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Synthesized nanostructures formation time effect on their morphological quality indicators – pore diameter increase in nanostructured coatings

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Abstract

The synthesis of nanostructures with adjustable quality, properties and sizes of nanoobjects remains a crucial issue in recent decades. An effective mechanism of quality control for nanostructures can be considered to determine the correlations between the synthesis conditions and their measured morphological properties.

The article focuses on the analysis of the basic mechanisms when synthesizing nanostructures of a given quality level on the surface of crystals. The type of dependence of the pore size on the nanostructures synthesis time has been determined experimentally. The article determines the regularities of pore formation in nanocoatings over time based on metrologically substantiated and valid results of representative studies of the nanostructures synthesis on the surface of indium phosphide, namely correlation dependences between the nanostructures formation time and their morphological properties, the main critical points of synthesis, that is, the start-point and the end-point of pore formation. The trend equation for the dependence of the pore diameter on the etching time has been set up by statistical techniques taking into account the specifics of the process, in particular, by the finite-difference method. The conducted researches allowed to understand the dynamics of the pore formation process and further possibility of forming nanostructures with the set parameters and quality level on the surface of semiconductors by varying its duration.

Keywords: synthesis; nanocoatings; pore formation; observations; statistical methods.

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1. Introduction

The synthesis of nanostructures with the controlled quality, properties and sizes of nanoobjects has remained a decisive issue in recent decades. Its solution is highlighted in "Strategic Research and Innovation Agenda for Nanomedicine, European Technology Platform on Nanomedicine, 2016–2030", "EU US Roadmap Nanoinformatics, 2017–2030", "Continuing to Protect the Nanotechnology Workforce: NIOSH Nanotechnology Research Plan for 2018-2025", "Key Priority Areas in the Development of Science and Technology in Ukraine until 2020". The reason for this is that nanotechnology today is an industry that distorts the rapid development of high-power computers and computing technology [1], electronics [2], solar and alternative energy [3], environmental research [4], biomedical [5] and information technology [6], etc.

However, the above only emphasizes theoretical relevance of the use of nanomaterials. Very few works focus on determining the actual impact of using nanomaterials on product quality [7] proceeding from the general principles of its assurance [8], the study of defects in nanomaterials and their correlation with material properties [9], as well as the level of quality of nanomaterials itself, etc., which is largely due to the lack of established criteria for the quality of nanostructures, a multifaceted approach to the assessment and management processes and methodology and research guidelines for its determination.

The most commonly used quality assurance tools are various methods of the Statistic Process Control (SPC) of production products [10]. Determination of correlations between synthesis conditions and measured morphological properties can be considered a viable quality control tool for nanostructures, because they are due to the emergence of quantum effects in the transition to nanoscale. As a result, such materials demonstrate an extremely large specific surface area; active surface states; ultra-small size and variety of nanomaterial types.

These and other properties account for high adsorption activity, accumulation capacity, changes in solubility, reactive and catalytic capacity; increase in the value of adsorption capacity of materials, etc. A significant number of scientific papers is concerned with solving these issues within the framework of a typical technology for creating nanostructures on the surface of crystals and their electrochemical processing [11, 12]. Etching time, impressed voltage as well as electrolyte concentration and composition, presence of defects and dislocations of the surface, type and orientation of the surface, etc are the dominant factors affecting the surface morphology of nanostructured semiconductors. It is barely possible to take into account all these factors when assessing the morphology of the synthesized nanosurface in one multiparameter model; however, a detailed study of each of them allows one to determine the basic mechanisms of nanostructures formation on the surface of semiconductors, as well as their parameters.

The suggested study focuses on determining correlation dependences between one of the most important factors, that is, nanostructures formation time on the semiconductors phosphide as well as their morphological properties, and primarily, the increase in pore diameters over time in a typical nanostructure synthesis process.

2. Research methodology

The type of dependence of the pore size on the nanostructures synthesis time has been determined experimentally. In this case, the chosen plates of single-crystal n-type indium phosphide (por-InP) with the surface orientation (111) have been electrochemically processed in a solution of hydrofluoric acid (HF:H2O:C2H5OH = 1:1:2) at a current density of 100 mA/cm^2 in a standard electrolytic cell [13]. We have conducted a series of 15 tests uniformly distributed within the crystal processing time interval of (3–30) min in order to determine correlations between the synthesis time and morphological parameters, with 5 observations in each test. The obtained test values are within the confidence intervals equal to ± 5% of the measured value for P = 0.95 [14]. After etching, the samples were dried and the morphology of the obtained nanostructures, namely the pore diameter, was studied using a JEOL 6490 scanning electron microscope. The micrographs were processed with the ImageJ software product.

