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Justification of the most rational method for the nanostructures synthesis on the semiconductors surface

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ABSTRACT

Purpose: of this paper is to justification the most rational method for the nanostructures synthesis on the semiconductors surface, which is capable of providing high quality synthesized nanostructures at low cost and ease of the process.

Design/methodology/approach: The choice of the optimal method of synthesis was carried out using the hierarchy analysis method, which is implemented by decomposing the problem into more simple parts and further processing judgments at each hierarchical level using pair comparisons.

Findings: The article describes the main methods of synthesis of nanostructures, presents their advantages and disadvantages. The methods were evaluated by such criteria as: environmental friendliness, efficiency, stages number of the technological process, complexity, resources expenditure and time and effectiveness. Using the hierarchy analysis method, has been established that electrochemical etching is the most important alternative, and when choosing a nanostructures synthesis method on the semiconductors surface, this method should be preferred. Such studies are necessary for industrial serial production of nanostructures and allow reducing expenses at the realization of the problem of synthesis of qualitative samples.

Research limitations/implications: In this research, the hierarchy analysis method was used only to select a rational method for synthesizing nanostructures on the semiconductors surface. However, this research needs to be developed with respect to establishing a correlation between the synthesis conditions and the nanostructures acquired properties.

Practical implications: First, was been established that the optimal method for the nanostructures synthesis on the semiconductors surface is electrochemical etching, and not lithographic or chemical method. This allowed the theoretical and empirical point of view to justify the choice of the nanostructures synthesis method in the industrial production conditions. Secondly, the presented method can be applied to the synthesis method choice of other nanostructures types, which is necessary in conditions of resources exhaustion and high raw materials cost.

Originality/value: In the article, for the first time, the choice of the nanostructures synthesis method on the semiconductors surface is presented using of paired comparisons of criteria and available alternatives. The article will be useful to engineers involved in the nanostructures synthesis, researchers and scientists, as well as students studying in the field of "nanotechnology".

Keywords: Hierarchies' analysis method, Chemical etching, Electrochemical etching, Lithographic etching, Nanostructures synthesis

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ANALYSIS AND MODELLING

1. Introduction

The current trend in the field of semiconductor technology is the nanostructuring of the surface of semiconductors in order to provide new properties that did not possess the source material [1,2]. It is known that nanostructured materials possess a complex of properties (physical, chemical, biological, mechanical, to name but a few), which often differ radically from the properties of the same substance in the monocrystalline phase [3,4]. Specific nanomaterials properties can be attributed [5,6]:

- the ability to accumulate;
- high chemical potential;
- a large specific surface of nanomaterials, which leads to an increase in the value of the adsorption capacity of materials;
- active surface states;
- microscopic sizes and variety of nanomaterials types;
- high adsorption activity, which is a consequence of a highly developed nanomaterial surface.

There are two ways of synthesizing nanostructures – "top-down" and "bottom-up". "Bottom-up" nanotechnology is a technology for obtaining nanostructured materials in which nanoparticles from atoms and molecules are realized, that is, an aggregation of the initial structural elements up to particles of nanometre size is achieved [7,8].

"Top-down" nanotechnology is a technology for obtaining nanostructured materials in which the nanometre size of particles is achieved by shredding large particles, powders, or solids of a solid [9,10]. At present, combined methods are actively developing [11].

However, the nanostructures properties and application area depend on the synthesis methods. There are several chemical [12,13] and physical methods that are successfully used for the manufacture of nanostructures of various materials [14,15]. Plasma surfacing methods such as impulse laser deposition, arc discharge, etc. are still popular [16,17]. However, most of these methods have limitations [18-21].

In this regard, it is relevant to justify the most rational method for the nanostructures synthesis on the semiconductors surface, which will be characterized by simplicity and efficiency.

Semiconductors, manufactured in the nanoscale, show a sharp change in optical and electronic properties [22]. These changes are primarily due to quantum-sized effects associated with quantization of the charge carrier's energy, whose movement is limited in one, two or three directions [23]. Properties of the resulting nanostructures, in turn, depend on the parameters of the source crystal and synthesis methods [24].

Among the many nanostructures synthesis methods, chemical and electrochemical methods occupy a special place, because of:

- cheapness [25];
- simplicity [26];
- a small number of technological steps [27];
- the short technological process time, and more [28].

