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**Chemistry**

# SURFACE MODIFICATION OF GALLIUM ARSENIDE BY ELECTROCHEMICAL METHODS IN DIFFERENT ELECTROLYTE COMPOSITIONS

***Yana Suchikova[1, ✉], Sergii Kovachov[1], Andriy Lazarenko[1], Hanna Lopatina[1], Natalia Tsybuliak[1], Olha Hurenko[1], Ihor Bohdanov[1]***

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**Abstract.** We present the study of the n-GaAs surface modification by the electrochemical etching in different electrolyte compositions. The possibility of forming the different micromorphology types on the identical GaAs samples, in particular the possibility of forming the crystallographic, defective-dislocation, and isotope interfaces, was investigated.

**Keywords:** micromorphology, electrochemical etching, electrochemical reaction, electrolyte, anodizing voltage.

## 1. Introduction

The electrochemical methods of semiconductor surface modification are widely used when the materials of electronic devices are manufactured.[1,2] Such methods include chemical,[3] electrochemical,[4,5] and photoelectrochemical[6] etching, as well as electrochemical[7] and chemical deposition.[8] All these modifications of the method are based on the crystal treatment with the acid or alkali solutions.[9,10] The result of such treatment can be the formation of the films on the crystal surface,[11,12] polishing,[13] surface passivation,[14,15] and the formation of the developed semiconductor nanorelief.[16,17] The main advantages of the electrochemical method are its simplicity, cheapness, process speed, and the lack of need to use high-tech and costly equipment.[18]

This method is traditionally used in order to obtain the porous layers on the silicon surface.[19,20] This technology is already well-developed, which allows producing the porous silicon on a commercial scale. The electrochemical methods are also actively used for the binary semiconductors of groups $A^2B^6$ and $A^3B^5$.[21,22]

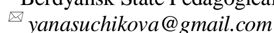
It should be noted that the semiconductors of group $A^2B^6$ are etched in the acid and alkali solutions much worse than the semiconductors of group $A^3B^5$ due to their peculiarities.[23] Therefore, other methods of surface modification, among which the methods of ion bombardment, thermal annealing, epitaxy, sol-gel methods, *etc.*[24,25] are used as a rule for the semiconductors of group $A^2B^6$. It should be noted that all these methods have their own peculiarities of implementation and ultimate goal, so they cannot be compared and prioritized.

Among all semiconductors, the largest variety of surface modification by the electrochemical methods was achieved for the crystals of type $A^3B^5$, including InP, GaAs, GaP.[26,27] Thus, the possibility for synthesizing the nanoneedles, nanowires, textured and porous surfaces, was repeatedly shown.[28,29] The heterostructures consisting of the layers of the semiconductor's own oxide can be also formed on the semiconductor surface by the electrochemical treatment methods.[30,31]

All this generates new interest in the surface modifications of the semiconductors of group A3B5 and stimulates the researchers to improve these methods.[32,33]

It should be noted that despite the implementation simplicity of the electrochemical treatment method of the semiconductors, the surface dissolution mechanism is quite a complex one and not been fully studied. This is primarily due to many factors on which the final result depends. Thus, during the electrochemical etching the morphological and chemical changes in the semiconductor surface are influenced by the electrolyte composition and concentration,[34] the value of applied potential,[35] treatment time,[36] electrolyte temperature, lighting, *etc.* Furthermore, it was reported about the self-organization processes of the nanostructure growth on the surface due to the influence of the surface and bulk defects.[37,38] It is also important to take into account the semiconductor characteristics, namely the conductivity type, surface orientation, type and concentration of the dopant, *etc.*[39,40]

In this study, we analyzed the influence of the electrolyte composition on the surface morphology of the gallium arsenide during the electrochemical etching in the acid solutions. This is not the first study of this type. Thus,

[1] Berdyansk State Pedagogical University

✉ *yanasuchikova@gmail.com*
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electrochemical etching of the gallium arsenide surface can lead to the formation of a dense porous layer.[41,42] Other studies indicate that the porous layer can consist of gallium or arsenic oxides.[43-45] However, so far not all GaAs surface modifications have been described, and the dissolution mechanism of this semiconductor during the electrochemical treatment has not been fully established. Furthermore, some results and conclusions can be generalized to a wider semiconductor class in order to establish a single mechanism of the nanorelief formation with the predetermined properties.

# 1. Introduction

## 2.1. Samples

A set of the same-type samples of the single-crystal gallium arsenide polished on both sides to a mirror shine, was used for the experiment. N-type conductivity samples, doped with antimony to the concentration of charge carriers 3×1019 $cm^{-3}$, were used. The samples were cut into ingots sized 1×2×0.2 cm. Before carrying out the experiment, the samples were cleaned with alcohol and washed in deionized water. After completion of the experiment, the samples were dried in a stream of nitrogen and kept in the open air for 3 months.

## 2.2. Device

The Teflon electrochemical cell was used for the n-GaAs electrochemical etching. The three-electrode mode was used. The platinum plate was used as the cathode, the semiconductor sample was used as the anode, the chlorine-argentum electrode EVL1M3 was used as the comparison electrode. The potentiostat of MTech SPG-500S model was used. The etching device was equipped with a Teflon stirrer to stir the electrolyte during the electrolysis and to outflow the reaction products from the semiconductor-electrolyte boundary. The platinum and semiconductor plates were placed parallel to each other and perpendicular to the electrolytic cell bottom. The distance between the anode and the cathode was 1 cm.

## 2.3. Experiment Methods

The semiconductor plates were subjected to the electrochemical treatment in the aqueous and alcohol acid solutions (for convenience, water and alcohol electrolytes, respectively). The following electrolyte sets were used (Table 1). Hydrochloric, hydrofluoric, and nitric acid solutions are selective etchants for GaAs.

The etching was carried out by the following method: After immersion of the semiconductor in the electrolyte solution, the crystal treatment began at a voltage of $U = 1$ V. After every minute, the anodizing voltage was increased by another 1 V, and so on. Such actions were carried out in order to determine the voltage $U_1$, at which the electrochemical dissolution process of the semiconductor begins (the first critical point, or the starting point of the electrochemical reaction).

**Table 1.** Electrolytes used for the experiment (v/v ratio)

| Sample No. | Etching agent |
|---|---|
| 1 | $HNO_3$:$H_2O$=1:4 |
| 2 | $HNO_3$:$H_2O$:$C_2H_5OH$ =1:4:2 |
| 3 | HF:$H_2O$=1:4 |
| 4 | HF:$H_2O$:$C_2H_5OH$=1:4:1 |
| 5 | HCl:$H_2O$=1:4 |
| 6 | HCl:$H_2O$:$C_2H_5OH$=1:4:2 |

At this moment, the behavior of the samples was visually observed and the current density values were recorded. A sharp increase in the current was observed at some value of the anodizing voltage (for each sample this value is individual). After some anodizing time, the current stopped rising, and was fixed at some value, or began to decrease. This meant that the active process of surface modification is being completed. The voltage value at this moment of the etching is the second critical point. The system was de-energized; the samples were kept in the same electrolyte solution for another 1 min. After that, the experiment was completed. All experiments were carried out in daylight at room temperature (293 K).

