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SPECIFIC FEATURES OF SURFACE RESEARCH OF $ZnO–SiO_2$ FILMS BY MULTIFRACTAL ANALYSIS

On the example of the multifractal (MF) analysis of the images obtained for the surfaces of nanofilms synthesized in the $ZnO–SiO_2$ system using the sol-gel technology, the specific features of this method relevant for measuring the quantitative surface characteristics have been discussed. As the input information for the implementation of this approach to the description of the surface state, Secondary-Electron Microscopy (SEM) images of the surfaces of specimens synthesized under given conditions are used. Numerical calculations of the generalized partition functions for the area and volume of spatial nanoforms show the linear dependences of those nano-geometric parameters of the surface on spatial dimensions, which is the main proof of their self-similarity and fractal symmetry. The necessity to enhance the reliability of determining the parameters of MF spectra is emphasized, and the factors responsible for the accuracy of the calculated absolute values of the Rényi numbers are analyzed. Recommendations have been made to minimize errors in order to obtain the most reliable data for the MF surface parameters. The dependences of the Rényi numbers on the temperature of the sol-gel synthesis of $ZnO–SiO_2$ layers are presented. For the further implementation of the multifractal analysis (MFA) results in physical calculations, the attention is attracted to the necessity of a correct choice of those Rényi numbers that include the required information about the simulated fractal parameter. The physical origins for the appearance of a relation between, on the one hand, the parameters of MF spectra for the surface area and the volume of nanoforms formed on the film surface and, on the other hand, the conditions of their synthesis have been discussed.

Keywords: nanorelief, multifractal analysis, determination errors of Rényi numbers, sol-gel technology, nanolayer surface.

1. Introduction

The monitoring of the state and the control over the parameters of nanoforms that were formed on a film surface during the synthesis process and, to a great extent, determine the main operational characteristics of optoelectronic devices comprise an important technical and scientific task. This is especially relevant, if the characteristic dimensions of the active zones in a future device become comparable with the characteristic dimensions of such a surface relief. Therefore, the further development and improvement of methods applied to experimentally research and mathematically describe such surfaces in the framework of small spatial scales has an important and challenging theoretical and practical value. One of the directions aimed at solving the problem of the

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mathematical description of the material surface state is connected with the application of fractal analysis (FA). The main advantage of such a non-trivial approach to the development of a mathematical description of the surface is its strict physical justification, which is based on the principles of self-similarity and fractal symmetry types.

We have accumulated a considerable experience in the experimental and theoretical studies of the surface layers of materials that were formed in a natural way during the film synthesis [1, 2], as well as in the studies of the fractal structure of a periodic relief created after the application of cyclic methods of metal processing [3, 4]. In the cited works, on the basis of the developed software, the multifractal (MF) spectra of the surface relief of the specimens were obtained, and their quantitative fractal parametrization was carried out. Those quantitative results were intended to assess the possibility of controlling the relief parameters by adjusting the surface fabrication conditions.

To control the state of the surface according to its MF parameters, it is enough, in principle, to know the main tendencies in its change depending on the technological conditions of the surface formation. In this case, the absolute value of those parameters is not extremely critical. Indeed, knowing such correlational dependences in the variations of the MF surface spectra, it is not difficult to perform such a correction of the technology. However, there are a number of fundamentally important physical characteristics of the surface whose values are strictly related to the absolute values of the fractal surface parameters. An example of such a parameter is the surface energy. For a fractal surface, its value depends on the absolute value of the surface Hausdorff dimension. The problems that arise when finding the absolute values of the fractal characteristics of physical systems are also pointed out in the main works concerning the multifractal analysis (MFA) applications [5–8].

The problem of high-precision determination of the values for the MF parameters automatically implies the necessity to discuss issues related to the specific features of corresponding experimental procedures and numerical (computational) algorithms. In essence, this means the necessity to discuss errors that arise at every stage when determining fractal characteristics. Naturally, it must be considered in close relation with the physical and technical factors responsible for the appearance of those errors. The experience gained by the authors in performing the MFA at the full scope – from synthesizing semiconductor layers under given technological conditions, through obtaining high-quality photographic images of the surface, to calculating the MFA spectra for the selected geometric surface parameters [1, 2] – allows such a generalization to be made.

Nowadays, an ultrathin layer of zinc oxide is being considered more and more frequently as a transparent electrode in modern IR photoelectronic and solar energy optoelectronic devices. Zinc oxide is a wide-bandgap semiconductor ($E_g = 3.32$ eV), which allows it to remain a transparent material in the visible and infrared intervals of electromagnetic wavelengths. Despite the substantial band-gap value, which is more typical of insulators, this material has a relatively low specific electrical resistance, which varies within an interval of 10^{-2}–10^{-4} Ω cm depending on the film defect state. The latter fact means that the material can be used as a conducting and optically transparent electrode.

An important parameter of the ultrathin layer is the surface morphology, which is determined by the surface relief of the layer. Therefore, the study of these parameters of the layers at the nanolevel is a primary task on the way to their further application in devices. In other words, the stated arguments make it possible to consider the MFA of the surface of ultrathin ZnO films as an important fragment of research concerning the technological process of formation of active device media for hetero-compositions on the basis of semiconductor solid solutions A_2B_6 [2].

Thus, the aim of this work was to use the fractal parametrization of the surface of ZnO films that were deposited by the sol-gel method in various modes, as an example to reveal the physical origins of the determination errors for the absolute values of the MF parameters and minimize those errors. In essence, this means the search for the main realization features of the MFA of the surface of the layers that are formed in a natural way at their synthesis.