Short-term etching of the crystal causes the formation of the etching figures (often pits) and the dissolution layers on its surfaces without the loss of macroscopic features (macromorphology) [29], while prolonged etching contributes to the macroscopic form emergence which is different from the original [30]. Both micro-and macro-morphology of crystals is determined by the processing parameters. In addition, crystals etching greatly affects at the chemical composition of its surface [31]. The chemical composition of gallium arsenide after electrochemical treatment is investigated in the paper [32]. It was shown, that under the light influence the arsenic oxide is formed on the structure surface. It has been established, that oxides clusters are formed only on those crystal parts that were illuminated during etching. Since the most semiconductors surface of the A_3B_5 group is characterized by a high density of surface states in the forbidden zone [33], then the Fermi level is fixed. Its position on the surface practically does not depend on the nature of adsorbed atoms [34]. This fact negatively affects the functioning of many micro and optoelectronic devices [35,36], preventing the semiconductors high potential be fully disclosed. However, all these research do not give a general idea of the mechanisms of the formation of the nanostructured layer during the surface treatment of semiconductors. This situation is due to the fact that most studies focus on establishing the influence of a particular factor on the nanostructuring process. While it is necessary to take into account a complex of factors and to study their correlation with the morphological nanostructures properties.

Synthesis nanostructures methods on the semiconductors surface determine the quality level of nanostructured surfaces [37,38]. Therefore, the investigation purpose is to study the basic methods of synthesis nanostructures on the semiconductors surface and to justification of the most rational method, which will enable the formation of high-quality nanostructures at a resources minimal cost.

2. Materials and methods of investigations

The choice of methods for the nanoparticles synthesis should be based on the following indicators: cost-effectiveness; environmental friendliness; the number of links in the technological process; the complexity of technological operations; the number of resources used.

Among the various methods, chemical etching; electrochemical etching; methods of lithography are the most common methods for forming the porous layers on the semiconductors surface [39,40].

Other methods to varying degrees should be considered as modifications presented above. Thus, photoelectrochemical etching is a variant of the electrochemical method with the only difference that etching does not occur in the dark, and samples are deliberately illuminated by lamps of varying power [41,42]. This method is used to accelerate etching and to form nanostructures on the surface of semiconductors of p-type. So, we have the task of choosing the optimal method for the synthesis of porous layers on the surface of semiconductors.

To determine the optimal method for the synthesis of nanostructures on the semiconductor surface, the example of the formation of porous nanostructures will be assessed. So, we will use the method of analysis of hierarchies (HAM) [43]. The basis of this method is the decomposition of the problem into more simple parts and further processing of judgments at each hierarchical level using pair comparisons. As a result, the relative degree (intensity) of the interaction of elements in the analyzed hierarchical level or the superiority of some elements over others can be expressed [44]. These judgments are provided with numerical evaluation.

At the first stage, an analysis of the goals is needed. The second stage is to build hierarchies. The highest level is our goal: The most rational method for the synthesis of nanostructures". Achievement of the goal occurs through the intermediate levels (criteria) to the lowest level, which is a list of alternatives. For convenience, the designation of criteria and possible alternatives, which in our opinion are the most decisive, are introduced in Table 1.

Table 1.
Designation of criteria and alternatives in the choice of optimal method for the synthesis of porous layers on the surface of semiconductor specimens

Criteria and alternatives			
No.	Marking	Name	Explanation
1	$C_{cost\text{-}effectiveness}$	The criterion of cost-effectiveness	Evaluated financial costs, which include: the cost of resources, equipment, for the technological process
2	$C_{ecological}$	The criterion of ecological friendliness	Ecological safety of technology and harmful production factors are assessed
3	C_{number}	The criterion for the number of links in the technological process	The stages number of a purely technological process is estimated. Preparation of samples for the process and post-processing are not taken into account since they are identical to all three selected synthesis technologies
4	$C_{complexity}$	The criterion of complexity	The implementation complexity of the technological processes, the complexity of the equipment used and the necessary personnel qualifications

Criteria and alternatives			
No.	Marking	Name	Explanation
5	$C_{resources}$	The criterion of resources	Resources number required for the technological process (samples, electrolytes, electrodes, masks, etc.)
6	C_{time}	The criterion of time	The time spent on conducting a technological operation of porous structure synthesis
7	$C_{performance}$	The criterion of performance	The achieved result will be the formation of a uniform porous layer on the semiconductor surface. Under uniformity we will understand the uniformity of the arrangement along the sample surface and the pore sizes distribution
Methods of synthesis			
No.	Marking	Name	
1	*ChE*	Chemical etching	
2	*ElChE*	Electrochemical etching	
3	*LE*	Lithographic etching	

Table 2.
Relative Weight Scale [45]

