task. For the first time, a study of the presented technique as to convergence, reproducibility and homogeneity, was conducted.

Keywords: GaP, Chemical composition, Porous semiconductors, Reproducibility, Convergence

Reference to this paper should be given in the following way:

S. Vambol, V. Vambol, Y. Suchikova, I. Bogdanov, O. Kondratenko, Investigation of the porous GaP layers' chemical composition and the quality of the tests carried out, Journal of Achievements in Materials and Manufacturing Engineering 86/2 (2018) 49-60.

MATERIALS

1. Introduction

The current trend of semiconductor technology is the surface nanostructuring in order to obtain materials having unusual properties in comparison with monocrystalline analogues [1,2]. Nanostructures are widely used in many branches of science and technology, in particular in:

- laser technology [3,4];
- solar power generation [5];
- touch-sensitive technologies [6];
- medicine [7];
- cosmetology [8];
- textile industry [9,10].

According to official statistics [11], 7497 industrial products containing nanostructures have been registered to date. Such wide application is due to the variety of nanostructures available, whose number exceeds 40 types [12,13]. Such a significant amount of synthesized nanostructures extends the scope of their application. However, due to this, there are environmental problems [14-16] and difficulties in establishing a unified approach to the nanomaterials production management and studying their properties. The main reasons for the lack of a uniform approach to the parameters measurement and evaluation of the nanostructures properties are: lack of clear requirements and standards for the nanomaterials quality; the absence of standard samples for most nanomaterials; insufficient number of certified techniques measurement, calibration, verification, etc.

Among the scores of techniques for the nanostructures synthesis, chemical and electrochemical methods occupy a special place [17,18], thanks to:

- low cost;
- simplicity;
- a few number of process stages;
- a short process duration, etc.

Short-term etching of the crystal causes the formation of the etching figures (the most frequently – pits) and the layers of dissolution on its surfaces without the loss of macroscopic properties (macromorphology) [19], while prolonged etching promotes the crystal development of a macroscopic shape which is other than the initial [20]. Both micro- and macro-morphology of crystals depend on the etching parameters and form the subject of theoretical and experimental study for many researchers [21,22]. In addition, etching of crystals affects the chemical composition of its surface greatly [23]. In study [24], the chemical composition of gallium arsenide after electrochemical treatment was investigated. It was demonstrated that under the light influence arsenic oxide is formed on the structure surface. It has been established that oxides clusters are developed only on those parts of the crystal that were illuminated during etching. Work [25] shows that in aqueous and acid solutions a significant oxidation of carbides occurs. It was shown that the morphology of the resulting structures depends on the oxidation conditions. The issues of determining the chemical equilibrium of the structures obtained remain unsolved in these works. Since the surface of most

semiconductors of the A3B5 group is characterized by a high density of surface conditions in the forbidden zone [26], then the Fermi level pinning occurs. Its position on the surface virtually does not depend on the adsorbed atoms nature [27]. This circumstance affects the work of many micro and optoelectronic devices adversely, interfering with full display of the semiconductors high potential [28].

To stabilize chemical and electrochemical properties, the method of chemical passivation is being actively introduced. The technology of the semiconductor surface passivation solves three important process tasks. First, it prevents the reaction of the semiconductor with the atmosphere throughout the lifetime of the semiconductor device (chemical passivation) [29]. Second, it eliminates the interface states from the prohibited area, and also prevents their further formation (electrical passivation) [30]. Third, it provides a sufficient barrier so that the semiconductor electrons should not be 'lost' in the passivating layer [31]. Thus, in [32], the influence of the sulfide passivation on the electronic properties of the Schottky contact Au/n-Hg₃In₂Te₆ was analysed. It was shown that the concentration of Te element decreased, and In-S and Hg-S bonds appeared on the surface after passivation. Meanwhile, the Fermi level was destroyed due to passivation with sulfide, which is confirmed by the growth of the work function. In addition, the leakage current of the Schottky contact Au/n-Hg₃In₂Te₆ was reduced due to a decrease in the surface states density. Thus, this method has an effective ability to reduce the leakage current and change the straightening behaviour. In [33], sulfide passivation was used to reduce the 'aging' of porous indium phosphide layers. With chemical passivation, a layer of oxide is removed from the semiconductor surface, in place of which a thin crystalline film of a chemically inert material is formed. Such a film can perform the properties of a superfine buffer layer and protect the semiconductor surface from the contact with aggressive components of the environment.

However, it is important to not only stabilize the properties of the already obtained compounds, but to control their chemical properties at the creation stage. Thus, in [34,35] it is noted that the analysis of synthesized nanostructures should be carried out at each stage of the life cycle. This will significantly improve the performance of the nanostructures-based devices. The main problem here is to ensure the reproducibility of the experiment [36] in order to have the possibility for further serial production of synthesized structures. For this purpose, indices based on statistical methods [37,38] should be used. Therefore, the analysis of the porous nanostructures properties and the

establishment of test quality is an actual applied and scientific issue. In this regard, the purpose of this study is to establish the quality of tests for determining the chemical composition of the porous surface obtained by the method of electrochemical etching, based on the convergence and reproducibility results indices.

To achieve this goal, the following tasks were solved:

- to obtain porous layers on the surface of gallium phosphide by electrochemical etching method and to stabilize their properties by passivation;
- to investigate the chemical composition of the gallium phosphide porous layers obtained by the electrochemical etching method;
- to evaluate the quality of tests based on the results convergence and reproducibility.

