Oxidation of the *n*-GaAs Surface: Morphological and Kinetic Analysis

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We study the directed oxidation processes of the *n*-GaAs surface as a result of the electrochemical treatment of a semiconductor in an aqueous-alcoholic solution of hydrochloric acid. The analysis of the voltampere characteristics was carried out in order to study the process kinetics, this made it possible to establish the formation stages of the oxide film and islands. The surface morphology was estimated according to the area characteristics, linear sizes, Solidity and Round islands. It was shown that the oxidation occurs by the Stranski-Krastanov mechanism. The formation study of own oxides on the GaAs surface is extremely important, because oxides can significantly impact the material properties. The native oxides of semiconductors are an inactive film that reliably protects the surface from environmental action and when interacting with aggressive substances. In addition, the native oxides of GaAs exhibit semiconductor properties that allow to create oxide/GaAs heterostructures with heterojunctions for optoelectronic applications.

Keywords: GaAs, Oxidation, Flade potential, Solidity, Round, Stranski-Krastanov mechanism, Layerplus-island growth.

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1. INTRODUCTION

Electrochemical treatment of semiconductor and metal surfaces is a widespread method of both scientific research and industrial production [1, 2]. Porous layers [3, 4], nanospots [5], nanoneedles [6], thin films [7], etc. were formed due to this method. The method has also gained special popularity for observing the growth defects of semiconductors [8]. The best results can be obtained for semiconductors of the A^3B^5 group and silicon due to the well-established technology and the presence of a large number of the selective herbalists [9].

GaAs electrochemical etching includes many stages, which can be conditionally divided into two: oxidation of surface atoms and dissolution of reaction products. Therefore, most electrolytes include both oxidizing and reducing agents. Hydrogen peroxide, bromine, water, alcohol are used as an oxidizing agent [10]. Acids and alkalis are used as a complex-forming agent [11]. Such solutions can be used not only for electrochemical etching of the semiconductor in order to form the microand macro-relief on its surface, but also for the directed synthesis of oxide layers and crystallites [12].

GaAs electrochemical etching in acidic electrolyte solutions is often accompanied by alternative processes, namely oxidation of the semiconductor of the semiconductor surface [13]. It is due to the deposition of reaction products on the semiconductor sample surface. In this regard, it is appropriate to talk about electrochemical oxidation processes, i.e., the creation of an oxide film or crystallites on the material surface as a result of oxidative-renewable reactions. In this case, structures with natural nanostructuring are quite often formed [14].

The formation of own oxide layers on the GaAs surface can significantly affect the material properties [15]. On the other side, own oxides can act as a passivating film, which prevents the material from breaking down in natural and aggressive environments [16]. Furthermore, most gallium and arsenic oxides are semiconductors, which provides the possibility for synthesizing the oxide/GaAs heterostructures as well as creating the heterostructures [17].

The electrochemical etching/deposition method is the most optimal for creating oxide layers and structures on the GaAs surface due to the existing undeniable advantages. This method is quite simple, allowing to synthesize both thin and thick films on surfaces of different shapes. The method has a high performance and low cost. If the technology is well-developed, the method allows to synthesize structures with controlled and predetermined properties. Along with this, it should be noted that the properties of the synthesized coatings are highly dependent on the treatment modes, the surface state of the output material and the electrolyte composition. This requires additional studies of the electrochemical treatment of materials, as well as the characteristics of the synthesized coatings.

In this paper, we study the oxidation of the n-GaAs surface, namely the process kinetics, the morphological characteristics of oxide formations, and the growth mechanism of the film and islands.

2. EXPERIMENT

2.1 Experiment Samples

The plates made of single-crystal gallium arsenide, grown by the Czochralski method from under the boron anhydride layer with angles of crystal growth from the seed to a specified diameter at a temperature of 35-90 °C were used for the experiment. The parameters of the output crystal are shown in Table 1.