## 2.4. Study Methods

The scanning electron microscope (SEO-SEM Inspect S50-B) was used to study the morphology of the GaAs modified surface. The quantitative and qualitative characteristics of the nanostructures were determined by the ImageJ software package. The component composition of the elements on the sample surface was studied by the energy dispersion analysis with AZtecOne spectrometer and X-MaxN20 detector.

# 3. Results and Discussion

As a result of the experiment, it was found that the active electrochemical reaction occurred in all compositions of the tested electrolytes. The critical starting points of the active electrochemical reaction and its completion were recorded for all studied samples. According to the results of the scanning electron microscopy, it was also found that the sample behavior was significantly varied in different electrolyte compositions during the electrochemical reaction. It was found that the surface microrelief is formed by different mechanisms, namely defective, isotropic and crystallographic mechanisms depending on the electrolyte anion involved in the electrochemical reaction. Let us consider these cases below.

## 3.1. Defective-Dislocation Microrelief

The GaAs electrochemical etching in $HNO_3$ acid solutions occurs by the defective-dislocation mechanism, at which the primary surface microrelief is formed by etching the surface defects and releasing the dislocations.

Fig. 1 shows the dependence of the anodizing current density on the etching time. It can be seen that a similar trend is observed in both compositions of the nitrogen electrolyte solution (with/without adding the ethanol). The current begins to increase almost immediately from the beginning of the electrochemical reaction. A sharp increase in the current density was observed already in the second minute of the etching in both aqueous and alcoholic electrolytes. This indicates the active electrochemical process.

For the aqueous electrolyte, a linear dependence was observed until the second critical point is reached. For the alcohol electrolyte, a certain plateau was observed in the current density values in the interval of 6–8 min of the etching. As a rule, this plateau indicates that there is an electrochemical reaction on the surface, but it doesn't move into the sample depth. Probably, the passivating oxide film, which is formed during the electrochemical treatment of the sample in the first minutes of the etching, was dissolved at this moment. The GaAs electrochemical etching in $HNO_3$ acid solutions occurs by the defective-dislocation mechanism, at which the primary surface microrelief is formed by etching the surface defects and releasing the dislocations.

Fig. 2 shows the photomicrograph of the GaAs surface after the electrochemical treatment in the aqueous (a) and aqueous-alcoholic (b) nitric acid solutions, respectively. It can be seen that the nitric acid is a selective etching agent for the n-GaAs there is a developed interface: on the surface, which can be described as a defective-dislocation one. The surface morphology of the GaAs sample, presented in Fig. 2a, shows the presence of the steps resulting from the etching of the so-called "dislocation walls". There are also many oxides on the surface. In Fig. 2a they are visible as white stripes and porous clouds. The transverse size of the strip is 100 nm; its length is 200 nm.

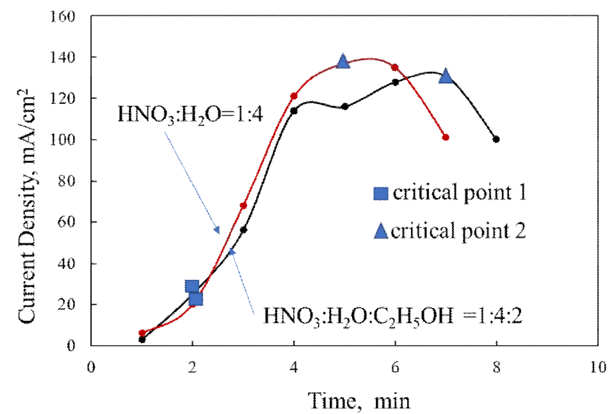



**Fig. 1.** Dependence of current density value on GaAs etching time for electrolyte solutions $HNO_3:H_2O=1:4$ and $HNO_3:H_2O:C_2H_5OH=1:4:2$

When adding the ethanol to the electrolyte, it is etched without forming the oxide islands (Fig. 2b). Instead, it is possible to observe the developed microrelief that contains the deep holes – the etching places of the dislocation. The plates stacked on top of each other are also observed. Thus, the etching in the nitric acid solutions is an anisotropic one against the n-GaAs and helps to detect surface defects.

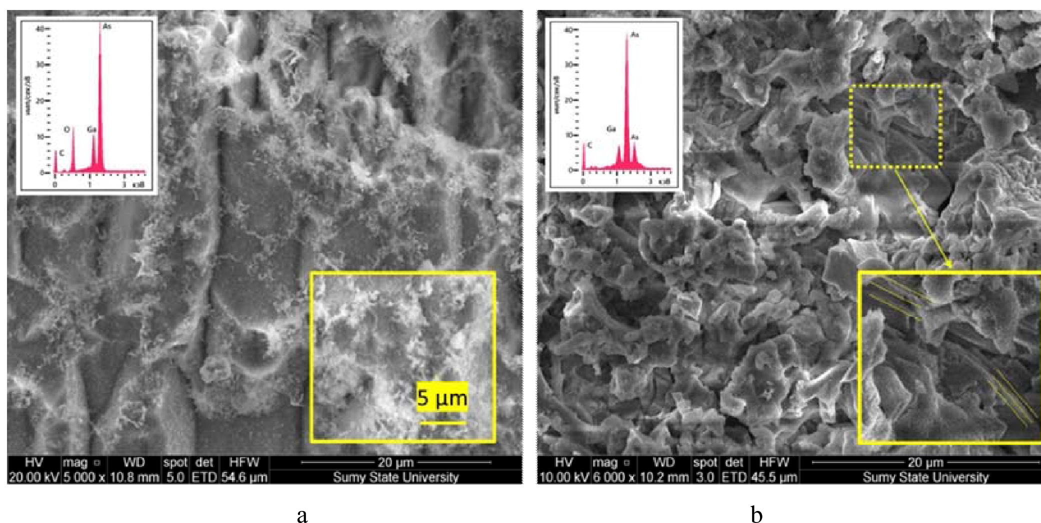



**Fig. 2.** SEM-image and EDX analysis of GaAs surface after electrochemical treatment in nitric acid solution: a – $HNO_3:H_2O=1:4$; b – $HNO_3:H_2O:C_2H_5OH=1:4:2$

Table 2 shows the proportion of components on the surface of the samples after electrochemical etching. It can be seen that in both cases there was a violation of stoichiometry in the direction of an excess of arsenic. A possible explanation for this is that arsenic binds better to oxygen ions in the electrolyte and is deposited on the surface of the sample in the form of an oxide. When ethanol is added to the electrolyte solution, we observe an almost complete absence of oxygen on the surface, which indicates that the reaction products did not settle on the surface of the sample.