2. Materials and research methods used to synthesize and analyse por-GaP properties

The samples of monocrystalline gallium phosphide grown by the Czochralsky method were selected for the experiment. The plates were polished on both sides. The samples overall dimensions – 5 x 5 x 1 mm. Before the experiment, the samples were subject to cleaned for degreasing and dust removal. Surface-oriented plates (100), doped with sulfur, of n-type conductivity were used in the experiment.

As a method for the porous layer formation on the mono-GaP surface, a method of electrochemical etching in hydrofluoric acid solution was chosen. The experiment was conducted in two stages. The purpose of the first stage was obtaining porous layers on the surface of gallium phosphide and their properties stabilization. For this purpose, 20 samples with the same initial properties were selected. Etching was carried out in aqueous-alcoholic solution of hydrofluoric acid in a ratio of HF:H₂O:C₂H₅OH=2:1:1. The etching duration was from 5 to 25 minutes, the current density was 75...150 mA/cm². To stabilize the chemical properties, all samples were passivated in the sulfide solution after the experiment. Passivation was carried out by samples exposure to Na₂S solution for 10 minutes. After passivation, the samples were dried in a stream of nitrogen.

At the second stage, the chemical properties of the porous samples were determined in order to be able to classify them as standard and test quality in terms of convergence, reproducibility and homogeneity. 10 samples obtained by electrochemical etching in a solution of

hydrofluoric acid were used as the source material for the study. These samples should have a homogeneous chemical composition and the components stability throughout their life cycle.

To determine the homogeneity of the test sample, a methodology ensuring the experiment results reproducibility and convergence shall be used. The convergence of the analysis should be understood as the quality of the measurements, which demonstrates the measurements results proximity to one another with measurements performed in the same conditions (within a short time period). The convergence of the analysis is characterized by the value of the root-mean-square error of a single measurement and is denoted as S_{rm} . The reproducibility of the analysis is understood as the quality of measurements, which reflect the proximity of the measurements results to one another with measurements performed in different conditions. The reproducibility of the analysis is characterized by the value of the relative standard deviation of the single definition and is denoted as S_{am} .

A study on the development of a standard sample was carried out using the EDAX method, an analytical method for elemental analysis of solids which is based on the analysis of the emission energy of its X-ray spectrum [39].

The micromorphology of the samples studied was investigated on a raster electron microscope.

To determine the concentration of elements on the sample surface, INCA.

Energy software from Oxford Instruments [40] was used, which is a platform for electron-probe microanalysis for raster and electronic microscopes. It contains the following elements:

- a personal computer with INCA Energy software;
- 'x-stream' and 'mics' modules;
- X-stream – microanalytical processor for receiving and analysing the spectrum;
- Mics – image capture system;
- X-MAX energy-dispersive detector.

INCA Energy software is based on navigators that run the operator through the necessary steps sequence. Every step of the navigators is provided by a separate screen that contains all the necessary analysis tools.

The software includes the main navigators (Fig. 1) [40]:

- analyser – qualitative and quantitative analysis of the chemical composition;
- Point & ID – automation of an electronic probe control and analysis with reference to an image;
- mapping – SmartMap – analysis of the elements spatial distribution.

The 'Mapping' Navigator collects the full spectral information about the sample with the corrected X-ray

spectra stored for each image point. The mapping algorithm [41] is given in Fig. 2.

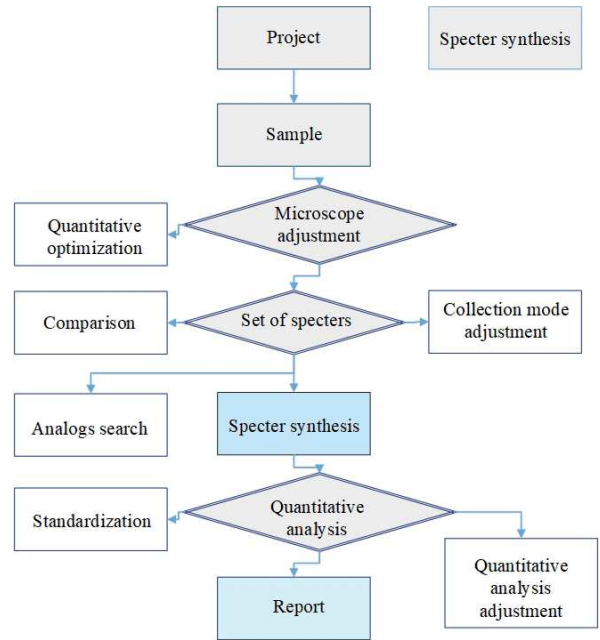


Fig. 1. Algorithm for collecting full spectral sample information using INCA Energy