The achievement of the indicated goal involves the solution of the following basic technical and mathematical tasks, which were the components of the conducted research:

• to analyze the technical limitations and the sources of errors that arise when obtaining images of

the film surface after the film synthesis; to estimate the magnitude of those errors;

• to consider the specific application features of the available software for processing the photographic images of the surface of semiconductor layers used when obtaining data on the MF spectra from various geometric parameters of nanoforms that were formed during the material synthesis process;

• to develop recommendations for minimizing the errors when calculating the MF parameters of the specimen surface.

Those tasks were solved using, as an example, the processing of photographic SEM images of the surface of sol-gel synthesized ZnO nanolayers.

2. Peculiarities of the Layer Synthesis and SEM Measurements

The process of producing ZnO–SiO_2 films, which was applied in this work, corresponds, in general, to a typical process of semiconductor layer deposition performed in the framework of the sol-gel technology [1, 2]. The following chemical reagents were used to form the layers: tetraethoxysilane $Si(OC_2H_5)_4$, ethyl alcohol (it was applied as a catalyst), hydrochloric acid (as a precursor), and crystalline hydrate of zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$.

The films were fabricated in several technological stages. First, the reaction of tetraethoxysilane ether hydrolysis was carried out at room temperature and in the presence of ethyl alcohol and hydrochloric acid with the addition of distilled water. The process of chemical interaction was accompanied by a vigorous stirring of the solution for 1 h. The resulting synthesized orthosilicic acid formed the main chain of the sol polymer molecule possessing film-forming properties [1, 2]. At the same stage, a calculated amount of the precursor, zinc nitrate salt, was introduced into the solution, which allowed the formation of a transparent silica solution with the required composition. The largest number of experiments on the layer synthesis were performed with a sol of the composition 50 wt% ZnO + 50 wt% SiO_2.

The obtained sol solution was deposited onto substrates, whose surfaces were preliminarily chemically etched using acid. Glass substrates were applied, which made it possible to minimize the influence of their crystallographic and mechanical properties on the ultimate properties of synthesized layers.

The next technological stage of the gel layer formation on the substrate surface was the centrifugation. As the control parameters of the process at this stage, we have selected the time of the sol deposition onto the substrate, the number of centrifuge revolutions, and the substrate location site on the rotating centrifuge unit. The main criterion for the quality of this technological stage was the production of continuous films of a required thickness. The following values of the indicated parameters of this process were found to be optimal. The prepared sol was held for 2 h before the deposition. A sol amount of 50 μl was deposited onto a horizontally oriented substrate. The centrifugation was carried out for 2 min at a rate of 3600 rpm.

At the final technological stage of the sol-gel film formation, the films were annealed in two stages: at low and high (final annealing) temperatures. This procedure allowed the morphological quality of the film surface to be substantially improved. The low-temperature stage was performed at temperatures of 80–90 °C. The temperature at the final annealing stage was varied from 200 to 500 °C. All specimens were annealed for 10 min at this stage.

The phase composition of the synthesized layers was monitored via X-ray diffractometric measurements [1, 2]. Distinct diffraction peaks in the diffractograms, which corresponded to the reflection of X-ray radiation from the planes with the crystallographic orientations (100), (002), and (101), were a strong confirmation of the existence of zinc oxide in a crystalline phase with the wurtzite structure. To study the surface morphology of the specimens, an FEI Quanta FEG 250 scanning electron microscope operating at a voltage of 10 kV was used.

Typical SEM and AFM (3D) images of the surfaces of the synthesized ZnO–SiO_2 layers are shown in Fig. 1. The 3D image allows one to understand why the Hausdorff dimension of such a developed surface exceeds the dimension 2 of an ideal flat surface. Indeed, the analysis of the relief 3D pattern testifies to the existence of interfacial micro-peaks and micro-depressions; each of them has a lateral surface and, as a result, contributes to the total surface area. This "lateral" surface makes the film surface dimension value larger than two, a value corresponding to an ideal plane. An analogous consideration of the arrangement of the nanostructure elements from the viewpoint of their "loose" layout with the formation

of cavities gives grounds to assert that the Hausdorff dimension for the volume of nanoforms cannot exceed three.

Similar SEM and AFM images of the surface were obtained for a number of films synthesized under various final annealing conditions, i.e., at the stage, when the surface relief was ultimately formed. Those data were the input information in the implementation of the method of coarsened partitions in the MFA.

Before proceeding to the discussion of the calculation results, it is necessary to determine the physical phenomena that are required to obtain high-quality images of the surface used as input data for the further analysis. An important stage of the technological part of the work, which can substantially affect the error value while determining the fractal parameters of the surface, is the stage of specimen preparation for SEM measurements. Before the image registration, the layer surface was cleaned with a stream of dry air. No chemical treatment (etching, washing) was carried out. We estimated the variations of the Rényi numbers for the surface without etching and after its chemical treatment (with a hydrochloric acid solution). By directly applying MFA operations to various layers, it was found that, as a rule, after the chemical cleaning, the surfaces gave larger values of the Rényi numbers for the areas and, accordingly, somewhat larger ones for the volumes. Such a result seems quite understandable due to the effects of a surface etching, which led to the formation of a nonplanar, developed surface. Calculations showed that the deviation of the Rényi numbers from the values for chemically untreated surfaces did not exceed 0.004 by magnitude.

When discussing the errors that arise in the determination of Rényi numbers, it is necessary to emphasize that the application of SEM spectroscopy allows the surface images to be obtained with a higher resolution as compared to AFM images [1, 2, 9]. This means that SEM photos make the fine component of the surface fractal structure visible, which is inevitably reflected in the shift of the whole MF spectrum toward higher Rényi numbers for the surface area or, equivalently, their small volume analogs. This circumstance explains a systematic deviation of the Rényi numbers for the films whose surface was studied using the AFM spectroscopy methods and the SEM analysis. Therefore, when comparing quantitative parameters that characterize the quality of the film surface, the method of obtaining the data has to be taken into account. This requirement is especially necessary, when high-quality layers are compared for which the contribution of small fractal forms available on their surfaces to the values of Rényi numbers becomes significant.