**Table 2.** Ratio of components on the surface of samples after electrochemical etching in nitric acid solutions (At %)

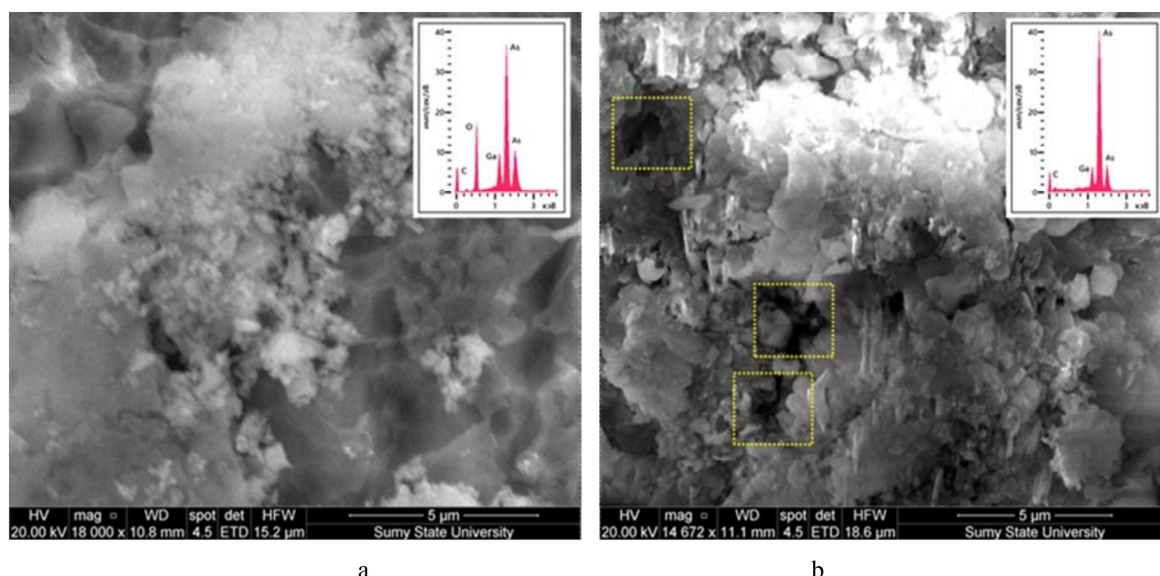
| Electrolyte | Ga | As | O |
|---|---|---|---|
| $HNO_3$:$H_2O$=1:4 | 30.51 | 50.44 | 19.05 |
| $HNO_3$:$H_2O$:$C_2H_5OH$ =1:4:2 | 42.34 | 56.60 | 1.06 |

## 3.2. Isotropic Microrelief

The GaAs electrochemical etching in the hydrofluoric acid solutions leads to the formation of the isotropic microrelief, *i.e.*, the relief without expressed growth directions of the pores and etching pits. The sample surface is characterized by a large number of small shallow pores. The absence of the pore advancement into the crystal volume is due to the fact that a dense passivating film is formed on the GaAs surface during the electrochemical etching, which prevents the advancement of the etching front into the crystal depth. Over time, this film is etched, forming networks of shallow holes on the GaAs surface. The formation of a loose oxide layer of the cloud type can also be observed (Fig. 3a). Such structures are formed during the deposition on the crystal surface of the reaction products adsorbed from the electrolyte solution. Most likely, the oxide is present on the surface in an amorphous state.

When the ethanol is added to the electrolyte solution, the surface becomes more relief (Fig. 3b). The presence of oxide is not observed on the surface. The large-scale etching pits can also be seen, which can indicate the etching process of the defects and dislocations. That is, the addition of ethanol to the HF aqueous solution allows the transition from the isotropic etching to the defective-dislocation one.

Fig. 4 shows the dependence of the current density on the etching time in the aqueous and alcoholic solutions of the hydrofluoric acid. It can be seen that in these electrolyte compositions the active electrochemical reaction begins later than for the nitrogen electrolytes – at the 3rd and 4th minutes for the alcohol and water electrolytes, respectively. The hydrofluoric acid is active against the GaAs surface, so it is etched not only in the defective areas of the sample but over the entire surface. We can observe the presence of a small plateau of the current density values for both alcohol and water electrolytes with the subsequent sharp rise. Such "steps" arise due to the fact that in the hydrofluoric acid it is etched due to two competing mechanisms: defective dislocation and sowing pore formation. Therefore, the preferred mechanism (especially for the water-electrolyte) is the sowing pore formation, which leads to the formation of the additive microrelief.




a b

**Fig. 3.** SEM-image and EDX analysis of GaAs surface after electrochemical treatment in the hydrofluoric acid solution: a – HF:$H_2O$=1:4; b – HF:$H_2O$:$C_2H_5OH$ =1:4:2

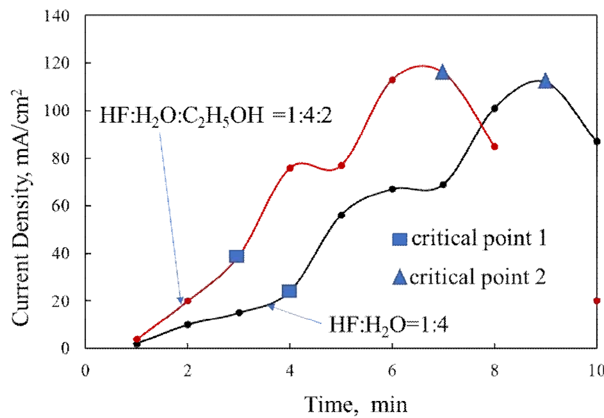



**Fig. 4.** Dependence of current density value on GaAs etching time for electrolyte solutions $HF:H_2O=1:4$ and $HF:H_2O:C_2H_5OH = 1:4:2$