Samples with sizes $1 \times 2 \times 0.2$ cm were cut by a string cutting with diamond spraying. Such cutting leads to mechanical damage to the sample surface, which is characterized by the appearance of roughness and chips. This can cause surface oxidation. In order to eliminate these phenomena, the surface was ground, polished and cleaned immediately before the experiment.

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Conductivity type	n	
Surface orientation	(111)	
Dopant	Sb	
Concentration of non-basic charge carriers, cm ⁻³	3×10 ¹⁹	
Syngonia	cubic	
Structure type	sphalerite	
Constant lattice, nm	0.5653	
Atomic density, cm ⁻³	4.43×10^{22}	
Structure of energy zones	straight-zone	
Width of prohibited zone, eV ($T = 300$ K)	1.43	
Connection nature	Ionic-covalent	

The samples were ground by an aqueous suspension of micropowder M10.

Diamond paste ASM 3/2 was used for mechanical polishing. An aqueous solution made of a mixture of hydrochloric and perchloric acids (HCl:HClO₄ = 1:1) was used for the chemical polishing. The samples were chemically treated for 5 min.

In order to clean and degrease the plate surfaces, they were washed in isopropyl alcohol, acetone and deionized water. Immediately after that, they were placed in the electrolyte solution without contact with air. Such thorough cleaning of semiconductor plates is required to eliminate the impact of the surface state on the course of the experiment.

2.2 Equipment

The experiment was carried out in a standard electrolytic cell (Fig. 1). The anode and cathode were fixed parallel to each other and perpendicular to the cell bottom at a distance of 1 cm. The Teflon cell was filled with an electrolyte solution. The cell was equipped with a stirrer for mixing the electrolyte during electrochemical treatment of crystals, removal of bubbles from the electrode surface and outflow of reaction products. The mixing mode of the electrolyte was used only in the first stages. The mixing mode was turned off for efficient electrochemical oxidation of the sample surface. A platinum plate was used as the cathode, and a semiconductor sample was used as the anode. A chlorineargentum comparison electrode was also used. The MTech SPG-500S potentiostat was used to observe the changes in the current values during the electrochemical treatment.

2.3 Experiment Method

The electrochemical etching method is characterized by the formation of adatoms, which consist of electrolyte ions and atoms of the sample surface, having broken bonds. Due to the application of an external potential, these adatoms are pulled from the semiconductor surface, which causes etching pits and a porous texture to be formed.

The opposite of this method is the electrochemical deposition method (in our case - oxidation), which is characterized by the application of the reaction products (sediment) on the electrode surface by passing the

current through the electrolyte solution saturated with the reaction products. Thus, these two electrochemical processes (etching and deposition) can flow simultaneously or cyclically, naturally changing each other. In this case, it is important to choose the treatment modes, on which the final result of the electrochemical reaction will depend.



Fig. 1 – Scheme of the electrolytic cell for *n*-GaAs oxidation

The electrochemical treatment of n-GaAs samples was carried out in HCl:H₂O:C₂H₅OH = 1:4:2 electrolyte solution.

The initial anodizing voltage was $U_0 = 1$ V. After every minute, the anodizing voltage was increased by 1 V to reach the value of $U_{end} = 10$ V. Then 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 a room temperature (20 °C).

2.4 Characterization

SEO-SEM Inspect S50-B scanning electron microscope was used to study the nanostructure morphology.

The element analysis on the synthesized structure surface was studied by the EDX AZtecOne spectrometer with the X-MaxN20 detector.

The morphological characteristics were studied by the ImageJ software package.

In order to describe the kinetics of the electrochemical process, the method of potential dynamics anode polarization was used, which is that the dependence of the anode current density on the polarized anode potential is registered during electrochemical treatment of the sample. The dependence is observed by means of the comparison electrode.

3. RESULTS

3.1 Volt-Ampere Characteristics of Electrochemical Reaction

Fig. 2 shows the diagram of the dependence of the current density on the applied potential taken during the electrochemical treatment of *n*-GaAs.