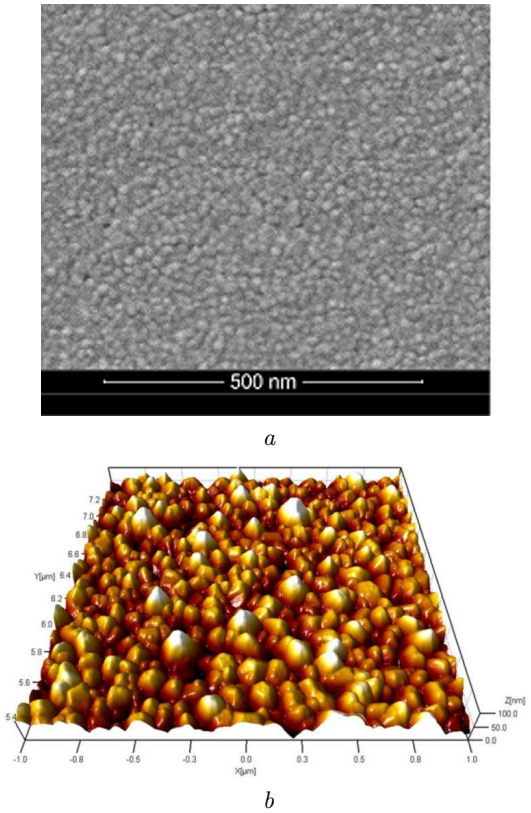

Fig. 1. Typical SEM (*a*) and AFM (*b*) images of ZnO–SiO_2 layers synthesized on glass substrates. The final annealing temperature was 200 °C for 10 min. The initial sol composition was 50 wt% ZnO + 50 wt% SiO_2 The linear scale of the photo is presented in the lower panel

In this work, before the MFA, the obtained SEM images were not artificially improved using a special software. At the same time, we estimated the influence of image corrections on the resulting MFA data, i.e., on the Rényi numbers. The calculations showed that the artificial processing of the images, e.g., by changing their sharpness, can lead to absolute variations of the Rényi numbers of an order of 0.01, which is quite substantial. Based on those data and in order to exclude the appearance of unnecessary uncertainties, we recommend not to perform any corrections of the images before subjecting them to the MFA.

The experience gained while calculating the MF spectra showed that the specified features of data preprocessing for the MFA have to be taken into account when processing the images numerically. Furthermore, the influence of those factors on the final MF parameter values can be minimized by the application of simple technical solutions and correct measurement operations. According to our estimations, the ignorance of those effects can lead to errors of up to 0.02 in the absolute values of the Rényi numbers or even to the total unobservability of the self-similarity effect and the fractal symmetry.

The most essential and important problems are revealed at the stage of digital image processing. The corresponding issues are discussed in the next section.

3. Specific Features of MF Spectrum Calculations

The principle point of the MFA application to the description of the specimen surface state is the specific choice of a physical parameter that most fully characterizes this state and allows the fractal parametrization. A clear selection of such a physical parameter will make it possible to use the quantitative information obtained about it in the subsequent comparative analysis of the surface state. In works [1, 2, 9], among possible geometric parameters that describe spatial forms formed on the film surface and the determination of which makes the calculation of the physical characteristics of the system in the fractal approximation possible, the surface area and the volume of the relief-forming nanoforms were chosen. It is obvious that the choice of the indicated scalar quantities is also the best from the mathematical viewpoint. Furthermore, the availability of a quantitative information about the MFA results obtained for the distributions of the surface nanoform areas and volumes will allow the recommendations to be made concerning the indicated geometric parameters of the system most accurately reflecting the surface state.

In essence, the aforesaid can be reduced to answering the question "Which of the indicated parameters is more sensitive to changes in the technological conditions for the relief creation (the synthesis of layers) and, therefore, can be most effectively used to monitor the surface quality. The availability of such quantitative data will make it possible to make an unambiguous choice between those system characteristics in order to control the relief parameters in practice. Further, it should be added that the fractal parameters of the surface, which are regarded as parameters that account for its complicated geometry, should be used to analyze and calculate its physical characteristics, for example, the surface energy. All the aforesaid should be considered as a physical justification of the necessity to perform the MFA of real surfaces with respect to both the areas and volumes of nanoforms that form the surface relief.

According to the principal works [5, 6] concerning the application of the FA to a number of physical systems, there is no direct correlation between the area and volume of fractal geometric figures. Such a theoretical conclusion means that the surface areas and elementary volumes of fractal figures located on the specimen surface form independent sets of measures, which allows them to be used as an independent input variable for the quantitative description of the surface relief. Such a formulation of the task, in essence, assumes the implementation of the MFA in two independent cases. The distribution of areas of elementary relief-forming nanoforms is used in one of them, and the volume distribution in the other.

The parameters of the MF spectra were determined using the method of coarsened partitions and following the standard procedure. It is known that this method is most effective for calculating the parameters of the multifractal spectra of systems [5–8]. According to this approach, the measure of each spatial cell was generated by partitioning the base space into N cells. As a cell measure by area, $\mu_{S,i}$, and volume, $\mu_{V,i}$, the relative sizes of the nanoform area and volume turned out in a cell were adopted as the area, $\mu_{S,i}$, and volume, $\mu_{V,i}$, respectively, cell measures. Then

$$\mu_{S,i} = \frac{S_i}{S}, \quad \mu_{V,i} = \frac{V_i}{V}, \tag{1}$$

where S_i and V_i are the surface area and the volume, respectively, of a small selected element of the surface relief, and

$$S = \sum_i^N S_i, \quad V = \sum_i^N V_i \tag{2}$$

are the area and volume, respectively, of the whole analyzed surface, which were found according for the data on its 3D image.