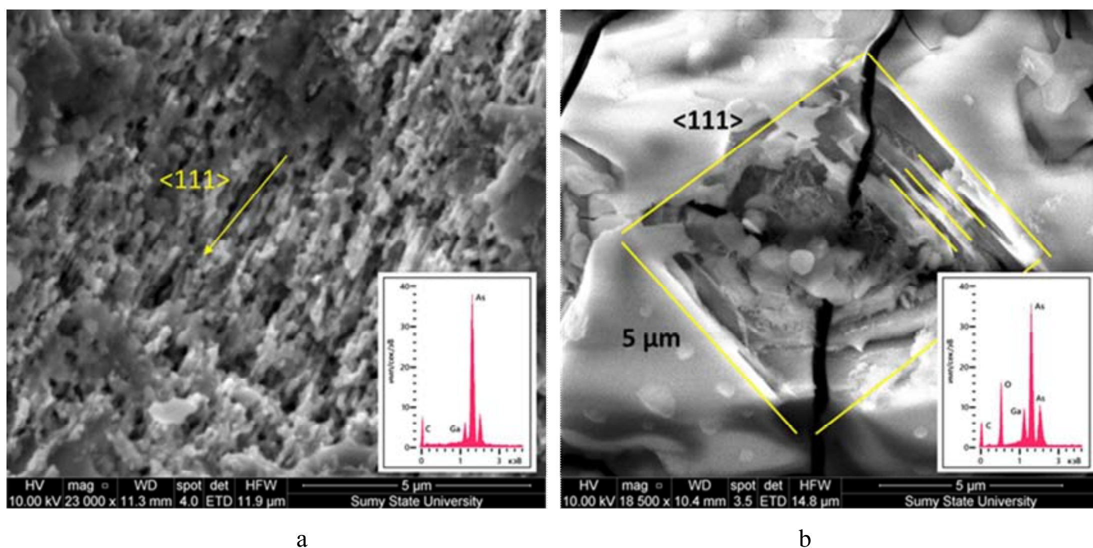
Table 3 shows the composition of samples after electrochemical etching in a hydrofluoric acid solution. In an aqueous solution of hydrofluoric acid, the electrochemical reaction occurred with significant oxidation of the surface. It is possible to observe almost complete overgrowth of the surface with an oxide film, which is confirmed by the above SEM data. As in the case of nitric acid, ethanol prevents reaction products from settling on the surface and better removes them from the electrolyte solution. Isolated clouds are observed, which are oxide inclusions on the surface.

**Table 3.** Ratio of components on the surface of samples after electrochemical treatment in hydrofluoric acid solutions (At %)

| Electrolyte | Ga | As | O |
|---|---|---|---|
| $HF:H_2O=1:4$ | 27.37 | 34.37 | 38.26 |
| $HF:H_2O:C_2H_5OH=1:4:1$ | 41.69 | 47.08 | 11.23 |

## 3.3. Crystallographic Microrelief

In our opinion, the most interesting case is the formation of a crystallographic microrelief on the GaAs surface. Such surfaces were obtained by electrochemical etching in the hydrochloric acid solutions. Thus, when using the aqueous electrolyte $HCl:H_2O=1:4$, the parallel etching pits, which are directed along the direction <111>, were formed on the n-GaAs surface (Fig. 5a). The pores were small enough and tightly packed. This pore type is called “crysto” due to its clear crystallographic direction. The GaAs etching in the HCl aqueous solution was without forming the oxide film.




a b

**Fig. 5.** SEM-image of GaAs surface after electrochemical treatment in nitric acid solution: a – $HCl:H_2O=1:4$; b – $HCl:H_2O:C_2H_5OH = 1:4:2$

When adding the ethanol to the electrolyte solution, a clear etching is observed in the crystallographic directions (Fig. 5b). The etching pit has a diamond shape, the faces of which coincide with the directions <111> A and <111> B. It can also be seen that the pore is etched in the layers, forming the steps. It has the shape of a regular quadrangular pyramid. The face length is 5 μm. Furthermore, the pore cracking along the pyramid diagonals can be observed. This indicates the etching of the dislocation, which came to the surface. That is, this microrelief type can be classified as a crystallographic-defective one, *i.e.*, mixed.

The hydrochloric acid shows a strong selectivity against the n-GaAs surface. When using the aqueous solution, the active increase in the current density is already observed in the second minute of the etching (Fig. 6). In

the third minute of the etching the process slows down a bit, but the current continues to increase. The plateau in the time interval of (3–5 min) is observed for the alcoholic solution of the electrolyte. This indicates that the main electrochemical processes are on the crystal surface. The acid anions, appropriate for the crystal surface, are not enough to carry out the etching in this mode. As the values of the applied potential increase, the process is intensified. In the interval of 5–6 min we can observe a sharp increase in the etching rate. Apparently, it was at this time that the etching front was advanced into the crystal depth and the crater-like crystallographic pores were formed.

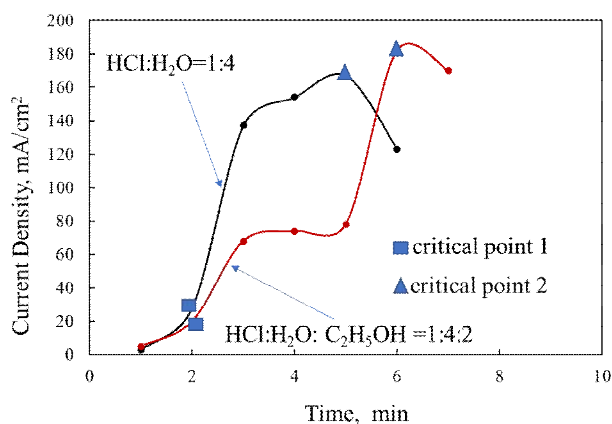



**Fig. 6.** Dependence of current density value on GaAs etching time for electrolyte solutions $HCl:H_2O=1:4$ and $HCl:H_2O:C_2H_5OH=1:4:2$

Table 4 shows the composition of the samples surface after electrochemical etching in hydrochloric acid solutions. In contrast to the previous two cases, the addition of ethane leads to the formation of an oxide film on the surface, while etching in an aqueous solution occurs almost without the precipitation of oxide compounds. This may be due to the high selectivity of hydrochloric acid toward the GaAs surface. From the first minutes of etching, the surface of the sample began to be etched without a transitional oxide stage. When ethanol is added, the sample solubility of the surface decreases, and in the first minutes of etching a dense oxide layer is formed, which is dissolved by the breakdown mechanism at later stages of etching.

**Table 4.** Ratio of components on the surface of samples after electrochemical treatment in hydrochloric acid solutions (At %)

| Electrolyte | Ga | As | O |
|---|---|---|---|
| $HCl:H_2O=1:4$ | 43.24 | 55.73 | 1.03 |
| $HCl:H_2O:C_2H_5OH=1:4:2$ | 32.72 | 29.35 | 37.93 |

## 3.4. Characterization of the Electrochemical Process

Thus, the developed morphology, formed on the surface of the gallium arsenide during the electrochemical etching in the acid solution has been shown by us. It is interesting to compare the behavior of the semiconductor samples in different electrolyte compositions. As noted in the “Experiment” section, we did not found the fixed treatment times, as well as the anodizing current and voltage. The etching process was with a gradual increase in the applied potential, and the conclusions about the stages of the electrochemical reaction were made according to the current values. When the current values were decreased, the process was stopped. Therefore, the treatment time is individual for each sample. Furthermore, the start and end time of the active phase of the electrochemical reaction (dissolution of the sample surface) was recorded. These values were obtained when analyzing the jumps of the anodizing current and fixing the critical points (Figs. 2, 4, 6).