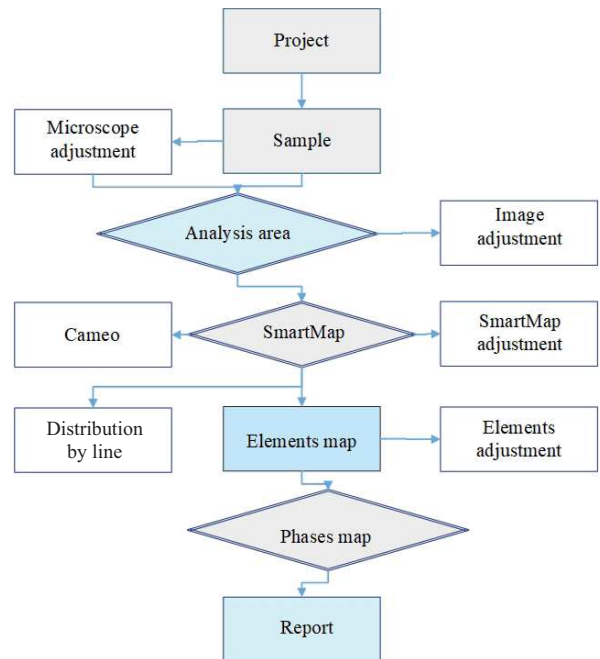


Fig. 2. Peak deconvolution algorithm for correct identification and calculation of the elements concentration at each point of the map

In the algorithm (Fig. 2) the steps perform certain functions [41] (Table 1).

Table 1.
Functions of decomposition steps for sample images mapping to perform spectral analysis

Step	Function
'Analysis area'	obtaining the area image in the secondary or displayed electrons
'SmartMap'	the choice of area for the X-ray mapping or a profile for studying intensity division
'The elements maps'	the random choice of element, analytical line, the window width. The possibility of mathematical operations between the maps, for instance, subtraction of the background
'Division along the line'	means the same as intensity-based division
'Cameo'	colour coding for X-ray spectrum visualization
'Phases map'	a tools set for phases division analysis
'Report'	report generation on each sample nature

Measurement of the elements concentration occurred on the side of the sample, which is covered by pores. One or more elements that are characterized by the concentration variability on the surface or in the volume of the standard sample material are, as a rule, the homogeneity indicator. In our case, the concentration of phosphorus was chosen. That is, we believe that the concentration of gallium will be higher, the lower the concentration of phosphorus is.

3. Results of GaP porous layers characteristics studies

3.1. Results of porous layers studies on the surface of gallium phosphide and the selection of a standard sample

Conducting a series of experiments resulted in obtaining porous layers on gallium phosphide surface. It was established that the morphology of the porous space correlates with the etching conditions. Pores are formed in a wide range of the formula-process factors. Almost all samples showed the appearance of etching pits. However, in case of short-term etching (less than 10 min), etching

pits had an individual nature. Their appearance is logically linked to etching of surface defects and segregation inhomogeneities. When etching duration exceeds 20 minutes, a net of tightly packed pores is developed. Some pores merge, forming massive etched areas. A uniform porous layer is formed within the range of etching time from 10 to 20 min.

The quantity and size of the pores are influenced by the anodizing current density. At low current density values (75 mA/cm^2) the surface porosity does not exceed the limit of 28%. As the current density increases, a sharp increase in the number of pores occurs on the crystal surface, the porosity reaches the values of 70%. However, when the limit value of current density is exceeded (for selected conditions – 150 mA/cm^2), the number of pores developed decreases. This is due to the course of an alternative process – electrochemical polishing of the gallium phosphide sample surface.

Regardless of the value of the surface porosity, pores have a circular cross-section in all samples studied. The average diameter of the pores varies from 140 nm to 330 nm, depending on the anodizing current density (75 mA/cm^2 and 125 mA/cm^2 , respectively).

The pores are current-oriented, which is characteristic of the chosen semiconductors surface (100) orientation type of A3B5 [42,43] group. The thickness of the porous layer varies from 7 to 30 μm and correlates with the anodizing current density.

Among all samples with a developed porous layer on the surface, we choose one that will be used as a reference sample for studying the reproducibility of the experiment results.

A sample was selected based on visual inspection, whose porous surface meets the requirements for samples to be used as buffer layers [20,44]. Such structures should have a uniform mesoporous layer with a surface porosity ranging from 30 to 70%. The conditions in which this sample was synthesized are as follows: etching time $t = 20 \text{ min}$, current density $j = 100 \text{ mA/cm}^2$, electrolyte $\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} \text{ 2:1:1}$. The micromorphology of this sample demonstrates a porous layer with an average pore diameter of 200...250 μm , with surface porosity making 31%, the thickness of a porous layer – 28.4 μm .

3.2. Results of gallium phosphide porous layers chemical composition studies and determination of the studies conducted quality

Monocrystalline gallium phosphide demonstrates the stoichiometric elements composition, that is, phosphorus

and gallium are present in equal shares. However, during etching of crystals, this equality can be distorted in the direction of gallium atoms' excess. This is due to a faster etching of the phosphorus substrate and can significantly affect the stoichiometric performance of the anodized samples. Therefore, the level of quality of the porous samples chemical composition should be determined by characterizing one of the elements, taking into account the non-stoichiometricity of the porous layers. To do this, one needs to analyse the content of the elements on the selected sample surface.

The chemical composition should be established proceeding from the possibility of determining the composition of all elements controlled throughout the concentrations range for a particular semiconductor brand. When creating standard samples, it is necessary to establish their operation period. For nano-structured samples it is appropriate to establish a term not exceeding three years, since the surface of nanostructures is very fragile and separation of part of the porous layer from the monocrystalline substrate can occur over time. Besides, the semiconductors surface is prone to oxidability. With the course of time, the porous layer may be skinned over with oxide film, which affects the sample chemical properties significantly.