Further, generalized partition functions were formed for the surface areas and the volumes of the cells with a given size:

$$Z_S(q, l_k) = \sum_{i=1}^{K} \mu_{S,i}^q, \quad Z_V(q, l_k) = \sum_{i=1}^{K} \mu_{V,i}^q, \tag{3}$$

where l_k is the normalized current value for the cube edge length used at the current step of the method of coarsened partitions, and q is a growth factor. In the calculations, the cell scales were changed (the sizes of the cubes were enlarged) according for the dependence $l_{k+1} = 2l_k$ $(k = 1, 2, 3, ...)$.

The calculation of the MF spectra requires the calculation of elementary surface areas and volumes of nanoforms that find themselves in a given spatial cell, when the method of coarsened partitions is applied. Of course, the initial information for such calculations was obtained from microphotographs. When calculating the volumes of surface nanoforms, the parameters of only those nanoforms that were directly responsible for the formation of the specimen surface relief were taken into account. This basic set of parameters included the total material volume calculated from the depth of the minimum depression to the height of the maximum peak on the surface. In essence, this choice of the volume of the entire analyzed state corresponded to the analysis of the state of the whole surface layer formed during the film synthesis.

The volumes of the prisms under the elementary surface sites were calculated using the formulas of classical geometry and the data for the surface equations, which, in turn, were found by approximating the digital image of a real surface using the triangulation method [1–4, 9]. The choice of this method for generating approximating surface equations was made due to its higher accuracy in comparison with the cube method. This reason becomes relevant, if the emphasis in calculations is shifted toward finding the absolute values of the Rényi numbers. Note that the transition from the method of calculating the surface area using the triangle method in calculations by the cube method gives a difference of up to 0.02 for the final values of the Rényi numbers D_0, D_1, and D_2. Such a value is comparable with the image registration errors discussed in Introduction. This result should be regarded as a confirmation of the necessity to correctly select the approximation methods

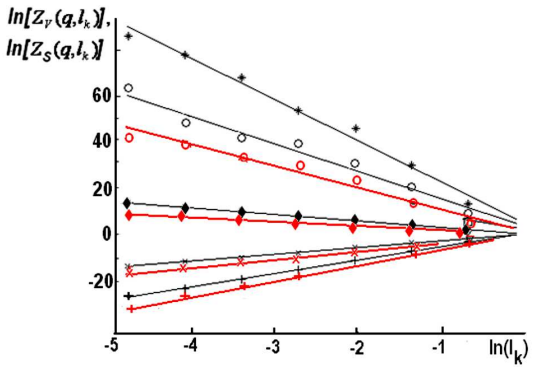

Fig. 2. Dependences of the generalized partition functions Z_S (black) and Z_V (red) on l_k for the nano-image presented in Fig. 1 for various $q = -3$ (∗), -2 (○), 0 (×), 2 (+), and 4 (♦)

when preprocessing initial data for the FA. Attention should be paid to the indicated feature when comparing the values of the Rényi numbers obtained by different authors and using different methods.

The calculation procedure for the characteristic MFA functions for each of the selected values of the growth factor q was terminated, when the magnitude of every next Rényi number $D(q)$ began to repeat the previous one to within a given accuracy. As a rule, for the indicated image sizes, the growth factor value did not exceed 30.

In Fig. 2, the experimental dependences of the generalized partition functions on $\ln l_k$ obtained for the surface areas and volumes of nanoforms located on the ZnO film surface, the photo of which is presented in Fig. 1, are exhibited. Within the whole set of q-values, a distinct tendency for the experimental data to group along straight lines is observed. This result proves the existence of a fractal symmetry for the indicated geometric parameters of nanoforms. Note that such plots were observed for the majority of the calculation results, which confirms once more the statement about the general character of the fractal symmetry in physical systems expressed in the principal works [5, 10].

At the same time, the existence of such linear dependences does not mean a high reliability of the calculation results obtained for the Rényi number on their basis, because they may reflect the influence of other factors, besides those that were taken into consideration. The main contribution to the error associated with the performance of MFA calculation procedures will be analyzed below when discussing the

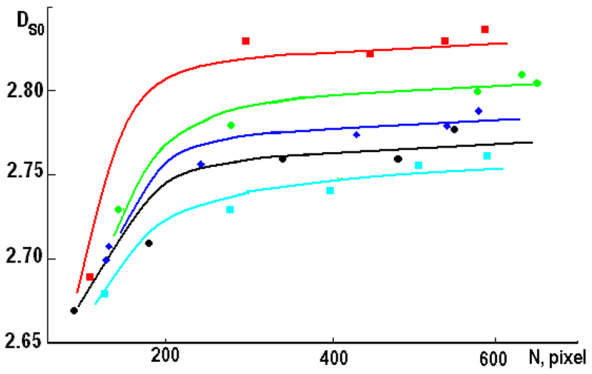

Fig. 3. Dependences of the Rényi number D_0 (the Hausdorff dimension) on the edge length (the number of pixels) of a square cut out from the original photo obtained for the surfaces of ZnO film synthesized using the sol-gel method at various temperatures t = 200 (red), 250 (green), 300 (blue), 350 (black), and 500 °C (blue-green curve). The solid curves were obtained by approximating the experimental results as cubic polynomials

sizes of statistical samples, i.e., the number of image pixels that would provide the account for all available elements with the fractal symmetry that are located on the surface when calculating the MFA spectrum.