Fig. 7 shows the time diagrams of the electrochemical treatment of the n-GaAs samples in different electrolyte compositions. The total treatment time $t_{sum}$ (meaning the time that the sample was etched when the external potential was applied) is most important for the aqueous solution of the hydrofluoric acid, least important for the aqueous solution of the hydrochloric acid (10 and 6 min, respectively). Thus, for the specified etching conditions and sample parameters, the hydrochloric acid shows greater selectivity against the n-GaAs surface compared to the hydrofluoric acid, *i.e.*, the reaction rate is higher when using the electrolytes based on the hydrochloric acid. It should be noted that the reaction rate is a parameter depending on many factors (state of the sample surface, its characteristics, external conditions of the experiment, *etc.*). Therefore, the results can significantly differ under other conditions.

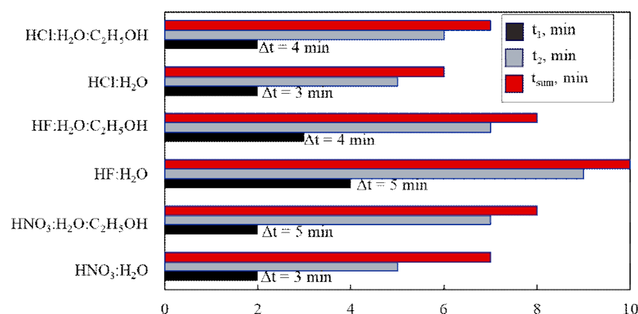



**Fig. 7.** Time diagrams of electrochemical treatment of n-GaAs samples in different electrolyte compositions. Fig.: $t_1$ is the start time of the active phase of the electrochemical reaction; $t_2$ is the end time of the active phase of the electrochemical reaction; $t_{sum}$ is the total time during which the electrochemical treatment of the sample was carried out

One of the characteristics of the electrochemical process is also the difference between the start and end time of the active phase of the electrochemical process $\Delta t = t_2 - t_1$. The highest value of $\Delta t = 2$ min corresponds to the aqueous solution of the hydrofluoric acid and the alcoholic solution of the nitric acid. This indirectly indicates that the etching process in these electrolyte compositions is uniform and slow. This result is well consistent with the results of the scanning electron microscopy - indeed, these samples have the most uniform surface microrelief (Figs. 1b, 3a). The aqueous solutions of the hydrochloric and nitric acid, on the contrary, correspond to the lowest value of $\Delta t = 3$ min. This means that the electrochemical process for this electrolyte type is very intense.

Fig. 8 shows the current density values during the GaAs electrochemical treatment at the beginning and after completion of the active phase of the electrochemical reaction. It can be seen that the highest current density values were recorded for the electrochemical reaction in the solutions of the hydrochloric acid.

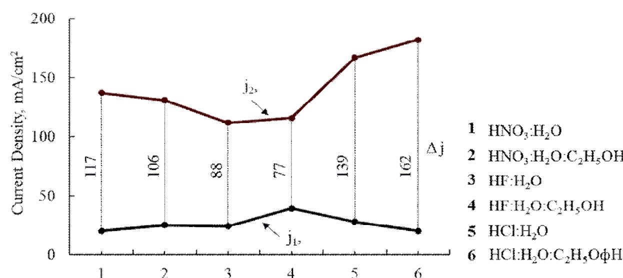



**Fig. 8.** Critical point values of current density for electrochemical treatment of n-GaAs samples in different electrolyte compositions: $j_1$ is the current density at the beginning of the active phase of the electrochemical reaction; $j_2$ is the current density at the end of the active phase of the electrochemical reaction, $\Delta j$ is the difference between $j_2$ and $j_1$

This indicates that in such electrolytes, the etching front is actively moving into the substrate depth, and the passivating coatings are not formed. Such results are well consistent with the results of SEM-analysis (Figs. 5a, b). For these electrolyte compositions, we also have the highest values of $\Delta j = j_2 - j_1$, namely 139 and 162 mA/cm$^2$ for the water and alcohol electrolytes, respectively. The high value of $\Delta j$ indicates that at the beginning of the electrochemical treatment of the GaAs in hydrochloric acid solutions the surface was not actively dissolved. Apparently, this is due to the acid concentration and its chemical activity against the n-GaAs surface. In this case, the applied potential is the decisive factor. As the potential increases over time, the electrochemical process of the crystal surface dissolution becomes faster. It should be also noted that the values of both $j_2$ and $\Delta j$ are higher for the alcoholic solution than for the aqueous solution. This indicates that in this case, the alcohol is a reaction accelerator, helping the outflow of the reaction products from the sample surface. The lowest value of $\Delta j$ is observed for the hydrofluoric acid solutions: 88 and 77 mA/cm$^2$ for the aqueous and alcohol electrolytes, respectively. Thus, the alcohol electrolyte has a lower value of $\Delta j$, which is primarily due to the fact that $j_1$ for the electrolyte $HF:H_2O:C_2H_5OH$ has the highest value compared to other electrolytes – 39 mA/cm$^2$. Therefore, this electrolyte composition is ideal for forming the dense porous layer on the n-GaAs surface. The values of $\Delta j$ for the electrolytes based on the nitric acid are quite adequate to the values of $j_2$ and $j_1$.

The critical values of the beginning voltage $U_1$ and the end voltage $U_2$ of the active phase of the electrochemical reaction are shown in Fig. 9. It can be seen that for the electrolytes, which contain the nitric and hydrochloric acid, the value of $U_1 = 2$ V. For the aqueous and alcoholic solutions of the hydrofluoric acid $U_1$ and $U_2$ the values are 4 and 3 V, respectively. Hence, the electrochemical reaction in the aqueous solution of the hydrofluoric acid was carried out the longest – $U_2 = 10$ V. The explanation for this phenomenon was higher because the voltage depends on the etching time according to the electrochemical treatment modes chosen by us. Note only that understanding the behavior of the GaAs semiconductor in different electrolyte solutions allows to create the nanostructures with predetermined controlled properties. As a result, the important point is the choice of the treatment mode – at the fixed (constant) values of the current or potential. The studies, presented by us, allow to choose a comfortable mode for achieving the planned result.