Fig. 2 – Scheme of the electrolytic cell for n-GaAs oxidation

Site 1 characterizes the active state of the semiconductor plate (anode). At this stage, etching of the GaAs surface is observed due to the extraction of gallium and arsenic atoms from the sample surface and their entry into the electrolyte solution. That is, there is the process of electrochemical dissolution of GaAs and ionization of its surface. It should be noted that the low value of the applied potential is sufficient for starting the etching process. This is due to the primary eradication of defective areas of the surface, which cause the area around them to be tensioned and are the embryos of etching pits. For initiating electrochemical etching of the entire sample surface, it is necessary to apply a much higher potential. Fig. 2 shows a plateau in the interval of 2-4 V, which is due to insufficient voltage in order to advance the etching front over the surface and into the sample volume. When the minimum required value of the anodizing voltage is reached, the active phase of electrochemical dissolution of the GaAs begins. This value depends on many factors and is selected individually for each case. In our case, the voltage at the beginning of active dissolution of the GaAs surface is $U_0 = 4$ V. The sample is actively dissolved, a gray sediment is observed on the cathode, and the electrolyte becomes pink. This indicates active dissolution of the entire surface (pore formation) and the entry of significant amounts of arsenic and gallium into the electrolyte. If the electrochemical reaction is stopped at this stage, then it is likely to obtain porous non-oxide layers of GaAs or the oxide concentration on the surface will be minimal.

The deposition of the reaction products on the anode begins along with this process. That is, at this time, the GaAs surface can be overgrown with an oxide film. The peak of the polarization curve $(j_{max} = 182 \text{ mA/cm}^2)$ corresponds to the maximum dissolution rate of the semiconductor sample surface. The maximum value of the current density corresponds to the value of the Flade potential V_f [18]. Exceeding the value of V_f will mean that the oxidation rate of the GaAs surface becomes higher than the dissolution rate.

Site 2 is characterized by a decrease in the current density values and indicates the transition of the GaAs (anode) surface from active to passive state. Surface oxidation leads to the formation of an oxide film. This layer prevents the entry of electrolyte ions to the GaAs surface. Accordingly, there is a decrease in the anode current values. As a rule, the electrochemical process should be stopped at this stage in order to obtain the samples passivated by an oxide film.

The voltage range from V_b to V_l , which corresponds to site 3, characterizes the passive state of the anode. At this stage of etching, the formation of an oxide film on the GaAs surface is observed. This, in turn, leads to a decrease in the rate value of the electrochemical reaction. The oxidation/dissolution rate of the semiconductor surface depends mainly on the concentration of particles and adatoms in the electrolyte, as well as the rate of their entry to the sample surface and removal of the reaction products. As can be seen from Fig. 2 at this stage, the rate of the electrochemical reaction does not depend on the potential values. It can be also seen that the current density value I_r (residual current), which corresponds to the potential V_b , is close to the initial anodizing current.

In site 4, there is an increase in the current density values. The kinetics of this process can be described as follows. The sample surface passivated by the oxide layer contains a large number of compounds, which are well-soluble in the electrolyte. For GaAs, such a compound is usually native oxide As₂O₃. If electrochemical etching is stopped, we will see the formation of oxide crystallites that densely cover the GaAs surface. If the electrochemical reaction continues, there is a "breakdown" of the oxide film. Etching of the oxide film with the formation of etching pits is observed in the breakdown places. This leads to an increase in the conductivity of the formed film and initiates the appearance of more etching pits and the advancement of the etching front into the sample depth.

3.2 SEM Analysis

Fig. 3 shows the surface morphology of gallium arsenide after electrochemical treatment. It can be seen that there is an array of crystallites – islands, which were formed during the electrochemical oxidation of the GaAs. Islands are spherical formations separated by grooves. Detailed observation allows to conclude that the grooves were formed at the late stages of etching as a result of cracking of the oxide film.

It can be also seen that the spherical crystallites have etched sites in the center. That is, the dissolution of the oxide film occurred by the breakdown mechanism, as described above.