Spectral analysis using the INCA Energy method was performed to study the element concentration on por-GaP porous surface. All elements were subject to analysis. The purpose of the analysis was to establish:

- the percentage ratio of gallium and phosphorus;
- presence of an oxide film or oxide crystallites on the sample surface;
- formation of the crystal electrochemical dissolution products.

The research was carried out on the entire surface of the sample in order to calculate the total spectrum of the elemental composition of the sample under study. The program interface and calculation results are given in Figure 3 and in Table 2.

Analysis of Figure 3 and Table 2 demonstrates that during anodizing, the stoichiometry of the crystals under study did not shift significantly towards gallium atoms excess. Oxygen is present at an insignificant concentration of 0.3%. This indicates the effectiveness of conducting the sulfide passivation of the sample surface following the electrochemical treatment. The presence of fluorine atoms that appeared on the surface as a result of the reaction with the electrolyte during etching, is observed in extremely low concentration. Based on these results, we can conclude that the sample possesses expected chemical characteristics.

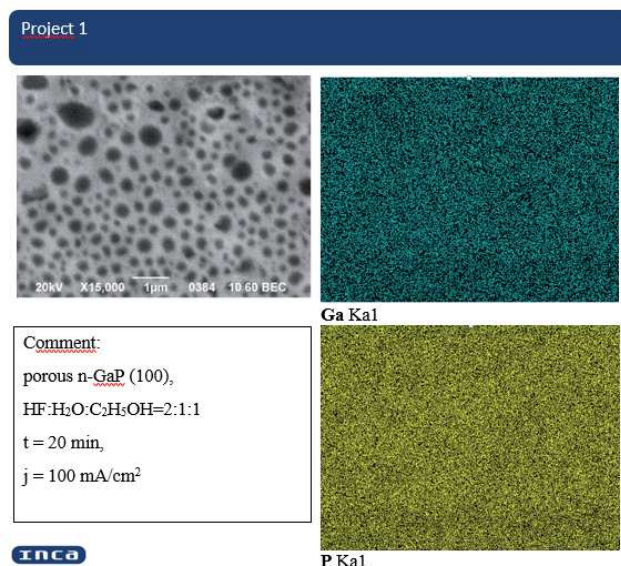


Fig. 3. Por-GaP spectral analysis results obtained by INCA Energy method

Table 2. Elements overall spectrum on por-GaP sample surface

Spectrum	O	F	P	Ga	Total
Overall spectrum	0.30	0.07	37.26	62.37	100.00
Mean value	0.30	0.07	37.26	62.37	100.00
Standard deviation	0.00	0.00	0.00	0.00	
Maximal value	0.30	0.07	30.26	62.37	
Minimal value	0.30	0.07	30.26	62.37	

The veracity of measurements depends on the degree of confidence in the result and is characterized by the probability that the true value of the parameter measured lies within the specified boundaries of the existing one. It should be noted that the results of measurements whose veracity extent is low, have no value. Along with such indices as accuracy, veracity and accuracy, the quality of measuring operations is also characterized by the convergence and reproducibility of the results. These indices are most common in assessing the quality of tests, since they characterize the tests accuracy.

3.3. Discussion of the study results with regard to the sample conformity, convergence, reproducibility and quality criterion homogeneity

The ratio of elements of monocrystalline stoichiometric gallium phosphide (Ga:P = 1:1) can be assumed by us as the standard values. To establish the distribution of elements on the sample surface, we will conduct a chemical analysis of the porous surface by EDAX method in 10x surface points (Fig. 4).

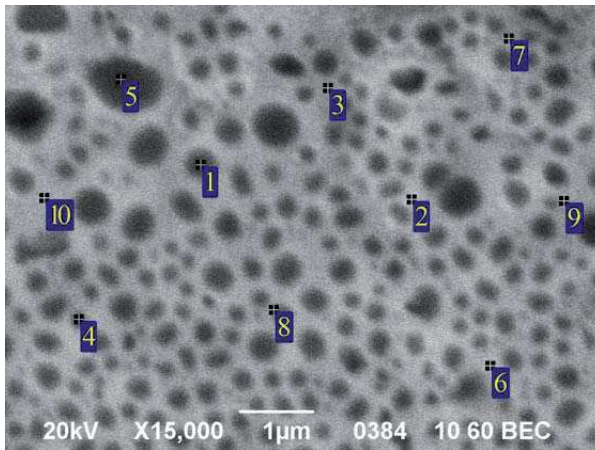


Fig. 4. Por-GaP micromorphology with selected points for chemical analysis by EDAX

Obviously, the same results are not produced by two or more tests of the same sample chemical composition by one method. Statistically justified estimates of the expected proximity of two or more results obtained by strict compliance with the test method [45].

In order to determine the homogeneity of the chemical composition of the test sample surface, a technique should be applied that ensures values [46] reproducibility and convergence.

Convergence studies were determined by a series of parallel measurements of phosphorus concentration in gallium phosphide porous samples. First a standard deviation was found using the formula:

$$S'_{\text{TM}} = \sqrt{\frac{\sum_{i=1}^{i=n} (c_i - \bar{c}_n)^2}{n-1}}, \quad (1)$$

where n – the number of measurements for one sample (in our case, 10 measurements were conducted);

\bar{c}_n – phosphorus average concentration which was taken into account based on n measurements;

c_i – phosphorus concentration.