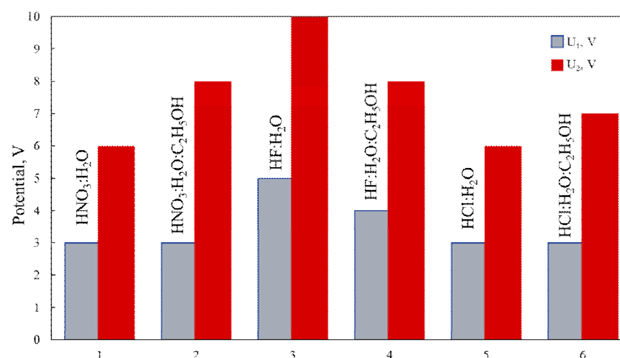



**Fig. 9.** Critical point values of applied voltage during electrochemical treatment of n-GaAs samples in different electrolyte compositions: $U_1$ is the current density at the beginning of the active phase of the electrochemical reaction; $U_2$ is the current density at the end of the active phase of the electrochemical reaction

Also, note that semiconductor etching is a multistage process involving the oxidation and subsequent dissolution of the formed oxide. It can be assumed that if

the concentrations of the oxidizing reagent are low, the reaction rate will determine the oxidation process, while if the concentrations are high, the reaction rate will be limited to the oxide dissolution. Furthermore, in some cases, the oxidation of the semiconductor surface does not occur at all, it can contribute to a higher rate of the electrochemical reaction and the formation of the developed micromorphology on the surface. It should be also noted that uneven etching of the crystal surface can occur when some areas of the surface behave as anodes or cathodes due to the variations in the material composition on the surface. Such behavior can be due to the presence of defects, inclusions, *etc*. Thus, the release sites of the dislocations on the surface can act as anodes. In this case, the formation of the dislocation etching pits is observed.

### 3.5. Limitations and Prospects for Further Research

It is worth noting that the electrochemical reactions that occur at the electrolyte/semiconductor interface are quite complex and depend on many factors. This is how electrochemical methods differ from many others. Thus, the result of the electrochemical dissolution of the crystal is simultaneously influenced by both the initial properties of the sample and the experimental conditions themselves. Therefore, changing any parameter changes the behavior of the entire system. The results presented in the article are valid only for the conditions described in the etching conditions article and for samples with characteristics identical to the selected ones. However, our studies help to partially understand how the composition of the electrolyte can affect the morphological characteristics of the samples. We did not focus our attention on the electrochemical processes themselves, which obviously require further research. Research is also needed to establish the influence of process mechanisms on the properties of crystals and their surface characteristics. Such studies are necessary to unify requirements for nanotechnological products and to establish optimal modes of electrochemical processing of crystals.

## 4. Conclusions

The modification of the n-GaAs surface in the electrolyte solutions by applying the external potential (electrochemical etching) is a complex physicochemical process that depends on many factors. The selection of the electrolyte concentration and composition allows to implement the controlled modification of the GaAs surface as well as to create the interface with a unique micromorphology. We demonstrate the synthesis on the n-GaAs surface of the defective-dislocation, isotropic and crystallographic morphologies in the aqueous and alcoholic solutions of the nitric, hydrofluoric, and hydrochloric acids, respectively.

Among the important observations of the experimental studies, presented in this paper, are as follows:

1. For initiating the active phase of the dissolution of the semiconductor surface, it is necessary to apply the appropriate voltage - the critical voltage of the beginning of the electrochemical reaction $U_1$.

2. For different electrolyte compositions the value of $U_1$ is determined individually. It should be noted that it depends not only on the acid composition and concentration in the electrolyte but also on other treatment modes and the state of the semiconductor surface.

3. During the GaAs electrochemical etching, the oxide films and islands are formed on the surface under certain conditions and electrolyte compositions. These films can be the passivating coating, on the other hand – they can impact the optical and physical properties of the devices, so their control is extremely important.

4. The electrochemical dissolution of the crystal is limited in time. There is a point at which the values of the anodizing current begin to decrease. This indicates that the active phase is being completed and the etching process can be stopped. The nature of this phenomenon should be discussed separately, but it can be said that it depends on the electrolyte depletion and partial passivation of the sample surface.

5. The introduction of the ethyl alcohol into the electrolyte solution allows to clean the surface from the formation of the oxide film by initiating a faster outflow of the reaction products from the sample surface. In some cases, the ethyl alcohol is also used as an accelerator of the electrochemical reaction.

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## References


[1] Fiuczek, N.; Sawicka, M.; Feduniewicz-Żmuda, A.; Siekacz, M.; Żak, M.; Nowakowski-Szkudlarek, K.; Muzioł, G.; Wolny, P.; Kelly, J.J.; Skierbiszewski, C. Electrochemical Etching of p-Type GaN Using a Tunnel Junction for Efficient Hole Injection. *Acta Mater.* **2022**, *234*, 118018. https://doi.org/10.1016/j.actamat.2022.118018

[2] Suchikova, Ya. Porous Indium Phosphide: Preparation and Properties. In *Handbook of Nanoelectrochemistry*: *Electrochemical Synthesis Methods, Properties, and Characterization Techniques*; Springer, 2016; pp 283-306.

[3] Surmeneva, M.A.; Khrapov, D.; Prosolov, K.; Kozadayeva, M.; Koptyug, A.; Volkova, A.; Surmenev, R.A. The Influence of Chemical Etching on Porous Structure and Mechanical Properties of the $Ti_6AL_4V$ Functionally Graded Porous Scaffolds Fabricated by EBM. *Mater. Chem. Phys.* **2022**, *275*, 125217. https://doi.org/10.1016/j.matchemphys.2021.125217

[4] Suchikova, J.A.; Kidalov, V.V.; Sukach, G.A. Preparation of Nanoporous n-InP(100) Layers by Electrochemical Etching in HCI Solution. *Funct. Mater.* **2010**, *17*, 131-134.

[5] Sychikova, Y.O.; Bogdanov, I.T.; Kovachov, S.S. Influence of Current Density of Anodizing on the Geometric Characteristics of Nanostructures Synthesized on the Surface of Semiconductors of $A_3B_5$ Group and Silicon *Funct. Mater.* **2019**, *27*, 29-34. https://doi.org/10.15407/fm27.01.29

[6] Weyher, J.L.; van Dorp, D.H.; Conard, T.; Nowak, G.; Levchenko, I.; Kelly, J.J. Chemical Etching of GaN in KOH Solution: Role of Surface Polarity and Prior Photoetching. *J. Phys. Chem. C* **2022**, *126*, 1115–1124. https://doi.org/10.1021/acs.jpcc.1c06528

[7] Çepni, E.; Özer, T.Ö. Electrochemical Deposition of Indium (III) Hydroxide Nanostructures for Novel Battery-Like Capacitive Materials. *J. Energy Storage* **2022**, *45*, 103678. https://doi.org/10.1016/j.est.2021.103678

[8] Han, Z.; Zhang, R.; Li, M.; Li, L.; Geng, D.; Hu, W. Recent Advances in Controlled Chemical Vapor Deposition Growth of Bilayer 2D Single Crystals. *J. Mater. Chem. C* **2022**, *10*, 13324-13350. https://doi.org/10.1039/D2TC01095J

[9] Heidarpour, A.; Faraji, M.; Haghighi, A. Production and Characterization of Carbide-Derived-Nanocarbon Structures Obtained by HF Electrochemical Etching of $Ti_3AlC_2$. *Ceram. Int.* **2022**, *48*, 11466-11474. https://doi.org/10.1016/j.ceramint.2022.01.003

[10] Suchikova, Y.A.; Kidalov, V.V.; Sukach, G.A. Influence of Type Anion of Electrolit on Morphology Porous InP Obtained by Electrochemical Etching. *Journal of Nano- and Electronic Physics* **2009**, *1*, 78-86.