It should be noted that mixing of the electrolyte, which was applied at the first stage of electrochemical treatment, leads to the formation of a dense film with the formation of a spheroidal structure.

When stirring the electrolyte, the outflow of the reaction products from the sample surface is faster than in the absence of stirring. This allows to "smooth" the surface and to form the uniform oxide layers with small protrusions (pseudospheres).

When the applied potential is increased and mixing is stopped, electrolyte anions are concentrated near the crystal surface, forming a Helmholtz-Gui transition layer at the semiconductor/electrolyte boundary. This causes the surface to be re-etched in places of inhomogeneities, protrusions and defects. Taking into account the fact that after the oxidation the GaAs surface was a set of spherical crystallites, it is logical to assume that

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Fig. 3- Morphology of the GaAs surface with the formed oxide layer after electrochemical treatment



Fig. 4 – Etching model of spherical oxide crystallites on the GaAs surface. The red sites show the concentration places of micro-stresses that initiate the breakdown of the oxide film

protrusions will be the highest sphere points. They have more energy due to the concentration of microstresses near the surface. This process model is shown in Fig. 4. The breakdown of the oxide film occurs as well as the formation of etching pits is observed in these sites (yellow sites in Fig. 3, red sites in Fig. 4).

Fig. 5 shows the diagrams of crystallite size distribution (the length and width of each island were estimated). We can see that the distribution is normal. Most crystallites have a size in the range of 1 to 5 μ m. The proportion of supermassive crystallites (which in at least one direction have a size of more than 9 μ m) does not exceed 0.1 %.

The crystallite shape is characterized by the Solidity and Round values.

Solidity characterizes the ratio of the area of the crystallite to the area of the convex hull:

$$S = Ar/Ar_c, \tag{3.1}$$

where Ar is the total area of the crystallite, Ar_c is the area of the convex hull of the crystallite.

Round is defined as the ratio of the area to the square of the major axis:

$$R = \frac{4Ar}{\pi l_{\max}^2},$$
 (3.2)

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Fig. 5 – Crystallite distribution in width (a) and in length (b)

where l_{max} is the major axis of the pore.

The roundness values, R = 1 and S = 1, indicate that the crystallite cross-section is an ideal circle. The closer the Round value to 0, the more elongated the crosssection will be, as well as the crystallite boundaries will be deformed at $S \rightarrow 0$.

Fig. 6 shows the crystallite distribution according to the characteristics of Solidity (a) and Round (b).

Analysis of Fig. 6 allows to conclude that the crystallites are mainly ellipsoidal, close to round. The range of Round values [0.7-0.9] includes 34 % of surface crystallites. 17 % of the particles have an almost perfect circle shape. Crystallites mostly have smooth boundaries. Thus, the calculation of the Solidity characteristic showed that 76 % of the crystallites are into the range of [0.87-1].

Fig. 7 shows the dependence between the characteristics of Round and Solidity. The array of values is in the upper right angle. This indicates that the more rounded the crystallite shape, the smoother its boundaries. On the other hand, the average value of the Solidity characteristic (S = 0.89) exceeds the average value of the Round one (R = 0.70).

4. DISCUSSION

The detailed analysis of the morphological characteristics is interesting in terms of the mechanisms of the crystallite formation. Ellipsoid crystallites with smooth boundaries indicate the earlier correct assumption that a dense oxide film, which later "spread" on the



Fig. 6 – Diagrams of crystallite distribution according to the characteristics of Solidity (a) and Round (b)



Fig. 7 – Diagram showing the dependence between the morphological characteristics of Round and Solidity of oxide crystallites

GaAs surface, was formed at the initial oxidation stages. This phenomenon is often caused by a mismatch between the crystal lattices of the oxide and the output semiconductor.