Relative standard measurement which characterizes the measurements convergence, is expressed by the formula:

$$S_{\text{TM}} = \frac{S'_{\text{TM}}}{\bar{c}_n}. \quad (2)$$

The calculation results are given in Table 3.

Table 3.

Data of measurements to determine the analysis technique convergence on the example of one sample

n	c_i	$(c_i - \bar{c}_n)^2$
1	0.37	0.000016
2	0.30	0.004356
3	0.40	0.001156
4	0.48	0.012996
5	0.28	0.007396
6	0.45	0.007056
7	0.43	0.004096
8	0.36	0.000036
9	0.29	0.005776
10	0.30	0.004356
$\bar{c}_n = 0.37$		$\sum (c_i - \bar{c}_n)^2 = 0.0472$

Having substituted the calculation results obtained in formulas (1) and (2), we will have:

- standard deviation – $S'_{\text{TM}} = 0.072449$;
- relative standard deviation – $S_{\text{TM}} = 0.197948$.

Validation of the parallel measurements results is carried out according to the three-sigma criterion:

$$[\bar{c}_n - c_{i_p}] > 3S'_{\text{TM}}\bar{c}_n$$

$$0.37 > 0.079549.$$

where c_{i_p} – concentration of phosphorus in the sample, calculated as per the i -th measurement element, which can be checked. This value can be omitted, because the difference in absolute value is taken into account.

Consequently, the calculation of convergence produces a positive result.

The technique reproducibility ascertainment was carried out in series (one series per day) for two samples for 2

days. The relative standard deviation was calculated using the formula,

$$S_{am} = \frac{S'_{am}}{\bar{c}}, \quad (3)$$

where \bar{c} – is phosphorus average concentration calculated based on five values of the measurements in two samples.

For each specimen, standard deviation was determined using the formula

$$S'_{am} = \sqrt{\frac{S_1^2 + S_2^2}{n}}, \quad (4)$$

where n – the number of samples;

S_1^2, S_2^2 – standard deviation, used with reference to the first and second samples respectively.

For each sample we calculate the standard deviation using to the formula

$$S_i = \sqrt{\frac{(c_i + c_{is})^2}{n-1}}, \quad (5)$$

where n – the measurements number;

c_i – phosphorus average concentration in the sample which is defined by five measurements.

c_{is} – phosphorus average concentration in the sample which is defined by two measurements.

The results of technique reproducibility are given in Table 4.

Table 4.
Data of the analysis technique reproducibility determination

Measuring number	1	2	3	4	5	c_i
Sample 1	0.39	0.33	0.35	0.41	0.29	0.078
Sample 2	0.32	0.36	0.37	0.48	0.33	0.064

After calculation using formulas (4) and (5) we will obtain:

- deviation for each sample – $S_1 = 0.2165; S_2 = 0.1756;$
- standard deviation – $S'_{am} = 0.2130.$
- relative standard deviation – $S_{am} = 0.5868.$

Thus, we can conclude that the testing technique presented is reproducible.

To study of phosphorus uniform distribution on the porous surface, was conducted on 10 samples and one measurement was performed for each of them. The

standard deviation characterizing the spread of results relative to their total average is found using the formula

$$S_i = \sqrt{\frac{\sum_{j=1}^m (\bar{c}_{mj} - \bar{c}_j)^2}{m-1}}, \quad (6)$$

where m – the number of measurements in a series;

\bar{c}_{mj} – phosphorus average concentration in the sample which is defined by m measurements.

\bar{c}_j – phosphorus concentration in the sample which is defined by j measurements.

The results of material homogeneity are given in Table 5.

Table 5.
Data for porous surface homogeneity determination

m	\bar{c}_j	$(\bar{c}_j - \bar{c}_{mj})^2$
1	0.35	0.001521
2	0.29	0.004761
3	0.37	0.000361
4	0.40	0.001681
5	0.33	0.000841
6	0.45	0.008281
7	0.41	0.002601
8	0.39	0.000961
9	0.32	0.001521
10	0.34	0.000361
$\bar{c}_{mj} = 0.36$		$\sum(\bar{c}_j - \bar{c}_{mj})^2 = 0.0229$

After calculation using formulas (6) we will obtain:

$$S_i = 0.0504.$$

In this case, variance will the following value:

$$S_{ord} = 0.14.$$

We compare the values of the sampling variances of two series of experiments based on Fisher's criterion F using the formula:

$$F = \frac{S_x^2}{S_y^2}, \quad (7)$$

where S_x^2 – the largest variance;

where S_y^2 – the least variance.

Thus, F will equal to:

$$F = 2.$$

For the level of significance $\alpha = 0.05$ and probability $p = 0.95$ value $F_{crit} = 3.18$.

Since $F = 2 < F_{crit} = 3.18$, than the sample porous surface is uniform.

Experimental studies have proved that due to its convergence, reproducibility, homogeneity, the sample chosen can be used as a standard enterprise sample when analysing the chemical composition of the porous gallium phosphide surface. In addition, the given method for determining the standard sample can be applied to other porous semiconductors. Conducting such studies is an important technological task that will allow us to create a series of standard samples of porous semiconductors of A3B5 group.