The data processing based on the obtained dependences of the generalized partition functions was carried out in accordance with the classic cornerstones of the MFA [4–7]. The parameters of a linear regression between the partition functions and the cell sizes were calculated in the framework of the least squares method for every selected value of the growth factor q. The data obtained for the linear regression coefficient were considered as a basis for the calculation of all MFA functions; namely, the generalized correlation functions $\tau(q)$, the spectra of fractal dimensions α, $f(\alpha)$, and the spectra of Rényi numbers for a current q-value, $D(q)$ [5–8]. All those functions were calculated numerically.

Because of the statistical basis of the fractal analysis, which implies the application of the least squares method when determining the Rényi numbers, its successful realization is possible only for samples with considerable sizes. Actually, this means the existence of a minimum possible image size of the researched surface, through which the fractal averaging is made. This condition can be reformulated for the case of image processing by imposing a restriction on the minimum pixel number, which has to be taken into account in the calculation program.

It is reasonable to take advantage of the standard FA software Gwiddion [11] in order to make allowance for the influence of the specimen pixel size (or, equivalently, the side length of a square image subjected to the processing) on the values of the Rényi numbers [2–4]. The application of our MFA software program [2–4] for the same purpose would be time-consuming, especially if processing the images with large pixel sizes. At the same time, the Gwiddion software program performs calculations rather quickly, it has no special restrictions on the processed image size, and its results obtained for the Hausdorff dimension completely coincide with the results of our software.

The calculation results obtained for the parameter D_0 for films synthesized at various temperatures are shown in Fig. 3. The plotted dependences were obtained, when an original image of the type shown in Fig. 1 was divided into smaller photos, which were later used to calculate the fractal parameters. The application of high-quality films with uniform surface properties in the measurements gave us hope to detect the indicated statistical effect. It was principally important that the fragments of the same photo were used in this procedure. Therefore, we may assert that those images were taken under the same conditions, only the dependence of the Rényi number D_0 on the sample size is registered, and it is not hidden by other photo effects.

For instance, Fig. 3 demonstrates that, for small image sizes, the value of D_0 changes substantially, if the size of the used image (the sample size) or the number of pixels in it increases. As the pixel number in the photo increases, the obtained dependences saturate and almost achieve a constant value. The presence of such a low-gradient section means that the calculated value of the Hausdorff dimension (the Rényi number D_0) ceases to depend on the calculation conditions. Just such values of the Rényi numbers have to be adopted as their true values. We did it in this work throughout the further analysis.

The results obtained for the dependence of the Rényi numbers on the processed image size made it possible to substantiate the minimum number of pixels in the image that provides the minimum error from this effect. We adopted that such a minimum size corresponded to the pixel number at a level of 270-300 along each side of the processed square image. With such a choice, the amount of output data for a further calculation of the areas of microscopic sites that

approximate the whole area of the surface relief was found to be quite sufficient for a stable implementation of the statistical component of the fractal analysis [1, 2, 5–9].

It should be emphasized that the application of images with small pixel sizes makes it possible to calculate the MF spectra rather quickly for the values of the growth factor q up to 80–100. At the same time, larger image pixel numbers lead to the narrowing of the convergence interval of the whole software due to the necessity to express small values of current variables as large negative power exponents of q. In turn, the limitation on the negative values of the growth factor q is a dangerous procedure, because there is a danger that not the total amount of the data on the MF spectrum of the system would be processed. Therefore, an important practical task when performing the calculations of MF spectra is to ensure a compromise between the processed image size and the q-value. The experience gained while performing calculations showed that the stable operation of the MFA software program [1, 2, 9] that was used in the analysis was observed for images of 300×300 pixels in size and a q-value not exceeding 30.

Thus, as the principle result of Fig. 3, one should recognize a substantial variation in the values of the Rényi numbers, if the size of the photos used for the fractal averaging changes. Indeed, the calculation uncertainty induced by the mentioned effect can reach a value of ± 0.15. This is almost an order of magnitude larger than the errors of technical origins discussed earlier. The circumstance makes it possible to assert that this stage of fractal calculations has to attract a special attention when determining the fractal characteristics of the epitaxial film surface.

The efficiency of the stated considerations concerning the method used to perform the MFA will be confirmed when describing the surfaces of nanofilms synthesized in the $ZnO–SiO_2$ system via the sol-gel technology. The results of such a processing will be commented from the viewpoint of revealing the dependences of the MF surface parameters on the technological conditions of the film synthesis.

4. Results and Discussion

As a proof that the indicated features have to be taken into account when performing the MFA in order to provide its information saturation and efficiency, let us consider its application on the example of the surface image processing of sol-gel synthesized films of the $ZnO–SiO_2$ system. A typical photo image is exhibited in Fig. 1.

According to the developed recommendations, at the first stage of the numerical data processing with the help of the standard software program Gwiddion [11], we searched for a size interval of the surface photo image in which the dependence of the Rényi number D_0 on the photo size was absent or relatively weak (Fig. 3). This procedure can be done rather simply, if the whole original image is used as input data for the calculation of the Hausdorff dimension (the Rényi numbers D_0) and, afterward, its fragments of various linear sizes (in pixels).

The found image size intervals served as a basis for choosing the final working size (300×300 pixels). Further, this value was fixed throughout the calculation cycle, and photos of this size were sent to the MFA program for the processing. Such an approach in calculations allowed us to assert about the minimization of the calculation errors induced by the indicated effect and hope for the reliability of the magnitudes of Rényi numbers that would be obtained using the MFA.