Table 2 summarizes the data on the maximum, minimum and mean values of the estimated morphological characteristics, namely the width, length, area of crystallites, their roundness (Round) and Solidity. It can be seen a significant spread between the maximum and minimum values of the linear sizes of crystallites. This characterizes the crystallite formation process as directed, i.e., there should be places of predominant cracking of the film, which are surface defects of the substrate (GaAs), dislocations and the growth degree of the oxide film. This is also indicated by comparing the minimum and maximum values of roundness. Here it can be also seen a significant spread with $\Delta R = 0.72$. The value of the crystallite area has a left-sided asymmetry (the average value is closer to the minimum one). This indicates that the film rupture process at the

stage of stopping the electrochemical reaction has not yet been completed. Upon further etching of the sample, the formation of even more small crystallites was observed.

That is, the GaAs surface is oxidized by the Stranski-Krastanov mechanism or the layer-plus-island growth (Fig. 8) [19, 20].

Table 2 – Maximum, minimum and average values of the morphological characteristics of oxide crystallites on the n-GaAs surface

Morphological characteristic	Max	Min	Average
Height, µm	11.63	0.11	3.88
Width, µm	12.9	0.12	3.46
Area, µm ²	3.59	1	1.49
Solidity	1	0.70	0.89
Round	1	0.28	0.70



Fig. 8 – Electrochemical oxidation mechanism of the n-GaA surface

According to this mechanism, an oxide film, the socalled wetting layer, is first formed on the GaAs surface. Stresses arise due to the mismatch between the lattice constants of the oxide layer and the semiconductor substrate in the wetting layer. Next, the wetting layer is deformed so that its lattice constant corresponds to that of GaAs. The local curvature of the deformed sites leads to the cracking of the film and the formation of islands – oxide crystallites.

Further etching of the etching pits on the island tops is not related to the Stranski-Krastanov mechanism but is due to the oxide breakdown because of the application of a very high potential and considerable time of the electrochemical reaction.

5. CONCLUSIONS

Directed oxidation of the n-GaAs surface was carried out by electrochemical deposition in an aqueousalcoholic hydrochloric acid solution. The study of the polarization curves allowed to establish the process kinetics and to describe the growth stages of the oxide layers. Thus, it was shown:

- at small potential values, the gallium arsenide surface is etched, as a result of which the electrolyte is saturated with gallium and arsenic atoms;
- when the Flade potential is reached, the current density has the highest value, which indicates the

high activity of the electrochemical process, this stage is characterized by simultaneous etching of the surface and deposition of the oxide layer;

- after the formation of a dense oxide layer on GaAs, there is a decrease in the current density values due to surface passivation, at this stage the oxide film begins to spread with the formation of spherical islands;
- if the electrochemical reaction continues, there is the breakdown of the oxide layer on the island tops with the formation of the etching pits;
- the breakdown of the oxide with the formation of the etching pits on the tops is due to the concentration of micro-stresses in these places.

The study of the morphological characteristics of the formed structures showed that, after electrochemical treatment, a system of densely packed oxide crystallites – islands – was formed on the n-GaAs surface:

• the crystallites mainly have a size in the range from 1 to 5 μ m, the average value of the area is 1.49 μ m², which indicates the left asymmetry of the distribution;

• Solidity (ratio of the area of the crystallite to the area of the convex hull) and Round islands (the ratio of the area to the square of the larger axis) were studied, and according to the results, the crystallites are ellipsoidal with smooth boundaries.