4. Conclusions

1. The results of the experimental study confirm the possibility of obtaining porous gallium phosphide using electrochemical etching technique with gallium phosphide meeting the requirements for specimens used as buffering layers for nitrides formation. This is achieved by the creation of certain formula and processing parameters and additional carrying out of sulfide passivation. The following optimal formula and processing parameters are recognized: etching time $t = 20$ min, current density $j = 100$ mA/cm², electrolyte HF:H₂O:C₂H₅OH 2:1:1. The passivation was carried out to prevent oxide film formation on the surface.
2. To study chemical composition of por-GaP surface the INCA Energy spectral analysis method and the analytical method of EDAX elemental analysis were used. It was established that the porous layers have an even distribution of elements along the surface with a stoichiometric violation in the direction of gallium atoms' excess. The excess of gallium atoms is due to a higher rate of phosphorus etching from the sample surface.
3. The assessment of the quality of tests with reference to indices of convergence, reproducibility and homogeneity, confirmed that the porous surface of the sample is homogeneous and the sample can be used as the enterprise standard sample when analysing the chemical composition of porous gallium phosphide surface. Besides, the given technique for determining the standard sample can be applied to other porous

semiconductors. Conducting such studies is an important technological task that will allow us to create a series of standard samples of porous semiconductors of A3B5 group.

Acknowledgements

The authors' team is grateful to the management of the Berdyansk State Pedagogical University and the National University of Civil Defence of Ukraine for the opportunity to conduct scientific research in the field of nanotechnology products' quality and safety.

Additional Information

The work was carried out within the framework of scientific state-supported studies:

- 'Nanostructured semiconductors for energy-efficient, environment-friendly technologies that increase the level of the urbosystem energy saving and environmental safety' (state registration number 0116U006961);
- 'Development of technology for assessing the quality and safety of nanotechnologies products during their life cycle' (state registration number 0117U003860).

References

- [1] L.A. Dobrzański, The examples of the research of the nanostructured engineering materials and the concept of the new generation of highly innovative advanced pioneering nanostructured composite materials, Archives of Materials Science and Engineering 82/1 (2016) 5-37, doi: 10.5604/18972764.1229403.
- [2] S.H. Gill, L. Seongha, L.D. Matthew, Q.J.-K.L. Fen, Highly Bendable Flexible Perovskite Solar Cells on a Nanoscale Surface Oxide Layer of Titanium Metal Plates, ACS Applied Materials and Interfaces 10/5 (2018) 4697-4704, doi: 10.1021/acsami.7b16499.
- [3] M. Suja, B. Debnath, S.B. Bashar, L. Su, R. Lake, J. Liu, Electrically driven plasmon-exciton coupled random lasing in ZnO metal-semiconductor-metal devices, Applied Surface Science 439 (2018) 525-532, doi: <https://doi.org/10.1016/j.apsusc.2018.01.075>.