The equation of the tendency of the dependence of the pore diameter on the etching time was established by statistical methods, in particular, by the method of finite differences in the form of a parabolic trend. Table 1 shows the final differences in the change in pore size during etching with indium phosphide.

Table 1

Final differences for pore size change during indium phosphide etching

Order finite difference	Formula
1st order finite difference	$\Delta_t^1 = d_1 - d_{t-1}$
1st order finite difference	$\Delta_t^2 = \Delta_t^1 - \Delta_{t-1}^1$
j-order finite differences	$\Delta_t^j = \Delta_t^{j-1} - \Delta_{t-1}^{j-1}$

where d_1, d_{t-1} – the function values in adjacent interpolation nodes, respectively;
Δ_t^1, Δ_{t-1}^1 – adjacent 1st order finite differences;
Δ_t^{j-1}, Δ_{t-1}^{j-1} – adjacent *j*-order finite differences.

The shape of the curve was chosen on the basis of the accepted quality criterion for the regression equation, which is the minimum sum of squares of the deviations of the actual values of the series level from the values of the levels calculated by the trend equation. The parameters of the trend equation were determined by the method of least squares (LS). In this case, the system of equations LS has the following form:

$$\begin{cases} a + b\sum t + c\sum t^2 = \sum d \\ a\sum t + b\sum t^2 + c\sum t^3 = \sum dt, \\ a\sum t^2 + b\sum t^3 + c\sum t^4 = \sum dt^2 \end{cases} \tag{1}$$

where *a*, *b*, *c* – equation parameters; *t* – etching time; *d* – pore diameter.

An important prerequisite for building a qualitative regression model for MNCs is the lack of correlation between any deviations and, in particular, between neighboring ones. In addition, when using MNC, it is assumed that the residual member has a constant dispersion. Therefore, the heteroscedasticity (sequence of random variables in which random variables have different variances) of the measured results was tested, for example, using the Durbin-Watson *DW* test, according to which, if the value of the Durbin-Watson statistics is the set of correlation coefficients for all differences is 2 (*DW* = 2), there is no autocorrelation of time series elements, *DW* < 2 – there is a positive autocorrelation, and if *DW* > 2 – a negative autocorrelation [15].

Estimation of determination of the sizes of an error or accuracy of the forecast of existence of correlations between etching time and morphological indicators of a porous surface of a semiconductor was carried out by means of Theil's discrepancy coefficient:

$$K_T = \frac{\sqrt{\sum (d_i - d)_2}}{\sqrt{\sum y_{\substack{2\\i}}}}, \tag{2}$$

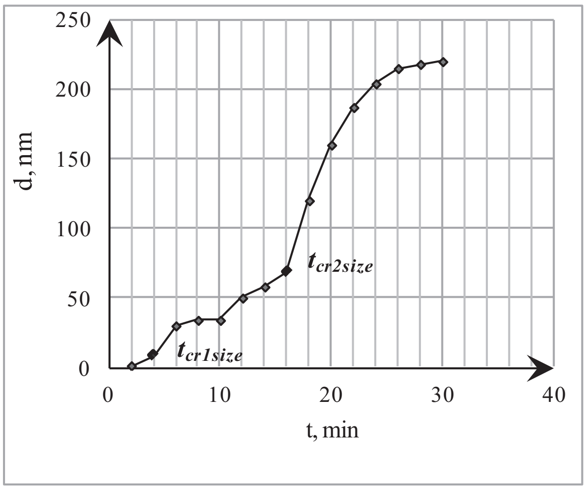

Fig. 1. The dependence of the pore size of the nanostructure on the etching time por-InP