Typical experimental dependences that form the basis of MFA and are the main evidence of the fractal symmetry that exists between the volumes and areas of surface microforms are presented in Fig. 2. This figure illustrates a typical dependence of the generalized partition functions $Z(q, l_k)$ for the surface areas and volumes of microforms on the edge length l_k of the spatial unit cell in the method of coarsened partitions for various q-values. It can be seen from the data that the plotted dependences have a tendency to group their data along the corresponding straight lines. Such a behavior is observed for both the surface areas and the volumes of microforms. The presented data make it possible to assert about the existence of the self-similarity and fractal symmetry between the indicated geometric parameters of the surface.

The availability of the indicated linear dependencies for various values of the parameter q at high values of the correlation coefficients in the least squares method allows us to assert the existence of the fractal symmetry and self-similarity in the system for various input variables. The latter is equivalent to the statement that just the MF spectrum is typical of such surfaces, and just the MFA is a promising method

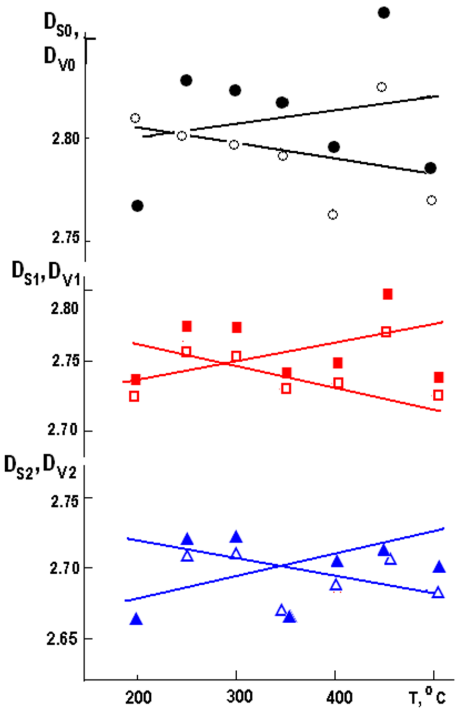

Fig. 4. Dependences of the Rényi numbers for the volumes ($D_{V,0}$, $D_{V,1}$, $D_{V,2}T$) and surface areas ($D_{S,0}$, $D_{S,1}$,$D_{S,2}$) of nanoforms and the MFA on the synthesis temperature of the films of the ZnO–SiO_2 system. Symbols denote experimental data obtained in this work. Black lines correspond to D_0, red ones to D_1, and blue ones to D_2

to describe the systems of this kind. Hence, these are the MF parameters of the system that should be used to describe the state of the surface of the specimens obtained using the sol-gel technology.

The analysis of typical calculation results obtained for the characteristic MFA functions $\tau(q)$, $f(\alpha)$, and $D(q)$ showed that they correspond to their canonical forms. This fact means that the sequence of Rényi numbers is descending, the functions $f(\alpha)$ have a characteristic maximum, and the dependences $\tau(q)$ have a cusp characteristic of the MFA. No specimen with deviations in the behavior of the characteristic functions from the forms predicted by the theory [5–8] was revealed among the analyzed images. This result is not a less important proof that a system of relief-forming microforms has the properties of self-similarity and fractal symmetry. Thus, the obtained data made it possible to apply the developed MFA software for the quantitative description of a fractal symmetry for the indicated geometric parameters of the relief-forming nanoforms and calculate the MF spectra and their parameters for the layer surface in the ZnO–SiO_2 system.

According to the recommendation given in works [5–8], the most informative for the quantitative description of the fractal structure of the surface are the Rényi numbers and the fractal ordering parameter $\Delta = D_1 - D_{q\to\infty}$ (the degree of fractal symmetry violation). The values of the Rényi numbers D_0, D_1, and D_2 calculated for various temperatures of the final layer annealing are presented in Fig. 4. Analogously to works [2, 9], during the MFA of the film surface of the ZnO–SiO_2 system, it is found that the magnitudes of the first Rényi numbers for the distributions of both the elementary areas and volumes of the elements of the nanofilm are quite close to one another, $D_0 \approx D_1 \approx D_2$. This fact was explained as a result following from the description of a rather smooth natural surface relief of a film by means of elements of rather small sizes. Therefore, the obtained surface approximations described the real surface rather accurately in the approximations for the degrees $q = 0, 1$, and 2. So, the closeness of the values of the obtained Rényi numbers was a result of this fact.

At the same time, one can see from Fig. 4 that the differences between the first Rényi numbers exceed the errors of their determination, which are estimated at a level of ± 0.01. Taking into account that the obtained fractal characteristics model the system through power-law functions, which strongly depend on the power exponent value, such variations of the Rényi numbers can substantially distort the real picture in physical calculations. Such a situation demands a discussion concerning which of those numbers is preferable when describing the thermodynamic properties of a system with the fractal symmetry.

Before discussing this issue, recall that $D_0 > D_1 > D_2$, and they have a physical interpretation. Namely, they are the Hausdorff, information, and correlation, respectively, dimensions for simulated system [5–8]. According to the MFA, the numbers D_0 are calculated by linearizing the dependence of the partition functions $Z_S(q = 0, l_k)$ or $Z_V(q = 0, l_k)$ on the cell size l_k, when the filling fraction $\nu_{V,i}^{q=0}$ of the current cell is raised to the zero power. Therefore, if the current cell contains even a small part of the studied parameter, its filling fraction is equated to one, which is evidently independent of the filling fraction itself. Such an approach can be considered as justi-

fied and giving a reliable information provided that unit cells of very small sizes are used in the method of coarsened partitions, and the surface relief is a smooth function. This is exactly the situation that was observed in work [2, 9] when analyzing the surface of a semiconductor film that was created in a natural way during the layer synthesis.