- [4] W. Matysiak, T. Tański, M. Zaborowska, Manufacturing process and optical properties of zinc oxide thin films as photoanode in DSSC, *Journal of Achievements in Materials and Manufacturing Engineering* 86/1 (2018) 33-40, doi: 10.5604/01.3001.0011.6016.
- [5] V.S. Prabhin, K. Jeyasubramanian, N.R. Romulus, N.N. Singh, Fabrication of dye sensitized solar cell using chemically tuned CuO nanoparticles prepared by sol-gel method, *Archives of Materials Science and Engineering* 83/1 (2017) 5-9.
- [6] K. Dhara, T. Ramachandran, B.G. Nair, T.G.S. Babu, Fabrication of Highly Sensitive Nonenzymatic Electrochemical H₂O₂ Sensor Based on Pt Nanoparticles Anchored Reduced Graphene Oxide, *Journal of Nanoscience and Nanotechnology* 18/6 (2018) 4380-4386, doi: <https://doi.org/10.1166/jnn.2018.15014>.
- [7] G.R. Serrano, S. Stafford, Y.K. Gun'ko, Recent Progress in Synthesis and Functionalization of Multimodal Fluorescent-Magnetic Nanoparticles for Biological Applications, *Applied Sciences* 8/2 (2018) 172(1)-172(23), doi: <https://doi.org/10.3390/app8020172>.
- [8] T.H. Shin, J. Cheon, Synergism of nanomaterials with physical stimuli for biology and medicine, *Accounts of Chemical Research* 50/3 (2017) 567-572, doi: 10.1021/acs.accounts.6b00559.
- [9] S. Vambol, V. Vambol, I. Bogdanov, Y. Suchikova, N. Rashkevich, Research of the influence of decomposition of wastes of polymers with nano inclusions on the atmosphere, *Eastern-European Journal of Enterprise Technologies* 6/10(90) (2017) 57-64, doi: <https://doi.org/10.15587/1729-4061.2017.118213>.
- [10] S. Ghasemi, M. Tajvidi, D.W. Bousfield, D.J. Gardner, Reinforcement of natural fiber yarns by cellulose nanomaterials: A multi-scale study, *Industrial Crops and Products* 111 (2018) 471-481, doi: <https://doi.org/10.1016/j.indcrop.2017.11.016>.
- [11] Nanotechnology Products Database (NPD). – URL: <http://product.statnano.com/>.
- [12] G. Chladek, A. Mertas, C. Krawczyk, R. Stencel, E. Jabłońska-Stencel, The influence of silver nanoparticles introduced into RTV-silicone matrix on the activity against *Streptococcus mutans*, *Archives of Materials Science and Engineering* 78/2 (2016) 59-65, doi: 10.5604/18972764.1226989.
- [13] Z. Sun, W. Blum, Hardening strain and recovery strain in nanocrystalline Ni investigated in tests with multiple stress changes, *Archives of Materials Science and Engineering* 79/2 (2016) 53-59, doi: 10.5604/18972764.1229421.
- [14] S. Vambol, V. Vambol, O. Kondratenko, I. Bogdanov, Y. Suchikova, Assessment of improvement of ecological safety of power plants by arranging the system of pollutant neutralization, *Eastern-European Journal of Enterprise Technologies* 3/10(87) (2017) 63-73, doi: <https://doi.org/10.15587/1729-4061.2017.102314>.
- [15] V. Vambol, Numerical integration of the process of cooling gas formed by thermal recycling of waste, *Eastern-European Journal of Enterprise Technologies* 6/8(84) (2016) 48-53, doi: 10.15587/1729-4061.2016.85455.
- [16] S. Vambol, Yu. Shakhov, V. Vambol, I. Petuhov, A mathematical description of the separation of gas mixtures generated by the thermal utilization of waste, *Eastern-European Journal of Enterprise Technologies* 1/2(79) (2016) 35-41, doi: <https://doi.org/10.15587/1729-4061.2016.60486>.
- [17] M.D. Gerngross, J. Carstensen, H. Föll, Electrochemical growth of Co nanowires in ultra-high aspect ratio InP membranes: FFT-impedance spectroscopy of the growth process and magnetic properties, *Nanoscale Research Letters* 9/1 (2014) 316(1)-316(10), doi: 10.1186/1556-276X-9-316.
- [18] S.O. Vambol, I.T. Bohdanov, V.V. Vambol, Y.O. Suchikova, Formation of filamentary structures of oxide on the surface of monocrystalline gallium arsenide, *Journal of Nano- and Electronic Physics* 9/6 (2017) 06016-06020, doi: 10.21272/jnep.9(6).06016.
- [19] E. Monaico, I. Tiginyanu, O. Volciuc, T. Mehrtens, A. Rosenauer, J. Gutowski, K. Nielsch, Formation of InP nanomembranes and nanowires under fast anodic etching of bulk substrates, *Electrochemistry Communications* 47 (2014) 29-32, doi: <https://doi.org/10.1016/j.elecom.2014.07.015>.
- [20] S. Vambol, I. Bogdanov, V. Vambol, Y. Suchikova, Research into regularities of pore formation on the surface of semiconductors, *Eastern-European Journal of Enterprise Technologies* 3/5(87) (2017) 37-44, doi: <https://doi.org/10.15587/1729-4061.2017.104039>.
- [21] N. Ma, Y. Chen, S. Zhao, J. Li, B. Shan, J. Sun, Preparation of super-hydrophobic surface on Al-Mg alloy substrate by electrochemical etching, *Surface Engineering* (2018) (Published online: 08 Jan 2018), doi: <https://doi.org/10.1080/02670844.2017.1421883>.
- [22] X. Qi, X. Fang, D. Zhu, Investigation of electrochemical micromachining of tungsten microtools,