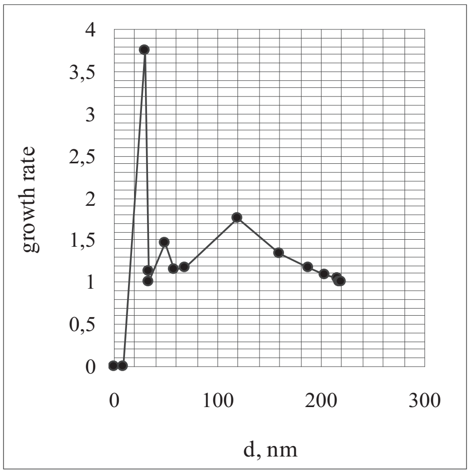

Fig. 2. The growth rate of pore diameter

which allows to calculate the root mean square value of the error of the forecast of increments, and its proximity to zero will indicate the relative accuracy of the forecast. The closer it is to zero, the more accurate the forecast results are [16].

The statistical significance of the obtained equation should be checked using the coefficient of determination and Fisher's test [17]:

$$R = 1 - \frac{\sum(d_i - d_t)_2}{\sum(d_i - \overline{d})_2}, \qquad (3)$$

which must be at least 50% (in this case, the multiple correlation coefficient exceeds the modulus of 70%); models with a coefficient of determination above 80% are defined as quite good (correlation coefficient exceeds 90%); the value of the coefficient of determination of 100% means a direct functional relationship between variables [18].

The analysis indicates that the experimentally obtained results as well as the suggested methodology are metrologically correct and can be used to study the formation of nanostructures on the semiconductor surface.

3. Results and their discussion

Fig. 1 and Fig. 2 demonstrate the results of measurements of the pore sizes of the nanostructure synthesized on the surface of indium phosphide and their growth rates obtained by calculating the differences of the first and second order equations of the trend of pore diameter versus etching time at different etching times, respectively.

When analyzing Fig. 1, it can be seen that the pore size largely depends on the etching time, that is, with an increase in the time of anodizing, the pores increase in size. This fact is undeniable and logical. Fig. 2 allows to see the key aspects of the pore growth. 3 main bursts of increase can be identified. There may be more bursts under different etching conditions; however, there are only three during a typical nanostructures synthesis. The key aspect for any etching conditions is the presence of the first burst when the pores start to actively grow. At this moment, the main array of etching pits nucleates on the crystal surface. Fig. 1 indicates that no pores are formed in the first minutes of the samples anodizing. At this stage, the uneven surface layer dissolves. The pores begin to grow from the first critical point of etching, $t_{cr1size}$. Throughout the next (10–15) minutes, the dependence is almost linear. This is an indication that etching pits on the crystal surface begin to actively nucleate during this time interval. Starting from the critical point $t_{cr2size}$, the pores begin to grow rapidly in a short span of time, that is, the etching rate at this time interval (Fig. 2) increases, which can be explained by the etching of massive defects and dislocations as well as the coalescence of pores into agglomerates and eventually, the formation of relatively large etching pits. Further, the growth of pores somewhat slows down due to a number of factors. First, the electrolyte is depleted with its ions no longer being sufficient for the electrochemical dissolution of the crystal. Second, dislocations and point defects (where etching pits have been previously nucleated) are already fully involved in the process of pore formation. Third, no active surface states remain on the semiconductor surface as a result of etching. The crystal ceases to be superficially tense. At this point, active pore formation can be considered complete.

Given the positive dynamics of pore diameter growth in the nanostructured coating over time (Fig. 1), the equation of its trend was determined on the basis of the previously adopted quality criterion. Table 2 presents the differences of the first and second order and the growth rate of the series, determined by formula (1) and Table 1, to construct this equation.

Based on the results, the system of the LS equations (1) has the following form:

$$\begin{cases} 16a + 240b + 4960c = 1606 \\ 240a + 4960b + 115200c = 35988 \\ 4960a + 115200b + 2852992c = 867904 \end{cases} . \qquad (4)$$

Table 2

Differences of the first and second order and the growth rate of the series for constructing the trend equation for the dependence of the pore diameter on the etching time

t	d_i	Δ^1_t	Δ^2_t	***Growth rate***
2	0	–	–	–
4	8	–	–	–
6	30	22	22	3.75
8	34	4	-18	1.133
10	34	0	-4	1
12	50	16	16	1.471
14	58	8	-8	1.16
16	68	10	2	1.172
18	120	52	42	1.765
20	160	40	-12	1.333
22	187	27	-13	1.169
24	204	17	-10	1.091
26	215	11	-6	1.054
28	218	3	-8	1.014
30	220	2	-1	1.009