The intensity of relative weight in points	Definition	Explanation
1	Equal weight	The weight of the two comparable criteria is equal or impossible to quantify / objectively assess
3	Moderate advantage over one another	Empirical experience and judgment give a slight advantage
5	Significant or strong advantage	The available evidence indicates a significant advantage
7	Very strong advantage	The advantage of one over the other is obvious
9	Absolute advantage	Evidence of the benefits of the criterion for all available features
2, 4, 6, 8	Intermediate solutions between two adjacent judgments	Applied in compromise judgments

To determine the performance of pairwise comparison of the criteria, it is necessary to arrange the assessment scale. The most convenient scale is proposed by T. Saati [45] (Tab. 2). Saati suggested using an expert method in which qualified experts is appointed who conduct an evaluation on the proposed scale. In our case, it is appropriate to rely on the results of empirical data and available data in the scientific publications of leading scientists and patents.

3. Results of investigation and discussion of them

To begin with, we give a brief description of the three selected methods, highlight their advantages and disadvantages.

Method 1. Chemical etching is realized by immersion of a semiconductor into a selective herbalist for a long time. Advantages of the method are [46]:

- low cost;
- a small number of links in the technological process (essentially only one – direct digestion);
- simplicity (does not require special equipment and complex technological operations);
- does not require any additional resources (only semiconductor and electrolyte);
- cost-effectiveness (low cost of the method due to the ease of its implementation and use of standard electrolytes).

Disadvantages of chemical etching are [47]:

- a significant time of operation (samples must be kept in an electrolyte for several hours, and sometimes even days);

- very low quality of the received porous layers (very often the etching occurs without pore formation, and with the formation of textured layers).

Method 2. Electrochemical etching is a kind of chemical etching, but differs in that during etching the samples are exposed to electric current. As a result of this treatment, a porous layer is formed on the semiconductor surface. In comparison with chemical etching, the disadvantages of electrochemical treatment can be considered [48]:

- the greater complexity of the technological process;
- the availability of equipment for conducting technological operations is necessary.

The main advantages before chemical etching can be attributed [49]:

- much less processing time (maximum 30-40 min);
- significantly better qualitative characteristics of synthesized porous layers (layers show high pore density, evenness distribution in size, and so on).

The number of process links, environmental friendliness and resource-consuming are at the same level with chemical technology.

Method 3. Lithographic method. With the help of lithography and photolithography, it is possible to obtain the best quality porous layers. This method is realized by applying to the surface of the crystal a template (mask). Further, ordinary electrochemical etching is carried out. The main advantage is the quality of nanostructures – porous layers are formed with predefined characteristics [50]. However, the method has several disadvantages, among which [51]:

- the high cost of technology;
- the complexity of technological processes;
- a large number of links in the technological process;
- the need to spend extra resources (mask patterns).

Based on existing experience [52,53] and the conditions of the task, it can be easily seen that the ecological friendliness quality criterion will have equal importance for all three alternatives. Therefore, for simplicity and convenience, this criterion from the matrix of pair comparisons can be removed.

Based on this, a simple hierarchical structure with one level of criteria (containing seven indicators) and a list of available alternatives (Fig. 1) can be constructed.

The evaluation of the process will be based on the principle of minimizing the time, resources, costs, complexity and process costs while achieving maximum results, ecological friendliness, and cost-effectiveness. In other words, the indicators are actually evaluated:

- maximal result;
- maximal cost-effectiveness;
- maximal ecological friendliness;
- minimal cost of resources;
- minimal processing time;
- minimal complexity of the process;
- the minimum number of links in the technological process.