- International Journal of Refractory Metals and Hard Materials 71 (2018) 307-314, doi: <https://doi.org/10.1016/j.ijrmhm.2017.11.045>.
- [23] V.P. Ulin, S.G. Konnikov, Nature of Electrochemical Pore Formation Processes in AlIBV Crystals (Part I), *Fiz. Tekh. Poluprovodn* 41/7 (2007) 854-866.
- [24] A. Udupa, X. Yu, L. Edwards, L.L. Goddard, Selective area formation of arsenic oxide-rich octahedral microcrystals during photochemical etching of n-type GaAs, *Optical Materials Express* 8/2 (2018) 289-294, doi: <https://doi.org/10.1364/OME.8.000289>.
- [25] M. Messner, D.J. Walczyk, B.G. Palazzo, Z.A. Norris, G. Taylor, J. Carroll, T.X. Pham, J.D. Hettinger, L. Yu, Electrochemical Oxidation of Metal Carbides in Aqueous Solutions, *Journal of The Electrochemical Society* 165/4 (2018) H3107-H3114, doi: [10.1149/2.0171804jes](https://doi.org/10.1149/2.0171804jes).
- [26] R. Liu, Z. Zheng, J. Spurgeon, X. Yang, Enhanced photoelectrochemical water-splitting performance of semiconductors by surface passivation layers, *Energy and Environmental Science* 7/8 (2014) 2504-2517, doi: [10.1039/C4EE00450G](https://doi.org/10.1039/C4EE00450G).
- [27] X. Huang, E. Lindgren, J.R. Chelikowsky, Surface passivation method for semiconductor nanostructures, *Physical Review B* 71/16 (2005) 165328, doi: <https://doi.org/10.1103/PhysRevB.71.165328>.
- [28] E. Oudot, Hydrogen passivation of silicon/silicon oxide interface by atomic layer deposited hafnium oxide and impact of silicon oxide underlayer, *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films* 36/1 (2018) 01A116, doi: <https://doi.org/10.1116/1.4999561>.
- [29] J. Pacyna, Crack resistance of tool steels corresponding with the chemical composition of their matrices, *Archives of Materials Science and Engineering* 86/1 (2017) 5-14, doi: DOI: [10.5604/01.3001.0010.4868](https://doi.org/10.5604/01.3001.0010.4868).
- [30] L.E. Black, A. Cavalli, M.A. Verheijen, J.E.M. Haverkort, E.P.A.M. Bakkers, W.M.M. Kessels, Effective Surface Passivation of InP Nanowires by Atomic-Layer-Deposited Al₂O₃ with PO_x Interlayer, *Nano Letters* 17/10 (2017) 6287-6294, doi: [10.1021/acs.nanolett.7b02972](https://doi.org/10.1021/acs.nanolett.7b02972).
- [31] A.M. Joseph, R.T. Kumar, Formation and investigation of low dimensional super paramagnetic α -manganese dioxide nano structures, *Materials Research Express* 5/1 (2018) 014002, doi: <https://doi.org/10.1088/2053-1591/aa9e5d>.
- [32] Q. Guo, L. Fu, H. Chen, Y. Li, H. Zheng, Effects of electrochemical sulfide passivation on electrical properties of Au/n-Hg₃In₂Te₆ Schottky contact, *Journal of Electron Spectroscopy and Related Phenomena* 222 (2018) 167-172, doi: <https://doi.org/10.1016/j.elspec.2017.03.019>.
- [33] Y. Suchikova, I. Bogdanov, S. Onishchenko, S. Vambol, V. Vambol, O. Kondratenko, Morphologies and photoluminescence properties of porous n-InP, *Proceedings of the IEEE 7th International Conference "Nanomaterials: Application & Properties"*, NAP, 2017, 01PCSI17-1-01PCSI17-5, doi: [10.1109/NAP.2017.8190154](https://doi.org/10.1109/NAP.2017.8190154).
- [34] R. Dhingra, S. Naidu, G. Upreti, R. Sawhney, Sustainable Nanotechnology: Through Green Methods and Life-Cycle Thinking, *Sustainability* 2 (2010) 3323-3338, doi: <https://doi.org/10.3390/su2103323>.
- [35] A. Resano-Garcia, S. Champmartin, Y. Battie, A. Koch, A. En Naciri, A. Ambari, N. Chaoui, Highly-repeatable generation of very small nanoparticles by pulsed-laser ablation in liquids of a high-speed rotating target, *Physical Chemistry Chemical Physics* 18/48 (2016) 32868-32875, doi: [10.1039/C6CP06511B](https://doi.org/10.1039/C6CP06511B).
- [36] R.I. MacCusprie, K. Rogers, M. Patra, Z. Suo, A.J. Allen, M.N. Martin, V.A. Hackley, Challenges for physical characterization of silver nanoparticles under pristine and environmentally relevant conditions, *Journal of Environmental Monitoring* 13/5 (2011) 1212-1226, doi: [10.1039/c1em10024f](https://doi.org/10.1039/c1em10024f).
- [37] M. Sobolak, P.E. Jagiełowicz, The methods of globoid surface modeling in CAD, *Archives of Materials Science and Engineering* 81/2 (2016) 76-84, doi: [10.5604/01.3001.0009.7102](https://doi.org/10.5604/01.3001.0009.7102).
- [38] P. Malara, L.B. Dobrzański, Screw-retained full arch restorations—methodology of computer aided design and manufacturing, *Archives of Materials Science and Engineering* 83/1 (2017) 23-29.
- [39] V. Kumar, D.K. Sharma, K. Sharma, D.K. Dwivedi, Investigation on physical properties of polycrystalline nickel sulphide films grown by simple & economical screen-printing method, *Optik-International Journal for Light and Electron Optics* 156 (2018) 43-48, doi: <https://doi.org/10.1016/j.ijleo.2017.10.169>.
- [40] Energy Dispersive Spectroscopy (EDS) Analysis / Oxford Instruments. – URL: <https://www.oxfordinstruments.com/products>.
- [41] Microanalysis system INCA Energy SEM / Electron microscopes. – URL: http://quantum.kz/Sistema_mikroanaliza_INCA_Energy_SEM/.

- [42] S. Langa, I.M. Tiginyanu, J. Carstensen, M. Christophersen, H. Föll, Self-organized growth of single crystals of nanopores, *Applied Physics Letters* 82/2 (2003) 278-280, doi: <https://doi.org/10.1063/1.1537868>.
- [43] S. Langa, J. Carstensen, M. Christophersen, K. Steen, S. Frey, I.M. Tiginyanu, H. Föll, Uniform and nonuniform nucleation of pores during the anodization of Si, Ge, and III-V semiconductors, *Journal of the Electrochemical Society* 152/8 (2005) C525-C531, doi: [10.1149/1.1940847](https://doi.org/10.1149/1.1940847).
- [44] S. Vambol, I. Bogdanov, V. Vambol, Research into effect of electrochemical etching conditions on the morphology of porous gallium arsenide, *Eastern-European Journal of Enterprise Technologies* 6/5(90) (2017) 22-31, doi: <https://doi.org/10.15587/1729-4061.2017.118725>.
- [45] A.P. Alivisatos, Perspectives on the physical chemistry of semiconductor nanocrystals, *The Journal of Physical Chemistry* 100/31 (1996) 13226-13239, doi: [10.1021/jp9535506](https://doi.org/10.1021/jp9535506).
- [46] C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chemistry and properties of nanocrystals of different shapes, *Chemical Reviews* 105/4 (2005) 1025-1102, doi: [10.1021/cr030063a](https://doi.org/10.1021/cr030063a).