In this case: a=-10.779; b=4.447; c=0.143 and the corresponding trend equation will the following form:

$$d=0.143t^2 + 4.447t - 10.779. \qquad (5)$$

It is established that for the obtained results

– K_T=0.00195, and thus we can conclude that the previous assumption about the presence of a correlation between the pore size and the time of electrochemical processing of the surface of indium phosphide in a solution of hydrofluoric acid is correct;

– R=95%, that is, the general variability of the pore diameter is due to a change in the time parameter and the parameters of the model are statistically insignificant.

We use the Durbin-Watson criterion in order to test the autocorrelation hypothesis. Table 3 displays the calculated data for analyzing the correlation of deviations.

According to Table 3 for n=16 and k=1 (significance level 5%), we determine that d_1=1.10; d_2=1.37. Since $1.10>0.95$ and $1.37>0.95<4-1.37$, there is residual autocorrelation [19].

Heteroscedasticity was checked using graphical (Fig. 3) analysis of residues (Table 3), which makes it possible to visually determine its presence [20].

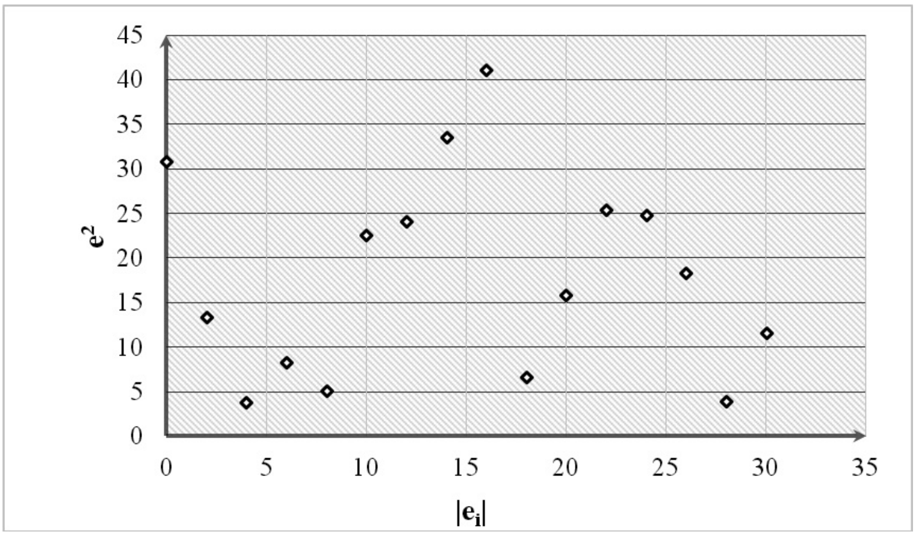

Fig. 3. Residues to test the hypothesis of heteroscedasticity

Table 3

Calculated data for analyzing the correlation of deviations

d	$d(t)$	$e_i = d\text{-}d(t)$	e^2	$(e_i - e_{i-1})^2$
0	-1.312	1.312	1.721	–
8	9.303	-1.303	1.698	6.837
30	21.065	8.935	79.839	104.821
34	33.974	0.0265	0.000701	79.367
34	48.029	-14.029	196.824	197.568
50	63.232	-13.232	175.095	0.635
58	79.582	-21.582	465.798	69.722
68	97.079	-29.079	845.612	56.206
120	115.724	4.276	18.288	1112.615
160	135.515	24.485	599.53	408.397
187	156.453	30.547	933.123	36.745
204	178.538	25.462	648.302	25.86
215	201.771	13.229	175.017	149.63
218	226.15	-8.15	66.422	457.079
220	251.676	-31.676	1003.399	553.495
$DW = \frac{\Sigma(e_i - e_{i-1})^2}{\Sigma e_i^2}$			0.95	

When analyzing Fig. 3, we can see that there are no regularities in the distribution of residuals while the hypothesis of heteroscedasticity absence is confirmed and the variance of deviations is constant. Despite the fact that a random deviation can take on any value for each specific observation, there is no reason that would predetermine higher or lower accuracy in such observations.