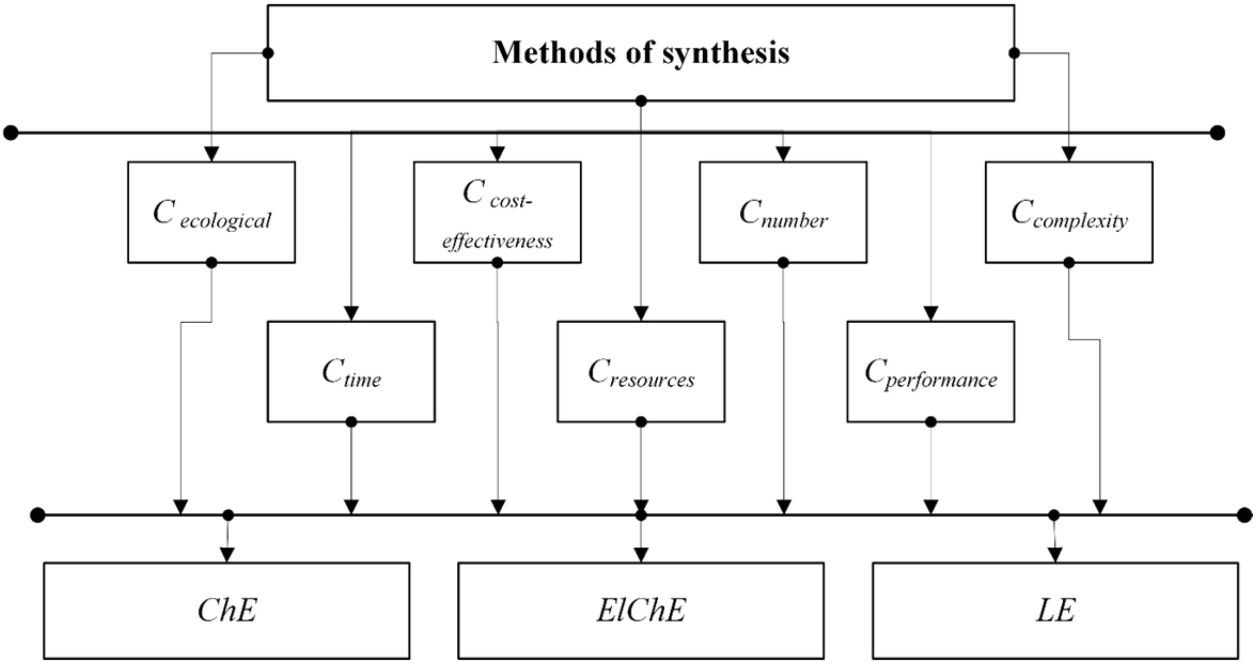

Fig. 1. The hierarchical structure of the choice of the optimal method for the synthesis of porous layers

In this approach, with a successful evaluation of the optimal method for the synthesis of nanoparticles, the most optimal result will be the one whose rates are the lowest. The matrix of pair comparisons for the level of criteria is presented as a table using the scale of the criteria (Tab. 3).

Table 3.
Matrix of pair comparisons for the level of criteria

Criteria	$C_{performance}$	$C_{complexity}$	C_{number}	C_{time}	$C_{resources}$	$C_{cost\text{-}effectiveness}$
$C_{performance}$	1	9	7	5	5	7
$C_{complexity}$	$^1/_9$	1	$^1/_3$	$^1/_3$	1	$^1/_3$
C_{number}	$^1/_7$	3	1	1	1	1
C_{time}	$^1/_5$	3	1	1	$^1/_3$	3
$C_{resources}$	$^1/_5$	1	1	3	1	5
$C_{cost\text{-}effectiveness}$	$^1/_7$	3	1	$^1/_3$	$^1/_5$	1

As it was previously mentioned, the most uniform porous layer is obtained by applying lithography technology. Therefore, in comparison with the chemical method of treatment, this method will have an absolute advantage, with the method of electrochemical treatment – a strong advantage. In turn, electrochemical etching has a significant advantage over the method of chemical etching.

The longest method of synthesizing porous layers on the surface of semiconductors is chemical etching, due to the fact that the rate of etching without the action of electric current is very low. Electrochemical and lithographic etching requires the same time for etching, but for lithography, it is necessary to carry out preliminary operations, which takes an extra-long time. Therefore, electrochemical etching has an absolute advantage over both methods. Lithographic etching in relation to the chemical has a strong advantage in the criterion of time.

Of course, lithography requires considerably more resources than two other methods. In turn, the methods of chemical and electrochemical treatment require almost the same amount of resources, so they will be given equal weight on the criterion of resources.

By the complexity of technological processes, lithography prevails. It is for this reason that this method is little used. The simplest is chemical etching, so it is given an advantage over others: it is absolute in relation to the method of lithography and strong in relation to electrochemical etching.

By the number of links in the technological process, chemical and electrochemical etching has an equal significance. The lithographic method requires a much larger number of process links, as shown previously.

The most expensive method is lithographic etching, while chemical and electrochemical processing is almost equal in value. Therefore, they will have absolute superiority over the lithographic method on the criterion of cost-effectiveness. Based on these inferences, a matrix of pair comparisons and also calculated values for different criteria levels are given in Table 4 and Table 5. Here W_s is normalized vector components, S is components sum of the normalized vector, and W is normalized value of vector components and λ_{max} is value of the maximum eigenvalue of the vector. The application of the proposed approach will be justified if the real situation turns out to be close to ideal. Therefore, as a measure of deviation of the real scheme from the ideal one, according to [44,45], the compatibility index (I_c) and the consistency relation (V_c) is used. If $I_c < 0.2$, then it is considered that the discrepancy between the ideal and real comparison schemes is within acceptable limits and the results obtained can be trusted. If this condition is not fulfilled, the task should be reviewed, the expert evaluations should be clarified and the matrix of pair comparisons should be re-formed.