Such a situation is partially excluded, if the emphasis in further physical calculations is shifted toward the application of the number D_1. Indeed, the calculation for the numbers D_1 involves the linearization of the partition functions $Z_S(q = 1, l_k)$ or $Z_V(q = 1, l_k)$. In this case, those functions are formed from the specific values of the relative surface area or volume of the substance in each cell. In this regard, it becomes clear why the parameter D_1 is called the information dimension [5–9]. Indeed, this is a number that includes an informational component about the most probable area (volume) spatial distribution of the substance. Therefore, when discussing the results of the fractal description of the system, besides the numbers D_0 (the Hausdorff dimension), the application of the set of the Rényi numbers D_1 (the information dimension) and D_2 (the correlation dimension) is also quite justified and useful in practice. Therefore, for their further physical applications and the discussion of the features of the fractal description of the nanolayer surface, those data are also exhibited in Fig. 4.

For the correct interpretation of the obtained data, one should bear in mind that, within the fractal formalism framework, a volume located near the surface and completely filled with the substance is assigned the $D_{V,0}$- and $D_{V,1}$-number values equal three, whereas the Rényi numbers equal two for a perfectly flat surface. The deviation of the Rényi numbers from the indicated values for a planar surface corresponds to the solution of the problem concerning the determination of the dimension of a surface that is not planar, but porous and developed at the nanolevel.

It is most effective to analyze the validity and information content of the obtained MFA data by considering their dependence on the technological parameters of the synthesis process. Really, exactly in such dependencies, the influence of various physical processes responsible for the surface relief state and governing the values of the fractal parameters can be detected rather distinctly. A set of such dependences of the Rényi numbers and the ordering parameters

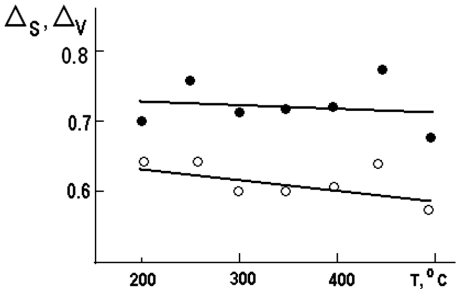

Fig. 5. Dependences of the ordering parameters for volumes (Δ_V, •) and surface areas (Δ_S, ○) of nanoforms on the synthesis temperature of the films of the ZnO–SiO_2 system

Δ's on the conditions of the final layer annealing are presented in Figs. 4 and 5. The straight lines in the plots were drawn according to the averaging of the experimental dependences of the MF parameters on the corresponding technological conditions in the framework of the least squares method. In essence, the presented results should be considered as the influence of the annealing temperature on the variation of the self-similarity and fractal-symmetry parameters of nanoforms on the specimen surface.

The data presented in Figs. 4 and 5 testify to the existence of stable relations between the MF parameters and the temperature of the layer synthesis for the distribution of both the surface areas and the volumes of nanoforms. This fact allows us to assert that it is the values of the MF parameters that quantitatively tracked and described the differences in the surface structure of the specimens with the same composition, but formed at different temperatures. Such a quantitative result is confirmed while visually analyzing the images of the layer surfaces. It follows from the photos that the sizes of the crystallites on the layer surface slightly increase, as the temperature grows. As a result, the fraction of areas with a flat surface appearing on the layer surface becomes larger. The latter is reflected in the results presented in Fig. 4, which quantitatively demonstrate that, as the substrate temperature increases, the dimension of the film surface area (the number D_S) decreases and approaches a value of two, whereas the corresponding parameter for their volumes (the number D_V) tends to grow and approach a value of three. Such profiles of the dependences under consideration reflect the system's tendency to faster form flat surfaces at higher substrate temperatures, when the rate of surface chemical reactions increases.

In Fig. 4, besides the dependences for the Rényi number D_0, the results of similar calculations for the Rényi numbers D_1 and D_2 are also depicted. The necessity to consider the behavior of these characteristic numbers was pointed out earlier. It follows from Fig. 4 that the indicated parameters change with the temperature in almost the same way as the number D_0. However, quantitative differences between their values are substantial. Concerning the aforesaid, we can assert that the data obtained for various Rényi numbers for the volumes and surface areas of microforms complement one another and form a common picture of the fractal symmetry in the system.

If different signs of the corresponding derivatives $\partial D_S/\partial T$ and $\partial D_V/\partial T$ are excluded from consideration, then the slope magnitudes of the dependences of all Rényi numbers on the temperature become practically identical. This fact was noticed when plotting the data, and the experimental results were straightened using the least squares method. It is impossible to make a strict theoretical justification for the physical or geometric origins of such a behavior of the indicated derivatives at the current stage of research. The absence of direct correlations between the volume and surface geometric parameters of any shapes (in particular, relief-forming forms) in the fractal approximation was marked in the principal works [5, 6, 10]. At the same time, the possibility of the existence of such a relation cannot be excluded; it can be observed in Fig. 4 as a synchronous behavior of the plots for the volume and surface parameters, when they were formed in a common physical process of crystal phase growth.

The results obtained for the Rényi numbers for the surface areas of nanoforms (Fig. 4) and their volumes lead to the following recommendation concerning the application of the MFA to the description of the surface state in the fractal approximation. When performing a complete analysis of the surface state of a substance with respect to the conditions of its synthesis and developing final recommendations concerning the correction of the phase formation conditions, it is advisable to use the whole complex of MF studies of the areas and volumes of the relief-forming surface nanoforms. Only their joint consideration will make it possible to reveal the physical factors responsible for the formation of such a surface and develop recommendations for the correction of surface properties. If the data body is limited or the complete set of parameters is absent, it may turn out at the preliminary research stage that the data on the distribution of the surface areas of microforms are more informative and, therefore, more useful. Therefore, when performing the MFA, just these results should be obtained and applied, first of all, when choosing processing conditions.