The emergence of autocorrelation can be caused by a number of factors. Firstly, by the autodependency of variables, that is, the longer the time, the greater the increase. Secondly, by the limiting factor, that is, self-organization of pore growth can prevent their appearance in certain areas while at other times they will continue to increase in size. Thirdly, there may be some other dependence, since, as noted earlier, the pore size is determined not only by the etching time, but also by other technological factors. This explains the extremely large variability of the surface morphology of nanostructured semiconductors. At the same time, the obtained results have given an option of determining the effect of one of the dominant factors in pore formation, namely the time of pore growth in a typical process of synthesizing nanostructures on the surface of semiconductors.

4. Conclusions and future scope

Based on the obtained results, we have analyzed the basic mechanisms of synthesizing nanostructures of a given quality level on the surface of semiconductors. Using metrologically substantiated and valid results of representative experimental studies of the nanostructures synthesis on the surface of indium phosphide, we have determined the regularities of pore formation in nanocoatings over time, namely correlation dependences between the nanostructures formation time and their morphological properties, the main critical points of synthesis, that is, the start-point and the end-point of efficient increase in pore diameters in the nanocoatings as well as the rate of their growth over time, allowing us to understand, adjust and describe the dynamics of the pore formation process, and thus enabling us to form nanostructures with the given parameters and quality level on the surface of semiconductors by varying the duration of the pore formation.

Вплив часу формування синтезованих наноструктур на морфологічні показники їх якості — зростання діаметра пор у наноструктурованому покритті

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Анотація

Синтез наноструктур на поверхні напівпровідників з регульованими якістю, властивостями і розмірами нанооб'єктів залишається вирішальним питанням останніх десятиліть. Дієвим механізмом контролю якості стосовно наноструктур можна вважати визначення кореляцій між умовами синтезу та виміряними їхніми морфологічними властивостями, які обумовлюються виникненням квантово-розмірних ефектів при переході до наномасштабу і характеризуються надвеликою питомою поверхнею, активними поверхневими станами, надмалими розмірами й різноманітністю типів наноматеріалів.

У статті проаналізовано й експериментально досліджено основні механізми синтезу наноструктур заданого рівня якості на поверхні напівпровідників. На основі метрологічно обґрунтованих і спроможних результатів репрезентативних досліджень синтезу наноструктур на поверхні фосфіду індію визначено закономірності процесу пороутворення у нанопокритті у часі: кореляційні залежності між часом формування наноструктур та їхніми морфологічними властивостями, основні критичні точки синтезу — початок та кінець пороутворення, темпи росту діаметрів пор з часом. Побудовано рівняння тренду залежності діаметра пор від часу травлення на базі статистичного методу кінцевих різниць у параболічному вигляді. Встановлено, що темпи росту діаметра пор на поверхні напівпровідника залежать від процесів, що відбуваються на межі розділу напівпровідник/електроліт. Крім того, перевірка гіпотези гетероскедантичності показала, що розмір пор зумовлюється не тільки часом травлення, а й іншими технологічними чинниками та вихідними параметрами напівпровідника. Проведені дослідження дозволили зрозуміти динаміку процесу пороутворення та дали змогу шляхом варіювання його тривалості формувати наноструктури із заданими параметрами та рівнем якості на поверхні напівпровідників.

Ключові слова: синтез; нанопокриття; пороутворення; спостереження; статистичні методи.

Влияние времени формирования синтезированных наноструктур на морфологические показатели их качества — увеличение диаметра пор в наноструктурированном покрытии

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Аннотация

Проанализированы и экспериментально исследованы основные механизмы синтеза наноструктур заданного уровня качества на поверхности полупроводников. На основе метрологически обоснованных результатов репрезентативных исследований синтеза наноструктур на поверхности фосфида индия определены закономерности процесса порообразования нанопокрытий во времени: корреляционные зависимости между временем формирования наноструктур и их морфологическими свойствами, основные критические точки синтеза – начало и конец порообразования, темпы роста диаметров пор, что позволило понять динамику процесса порообразования и путем варьирования его продолжительности формировать наноструктуры с заданными параметрами и уровнем качества на поверхности полупроводников.

Ключевые слова: синтез; нанопокрытия; порообразование; наблюдения; статистические методы.

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