[11] Roldan, T.; Méndez-Blas, A.; López-Cruz, E.; Calixto, M. E. Semiconducting $Cu_2Se$ Thin Films Obtained by Electrochemical Deposition for Possible Applications in Thermoelectric Systems. *MRS Adv.* **2022**, *7*, 1-4. https://doi.org/10.1557/s43580-021-00197-9

[12] Çetinel, A. Characterization of Octahedral $Cu_2O$ Nanostructures Grown on Porous Silicon by Electrochemical Deposition. *Mater. Chem. Phys.* **2022**, *277*, 125532. https://doi.org/10.1016/j.matchemphys.2021.125532

[13] Abouelata, A.M.A.; Attia, A.; Youssef, G.I. Electrochemical Polishing Versus Mechanical Polishing of AISI 304: Surface and Electrochemical Study. *J. Solid State Electrochem.* **2022**, *26*, 121-129. https://doi.org/10.1007/s10008-021-05037-2

[14] Suchikova, Y.O. Sulfide Passivation of Indium Phosphide Porous Surfaces. *Journal of Nano- and Electronic Physics* **2017**, *9*, 01006. http://dx.doi.org/10.21272/jnep.9(1).01006

[15] Zeng, Y.; Gossage, Z.T.; Sarbapalli, D.; Hui, J.; Rodríguez□López, J. Tracking Passivation and Cation Flux at Incipient Solid□Electrolyte Interphases on Multi□Layer Graphene using High Resolution Scanning Electrochemical Microscopy. *ChemElectroChem* **2022**, *9*, e202101445. https://doi.org/10.1002/celc.202101445

[16] Guo, H.; Cao, S.; Li, L.; Zhang, X. A Review on the Mainstream Through-Silicon via Etching Methods. *Mater. Sci. Semicond. Process.* **2022**, *137*, 106182. https://doi.org/10.1016/j.mssp.2021.106182

[17] Suchikova, Y.A.; Kidalov, V.V.; Sukach, G.A. Influence of the Carrier Concentration of Indium Phosphide on the Porous Layer Formation. *Journal of Nano- and Electronic Physics* **2010**, *2*, 75-81.

[18] Vambol, S.; Vambol, V.; Suchikova, Y.; Deyneko, N. Analysis of the Ways to Provide Ecological Safety for the Products of Nanotechnologies Throughout their Life Cycle. *East.-Eur. J. Enterp. Technol.* **2017**, *1*, 27-36. https://doi.org/10.15587/1729-4061.2017.85847

[19] Ge, D.; Rezk, A.; Zhao, C.; Hu, Z.; Zhang, L. Experimental Research on Damage and Formation Limits on Porous Silicon Materials by Electrochemical Etching Method. *J. Mater. Res.* **2022**, *37*, 876-886. https://doi.org/10.1557/s43578-021-00471-4

[20] Dawood, N.S.; Zayer, M.Q.; Jawad, M.F. Study of the Vacuum Pressure Sensing from the Electrical Resistance Response of Porous Silicon Fabricated via Photo-Electrochemical. *Journal of Applied Sciences and Nanotechnology* **2022**, *2*, 28-36. https://doi.org/10.53293/jasn.2021.3763.1041

[21] Shushanian, A.; Iida, D.; Zhuang, Z.; Han, Y., Ohkawa, K. Analysis of the n-GaN Electrochemical Etching Process and its Mechanism in Oxalic Acid. *RSC Adv.* **2022**, *12*, 4648-4655. https://doi.org/10.1039/D1RA07992A

[22] Suchikova, Y.A.; Kidalov, V.V.; Sukach, G.A. Influence of Dislocations on the Process of Pore Formation in n-InP (111) Single Crystals. *Semiconductors* **2011**, *45*, 121-124. https://doi.org/1134/S1063782611010192

[23] Atrashchenko, A.V.; Katz, V.N.; Ulin, V.P.; Evtikhiev, V.P.; Kochereshko, V.P. Fabrication and Optical Properties of Porous InP Structures. *Physica E Low Dimens. Syst. Nanostruct.* **2012**, *44*, 1324-1328. https://doi.org/10.1016/j.physe.2012.02.012

[24] Karipbayev, Z.T.; Kumarbekov, K.; Manika, I.; Dauletbekova, A.; Kozlovskiy, A.; Sugak, D.; Ubizskii, S.; Akilbekov, A.; Suchikova, Y., Popov, A.I. Optical, Structural, and Mechanical Properties of $Gd_3Ga_5O_{12}$ Single Crystals Irradiated with $^{84}Kr+$ Ions. *Phys. Status Solidi B Basic Res.* **2022**, *259*, 2100415. https://doi.org/10.1002/pssb.202100415

[25] Popov, A.I.; Balanzat, E.F Centre Production in CsI and CsI-Tl Crystals under Kr Ion Irradiation at 15 K. *Nucl. Instrum. Methods Phys. Res. B* **2000**, *166*, 545-549. https://doi.org/10.1016/S0168-583X(99)00789-2

[26] Cao, X.; Zhang, Y.; Ma, C.; Wang, Y.; Brechtken, B.; Haug, R. J.; Rugeramigabo, E.P.; Zopf, M.; Ding, F. Local Droplet Etching on InAlAs/InP Surfaces with InAl Droplets. *AIP Adv.* **2022**, *12*, 055302. https://doi.org/10.1063/5.0088012

[27] Kovachov, S.S.; Bogdanov, I.T.; Pimenov, D.O.; Bondarenko, V.; Konovalenko, A.; Skurska, M.; Konovalenko, I.S.; Suchikova, Y.O. Chemical Evaluation of the Quality of Nanostructures Synthesized on the Surface of Indium Phosphide. *Arch. Mater. Sci. Eng.* **2021**, *110*, 18-26. https://doi.org/10.5604/01.3001.0015.3592

[28] Monaico, E.V.; Morari, V.; Ursaki, V.V.; Nielsch, K.; Tiginyanu, I.M. Core–Shell GaAs-Fe Nanowire Arrays: Fabrication Using Electrochemical Etching and Deposition and Study of Their Magnetic Properties. *Nanomaterials* **2022**, *12*, 1506. https://doi.org/10.3390/nano12091506