Not less important parameters of the MF spectrum for the volumes and surface areas of nanoforms are the fractal ordering parameters Δ_S and Δ_V. Their dependences on the final annealing temperature in the framework of the sol-gel method are shown in Fig. 5. The data in Fig. 5 demonstrate a steady tendency of the system to narrow the width of its MF spectrum, as the final annealing temperature increases. Such a tendency of the analyzed dependences reflects the system's "intention" to form "monofractal" structures on the surface, which are characterized by a reduction in the values of the fractal ordering parameters and a narrowing of the spectrum of Rényi numbers. Thus, it can be asserted that the data obtained for the MF parameters of the system quantitatively confirmed that the increase of the temperature of layer synthesis within the indicated interval leads to an increase of the planarity of the obtained layers, i.e., to the formation of a less "defect" surface, whose geometry becomes closer and closer to planar.

Attention is attracted by practically parallel variations of the temperature dependences of the ordering parameters in Fig. 5. This fact means that these parameters of the fractal spectrum for the volumes and surface areas of the synthesized nanoforms have the same feature in their behavior as the corresponding Rényi numbers (Fig. 4). This situation can be considered as a kind of confirmation of the existence of a relation between the volume and surface parameters of nanoforms formed in a natural way on the film surface.

It should also be noted that the typical values of the fractal ordering parameters Δ_S and Δ_V are relatively high, which corresponds to a substantial width of the fractal spectrum for the geometric elements of the surface. The data obtained for those parameters show that their typical values are at the level of 0.67–0.77. On the other hand, for rather high-quality and homogeneous surfaces of polycrystalline Zn–Cd–Te epitaxial films, the corresponding parameters do not exceed 0.35 [2, 9].

5. Conclusions

The discussion concerning the peculiarities in the implementation of the MFA and the interpretation of the MF parameters that quantitatively characterize the geometry of nanoforms on the surface of the films of the ZnO–SiO_2 system synthesized using the sol-gel technology allowed us to draw the following conclusions.

1. Conditions for producing high-quality ZnO–SiO_2 layers under various final annealing temperatures in the framework of the sol-gel technology have been found and implemented. The surfaces of the synthesized layers have been studied using the SEM method with regard for the dependence on the temperature of their final formation.

2. The MFA has been applied to process the SEM images of the surface of the layers produced using the sol-gel method. The MF spectra from the surface areas and volumes of the relief-forming nanoforms that were formed on the layer surfaces have been calculated and analyzed.

3. Recommendations have been made to provide a high efficiency of calculations of the absolute values of fractal parameters for the surface areas and volumes of the relief-forming nanoforms. It is shown that the largest uncertainty of the MFA application to the description of a surface relief can be associated with an incorrect choice of the dimensions of the images for which the fractal averaging is performed.

4. By accounting for the indicated features of the MFA implementation and the interpretation of the obtained MFA parameters, we managed to demonstrate the existence of a correlation between the Rényi numbers, the ordering parameters, and the technological conditions of the final annealing process for the layers in the ZnO–SiO_2 system. The analysis of the relations between the MF parameters and the layer synthesis temperature made it possible to quantitatively confirm the fact of producing the layers with a higher degree of their fractal symmetry (i.e., more structurally perfect) by increasing the annealing temperature from 200 to 500 °C.

5. The obtained data on the relation between the MF surface parameters of the ZnO layers and the annealing temperature of the latter make it possible to substantiate the choice of conditions for a technological process aimed at the formation of heterostructures on the basis of ultra-thin 0.1-μm-films with a given surface relief.

The realization of those recommendations will considerably enhance the reliability of the values determined for the fractal parameters of the surface nanorelief. This circumstance will be a stimulus for the further application of the FA while developing the effective and data-intensive quantitative methods for the description of the state of complicated surfaces and the usage of such data in physical and technical calculations.

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ОСОБЛИВОСТІ ДОСЛІДЖЕНЬ ПОВЕРХНІ ПЛІВОК $ZnO–SiO_2$ МЕТОДОМ МУЛЬТИФРАКТАЛЬНОГО АНАЛІЗУ

На прикладі мультифрактального аналізу (МФА) зображень поверхонь наноплівок, що синтезувалися золь-гель технологією в системі $ZnO–SiO_2$, обговорюються особливості застосування цього методу при отриманні кількісних характеристик поверхні. Вхідною інформацією для реалізації цього підходу до опису стану поверхонь були Second electron microscopy (SEM) зображення поверхні зразків після їх синтезу в заданих умовах. Чисельними розрахунками узагальнених статистичних сум для площі та об'ємів просторових наноформ показано існування їх лінійних залежностей від просторових розмірів, що є основним доказом наявності самоподібності та фрактальної симетрії серед зазначених геометричних параметрів поверхні. Наголошується на необхідності підвищення надійності визначення параметрів МФ спектрів та аналізуються причини, що контролюють точність абсолютних значень чисел Реньї. Вироблено рекомендації для мінімізації похибок з метою отримання найбільш вірогідних даних щодо МФ параметрів поверхні. Наведено залежності чисел Реньї від температури синтезу шарів $ZnO–SiO_2$ золь-гель методом. Звертається увага на те, що для подальшого застосування результатів МФА у фізичних розрахунках необхідно коректно вибирати ті числа Реньї, які несуть у собі необхідну інформаційну компоненту за модельованим фрактальним параметром. Обговорюються фізичні причини появи взаємозв'язку між параметрами МФ спектрів для площі поверхні та об'ємів наноформ, що формуються на поверхні плівок, та умовами їх синтезу.

Ключові слова: нанорельєф, мультифрактальний аналіз, похибки визначення чисел Реньї, золь-гель технологія, поверхня наношарів.