Table 4.
Matrix of pair comparisons for levels of criteria

	ChE	***ElChE***	***LE***
	$C_{performance}$		
ChE	1	7	9
ElChE	1/7	1	3
LE	1/9	1/3	1
	C_{time}		
ChE	1	9	7
ElChE	1/9	1	1/5
LE	1/7	5	1
	$C_{resources}$		
ChE	1	1	1/9
ElChE	1	1	1/7
LE	9	7	1
	$C_{complexity}$		
ChE	1	1	1/9
ElChE	1	1	1/7
LE	9	7	1
	C_{number}		
ChE	1	1	1/9
ElChE	1	1	1/5
LE	9	5	1
	$C_{cost\text{-}effectiveness}$		
ChE	1	1	$^1/_9$
ElChE	1	1	$^1/_5$
LE	9	5	1

Table 5.
Calculated values for different levels of criteria

Indicator	$C_{performance}$	$C_{complexity}$	C_{number}	C_{time}	$C_{resources}$	$C_{cost\text{-}effectiveness}$
Ws	$\begin{pmatrix}17\\4.143\\1.444\end{pmatrix}$	$\begin{pmatrix}17\\1.311\\6.143\end{pmatrix}$	$\begin{pmatrix}2.111\\2.143\\17\end{pmatrix}$	$\begin{pmatrix}2.111\\2.143\\17\end{pmatrix}$	$\begin{pmatrix}2.111\\2.2\\15\end{pmatrix}$	$\begin{pmatrix}2.111\\2.2\\15\end{pmatrix}$
S	22.587	24.454	21.254	21.254	19.311	19.311
W	$\begin{pmatrix}0{,}753\\0{,}183\\0{,}0639\end{pmatrix}$	$\begin{pmatrix}0{,}695\\0{,}0536\\0{,}251\end{pmatrix}$	$\begin{pmatrix}0{,}0993\\0{,}101\\0{,}8\end{pmatrix}$	$\begin{pmatrix}0{,}0993\\0{,}101\\0{,}8\end{pmatrix}$	$\begin{pmatrix}0{,}109\\0{,}114\\0{,}777\end{pmatrix}$	$\begin{pmatrix}0{,}109\\0{,}114\\0{,}777\end{pmatrix}$
λmax	3.3	3.734	3.004	3.004	3.016	3.016
I_c	0.15	0.367	0.002	0.002	0.008	0.008
V_c	0.259	0.633	0.0034	0.0034	0.0038	0.0038

Then hierarchical synthesis is necessary. The calculation of the priority vectors is carried out in the direction from the lower levels to the upper ones, taking into account the specific relationships between the elements belonging to different levels. The calculation is made by multiplying the corresponding vectors and matrices.

The Table of priorities correspondence (Tab. 6) is constructed from a smaller value to a larger one. As already mentioned above, for the predominant criterion value, we took the smallest index, so the table of priority vectors should be analyzed in the same way. In our case, the lowest priority vector has electrochemical etching, so it is the most important alternative, and the advantage of choosing the method of synthesis of nanostructures on the surface of semiconductors should be given precisely to this method.

Table 6.
A table of priorities for available alternatives

No.	Value of the priority vector	Method
1	0.1376	Chemical etching
2	0.3697	Electrochemical etching
3	0.4928	Lithographic etching

The second place is the lithographic method, which is logical – for the best result, you need to spend the most resources. That is, this method is recommended only in those cases where the main goal is to obtain the maximum result. It is not recommended to use chemical etching for the synthesis of a uniform porous layer on the surface of semiconductors.

In order to achieve the goal of forming a uniform porous layer, it is necessary to control the process of electrochemical etching.

4. Conclusions

Using the hierarchy analysis method, the following has been established:

1. Electrochemical etching is the most important alternative, and when choosing a nanostructures synthesis method on the semiconductors surface, this method should be preferred.
2. Lithographic method can be recommended only in cases where the main goal is to obtain the maximum result.
3. To achieve the goal of uniform porous layer forming, it is necessary to control the process of electrochemical etching.

During this investigation, the methods were evaluated by such criteria as: environmental friendliness, efficiency, stages number of the technological process, complexity, resources expenditure and time and effectiveness.

However, the expert assessment results should not be absolutized and perceive them as an indisputable truth. This method is appropriate to apply along with other research methods, preferring results that are based on fairly accurate predictive models of the pores formation on the semiconductors surface.

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