The conducted studies allow to conclude that the

REFERENCES

- N. Guo, H. Xue, A. Bao, Z. Wang, J. Sun, T. Song, Q. Wang, *Angew. Chem.* 132 No 33, 13882 (2020).
- J.A. Suchikova, V.V. Kidalov, G.A. Sukach, *Func. Mater.* 17 No 1, 13 (2010).
- 3. S. Lee, J. S. Kang, D. Kim, *Materials* 11 No 12, 2557 (2018).
- J.A. Suchikova, V.V. Kidalov, G.A. Sukach, *ECS Transac.* 25 No 24, 59 (2009).
- B. Long, H. Yang, M. Li, M.S. Balogun, W. Mai, G. Ouyang, S. Song, *Appl. Catal. B: Envir.* 243, 365 (2019).
- D. Pei, J. Bao, Y. Li, Y. Li, H. Wang, H. Lu, Z. Wang, J. Energy Storage 51, 104483 (2022).
- R. Meija, V. Lazarenko, A. Skrastina, Y. Rublova, J. Andzane, V. Voikiva, D. Erts, *Batteries* 8 No 3, 25 (2022).
- Y.A. Bioud, A. Boucherif, M. Myronov, A. Soltani, G. Patriarche, N. Braidy, R. Arès, *Nat. Commun.* 10 No 1, 1 (2019).
- Y.O. Sychikova, I.T. Bogdanov, S.S. Kovachov, *Func. Mater.* 27 No 1, 29 (2019).
- D. Zhuang, J.H. Edgar, *Mater. Sci. Eng.: R: Reports* 48 No 1, 1 (2005).

GaAs surface is oxidized by the Stranski-Krastanov mechanism, which is characterized as a layer-plusisland growth.

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- E. Monaico, I. Tiginyanu, V. Ursaki, *Semicond. Sci. Technol.* 35 No 10, 103001 (2020).
- A. Henni, N. Harfouche, A. Karar, D. Zerrouki, F. X. Perrin, F. Rosei, *Solid State Sci.* 98, 106039 (2019).
- S.O. Vambol, I.T. Bohdanov, V.V. Vambol, T.P. Nestorenko, S.V. Onyschenko, J. Nano- Electron. Phys. 9 No 6, 06016 (2017).
- V.M. Kalygina, A.N. Zarubin, Y.P. Nayden, V.A. Novikov, Y.S. Petrova, O.P. Tolbanov, T.M. Yaskevich, *Semiconductors* 45 No 8, 1097 (2011).
- G. Deng, K. Saito, T. Tanaka, Q. Guo, *Opt. Mater.* 116, 111078 (2021).
- L. Zhou, B. Bo, X. Yan, C. Wang, Y. Chi, X. Yang, *Crystals* 8 No 5, 226 (2018).
- B.L. Ong, S.W. Ong, A. Rusydi, E.S. Tok, *Appl. Surf. Sci.* 530, 147256 (2020).
- M.R. Pinto, G.F. Costa, E.G.Machado, R. Nagao, *Chem-ElectroChem.* 7 No 14, 2979 (2020).
- 19. R. Franchy, Surf. Sci. Rep. 38 No 6-8, 195 (2000).
- A. Baskaran, P. Smereka, J. Appl. Phys. 111 No 4, 044321 (2012).

Оксидування поверхні n-GaAs: морфологічний та кінетичний аналіз

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Ми досліджуємо процеси направленого оксидування поверхні *n*-GaAs, які відбуваються в результаті електрохімічної обробки напівпровідника в водно-спиртовому розчині соляної кислоти. Аналіз вольт-амперних характеристик проведено з метою дослідження кінетики процесу, це дало змогу встановити етапи утворення оксидної плівки та острівців. Морфологія поверхні оцінена за характеристиками площі, лінійних розмірів, цільності (Solidity) та округлості (Round) острівців. Показано, що оксидування відбувається за механізмом Странського-Крастанова. Дослідження формування власних оксидів на поверхні GaAs є вкрай важливим, адже, оксиди можуть істотно впливати на властивості матеріалу. Власні оксиди напівпровідників є пасивуючою плівкою, яка надійно захищає поверхню від дії навколишнього середовища та при взаємодії з агресивними речовинами. Крім того, власні оксиди GaAs проявляють напівпровідникові властивості, що дозволяє створювати гетероструктури оксид/ GaAs з гетеропереходами для оптоелектронних застосувань.

Ключові слова: GaAs, Оксидування, Фладе-потенціал, Цільність, Щкруглість, Механізм Странського-Крастанова, Механізм пошарового-плюс-острівкового зростання.