[29] Vambol, S.O.; Bogdanov, I.T.; Vambol, V.V.; Suchikova, Ya.O.; Kovachov, S.S. Correlation between Technological Factors of Synthesis of por-GaP and its Acquired Properties. *Nanosystemy, Nanomaterialy, Nanotehnologii* **2018**, *16*, 657-670.
[30] Suchikova, Y.; Lazarenko, A.; Kovachov, S.; Usseinov, A.; Karipbaev, Z.; Popov, A. I. Formation of Porous $Ga_2O_3$/GaAs Layers for Electronic Devices. In *2022 IEEE 16th International Conference on Advanced Trends in Radioelectronics, Telecommunications and Computer Engineering (TCSET)*; Lviv-Slavske, 2022. https://doi.org/10.1109/TCSET55632.2022.9766890
[31] Dontsova, T.; Kutuzova, A.; Hosseini-Bandegharaei, A. Characterization and Properties of Titanium (IV) Oxide, Synthesized by Different Routes. *Chem. Chem. Technol*. **2021**, *15*, 465-474. https://doi.org/10.23939/chcht15.04.465
[32] Deivasigamani, P.; Ponnusamy, S.K., Sundararaman, S.; Suresh, A. Superhigh Adsorption of Cadmium (II) Ions onto Surface Modified Nano Zerovalent Iron Composite (CNS-nZVI): Characterization, Adsorption Kinetics and Isotherm Studies. *Chem. Chem. Technol*. **2021**, *15*, 457-464. https://doi.org/10.23939/chcht15.04.457
[33] Prudius, S.; Hes, N.; Trachevskiy, V.; Khyzhun, O.; Brei, V. Superacid $ZrO_2$–$SiO_2$–$SnO_2$ Mixed Oxide: Synthesis and Study. *Chem. Chem. Technol* **2021**, *15*, 336-342. https://doi.org/10.23939/chcht15.03.336
[34] Beji, L.; Sfaxi, L.; Ismail, B.; Zghal, S.; Hassen, F.; Maaref, H. Morphology and Photoluminescence Studies of Electrochemically Etched Heavily Doped p-Type GaAs in HF Solution. *Microelectronics J*. **2003**, *34*, 969-974. https://doi.org/10.1016/S0026-2692(03)00183-6
[35] Langa, S.; Tiginyanu, I.M.; Carstensen, J.; Christophersen, M.; Föll, H. Formation of Porous Layers with Different Morphologies during Anodic Etching of n□InP. *Electrochem. solid-state lett*. **2000**, *3*, 514-516.
[36] Spiecker, E.; Rudel, M.; Jäger, W.; Leisner, M.; Föll, H. Morphology, Interface Polarity and Branching of Electrochemically Etched Pores in InP. *Phys. Status Solidi A* **2005**, *202*, 2950-2962. https://doi.org/10.1002/pssa.200521098
[37] Guo, N.; Xue, H.; Bao, A.; Wang, Z.; Sun, J.; Song, T.; Ge, X.; Zhang, W.; Huang, K.; He, F. et al. Achieving Superior Electrocatalytic Performance by Surface Copper Vacancy Defects during Electrochemical Etching Process. *Angew. Chem*. **2020**, *132*, 13882-13888. https://doi.org/10.1002/ange.202002394
[38] Faktor, M.M.; Stevenson, J.L. The Detection of Structural Defects in GaAs by Electrochemical Etching. *J. Electrochem. Soc*. **1978**, *125*, 621. https://doi.org/10.1149/1.2131512
[39] Bohdanov, I.; Suchikova, Y.; Kovachov, S.; Peregudova, V.; Dauletbekova, A.K.; Popov, A.I. Investigation of Critical Points of Pore Formation Voltage on the Surface of Semiconductors of A3B5 Group. In *2021 IEEE 12th International Conference on Electronics and Information Technologies, ELIT 2021*; Lviv, 2021; pp 190-193. https://doi.org/10.1109/ELIT53502.2021.9501107
[40] Naddaf, M. Formation of Superhydrophobic Porous GaAs Layer: Effect of Substrate Doping Type. *Bull. Mater. Sci*. **2022**, *45*, 89. https://doi.org/10.1007/s12034-021-02639-4
[41] Bioud, Y. A.; Boucherif, A.; Belarouci, A.; Paradis, E.; Drouin, D.; Arès, R. Chemical Composition of Nanoporous Layer Formed by Electrochemical Etching of p-Type GaAs. *Nanoscale Res. Lett*. **2016**, *11*, 446. https://doi.org/10.1186/s11671-016-1642-z
[42] Vambol, S.; Bogdanov, I.; Vambol, V.; Lopatina, H.; Tsybuliak, N. Research into Effect of Electrochemical Etching Conditions on the Morphology of Porous Gallium Arsenide. *East.-Eur. J. Enterp. Technol*. **2017**, *6*, 22-31. https://doi.org/10.15587/1729-4061.2017.118725
[43] Suchikova, Y.O.; Kovachov, S.S.; Lazarenko, A.S.; Bardus, I.O.; Tikhovod, K.; Hurenko, O.I.; Bohdanov, I.T. Oxidation of the n-GaAs Surface: Morphological and Kinetic Analysis. *Journal of Nano- and Electronic Physics* **2022**, *14*, 03033. https://doi.org/10.21272/jnep.14(3).03033
[44] Vambol, S.O.; Bohdanov, I.T.; Vambol, V.V.; Suchikova, Y.O.; Kondratenko, O.M.; Nestorenko, T.P.; Onyschenko, S.V. Formation of Filamentary Structures of Oxide on the Surface of Monocrystalline Gallium Arsenide. *Journal of Nano- and Electronic Physics* **2017**, *9*, 06016. https://doi.org/10.21272/jnep.9(6).06016
[45] Md Taib M.I.; Zainal, N.; Hassan, Z. Improvement of Porous GaAs (100) Structure through Electrochemical Etching Based on DMF Solution. *J. Nanomater*. **2014**, *2014*, 294385. https://doi.org/10.1155/2014/294385

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## МОДИФІКАЦІЯ ПОВЕРХНІ АРСЕНІДУ ГАЛІЮ ЕЛЕКТРОХІМІЧНИМИ МЕТОДАМИ В РІЗНИХ КОМПОЗИЦІЯХ ЕЛЕКТРОЛІТІВ

***Анотація.*** *Висвітлено дослідження модифікації поверхні n-GaAs методом електрохімічного травлення в різних композиціях електролітів. Досліджено можливість формування різних типів мікроморфології на ідентичних зразках GaAs, зокрема формування кристалографічних, дефектно-дислокаційних та ізотропних інтерфейсів.*

***Ключові слова:*** *мікроморфологія, електрохімічне травлення, електрохімічна реакція, електроліт, напруга анодування.*