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SEM Investigation of ZnO and CdO–ZnO Layers Grown by Sol-Gel Technology and a Multifractal Analysis of their Surface Depending on Synthesis Conditions

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Abstract

Introduction. Super-thin films of zinc oxide regarded as transparent electrodes can be integrated in effective semiconductor heterostructures for use in modern infrared photo electronics and solar power installations. The most important parameter of zinc oxide thin layers is their surface nanorelief, which can be effectively studied using SEM spectroscopy. SEM images allow for a quantitative description of the surface depending on the synthesis conditions using the method of multifractal analysis. Such an approach reveals quantitative relationships between the fractal parameters of the surface topography of the layers in these systems and the temperature regimes used for their final annealing in conventional sol-gel technology.

Aim. To reveal quantitative relationships between the fractal parameters of the surface topography of layers in the Zn–O & Zn–Cd–O systems and the temperature conditions of their final annealing. The MFA method was used for a quantitative description of the surface state depending on the synthesis conditions.

Materials and methods. Super-thin films in the ZnO and ZnO–CdO systems were synthesized using a modified sol-gel technology. The temperature-concentration ranges of the parameters of the modified technological process, which allows high-quality layers of the material to be reproducibly obtained on a glass substrate, were determined. The surface morphology was investigated by SEM spectroscopy depending on the temperature of the final annealing of the layers. SEM images of the surface served as a basis for multifractal analysis (MFA) of the surface area and volume of nanoforms, which are formed on the surface of the obtained layers thus determining their surface relief.

Results. Renyi's numbers and the parameters of fractal ordering in MFA were chosen as fractal parameters for describing the nano-geometry of the layer surface. MFA was applied to the description of both the surface areas and volumes of nanoforms. Quantitative correlations between Renyi's numbers, as well as the parameters of fractal ordering for the areas and volumes of surface nanoforms, and the temperature of the final annealing were found.

Conclusion. The numerical values of Renyi's numbers for the surface and volume characteristics of the surface of layers were used to assess the effect of the fractality of the surface on the molar surface energy of the film. Consideration of the fractal geometry of nanoforms with their characteristic sizes smaller than $5\cdot10^{-3}$μm shows the possibility of both an increase in the surface energy of the resulting film and its decrease when changing the characteristic sizes of nanoforms. The latter effect is due to the formation of a highly porous surface at the nano level.

Keywords: surface structure, crystal morphology, second electron microscopy, oxides, zinc compounds

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Introduction. The development of a reproducible technology for the formation of transparent electrodes is part of physical, chemical and technological problem of obtaining the effective semiconductor hetero structure for modern infrared photo electronics and solar power. Currently, a superthin layer of zinc oxide is viewed as a transparent electrode in such devices. Zinc oxide is a wide-gap semiconductor $\left(E_g = 3.32\,\text{eV}\right)$, which allows it to be a transparent material in the visible and infrared range of electromagnetic wavelengths. Despite the significant band gap, which is more typical for dielectrics, this material has a relatively low electrical resistivity, which depending on the defective state of the film, is in the range of $10^{-2}\ldots10^{-4}$ Ohm·cm. The latter means that the material can be used as a conductive optically transparent electrode. An equally important advantage of the material is the rather high chemical stability of the compound with its low toxicity.

Super thin films of zinc oxide are usually synthesized using traditional sol-gel technology. The main stages of this process are well known and their conditions are analyzed in sufficient detail [1–3]. One of the important advantages of the sol-gel process of material synthesis is relative independence of the stages of its implementation. This situation opens up the possibility of its phased modernization. The most important contributes to the sol-gel process, which are subject to detailed study and improvement, were the stage of formation of the initial gel and the stage of searching for optimal temperatures during their annealing, when the final properties of the layers are formed. Naturally, the emphasis will be put on the analysis of the influence of the conditions for carrying out these stages of the sol-gel process on the final properties of the films.

The most important parameter of the thin layer is the morphology of its surface, which is determined by its surface relief. It can be argued that the surface relief of the layers is a mirror in which all the selected conditions of the synthesis of the layer are reflected. Therefore, the study of the surface topography of layers at the nanoscale, as well as the implementation of its quantitative description, is an important task at the stage of development of controlled technologies for obtaining material for its further use in electronic devices.

One of the most effective and visual methods for studying the surface of semiconductor layers at the nanoscale is SEM spectroscopy. The high resolution for surface elements in the resulting images opens the possibility of the effective use of such data for their further mathematical processing in order to obtain quantitative characteristics of the surface of the layers. As such a mathematical method for analyzing the geometric parameters of complex surface nanoforms the multifractal analysis (MFA) has been used. It is fractal analysis that makes it possible to quantitatively characterize the parameters of nanoforms that form a surface relief and which are very difficult to describe by the classical geometric figures.

At the same time, the experience of using fractal analysis to quantitatively describe the surface state shows that using only the Hausdorff'sdimension of the corresponding surface as an output parameter significantly limits the informative volume of such quantitative data [3, 5–11]. This is due to the relatively weak dependence of the power exponent (Hausdorff's dimension) in the corresponding power series on the shape of the surface under consideration. This drawback of fractal analysis is eliminated during the transition to MFA, when the entire spectrum of Renyi′snumbers is used for the quantitative description of complex geometric shapes, and not just its particular case of the Hausdorff′s dimension.

This situation made it possible to formulate the following approach to quantitative studies of the relationship between surface relief parameters and the conditions of the final annealing of the layers of the Zn–O and Zn–Cd–O systems in the process of sol-gel synthesis. Thus, the purpose of this work is to search for quantitative relationships between the fractal parameters of the surface topography of the layers of these systems and the temperature conditions of the final annealing of the layers. For a quantitative description of the surface state, depending on the synthesis conditions, the MFA method was used. The surface area and the volume of nanoforms were chosen as geometric parameters for the fractal description of the surface. Naturally, this kind of geometric parameters were found by numerically processing the corresponding SEM images. The practical implementation of the procedures described above made it possible to obtain quantitative relationships between the parameters of the MF spectra for the volume and surface area of nanoforms that are formed on the surface of layers synthesized by the sol-gel method, i. e. to achieve the goals set before work.

It is necessary to point out that previously we successfully applied a similar approach in [6–10] to search for the relationships between the parameters of MF spectra from the surface of the layers and the conditions for the synthesis of superthin $Zn_xCd_{1-x}Te$ solid solution films by vacuum technologies.

The significance of the obtained quantitative data on fractal characteristics of the surface of the layers for further theoretical studies is shown by their use for analyzing the dependence of the molar surface energy on the parameters of the nanorelief of the surface. The performed analysis shows that the data on the fractal parameters of the surface make it possible to estimate the contribution of surface energy to the overall energy balance of the nanosystem.

Methods.

1. Peculiarities of the synthesis of layers by the sol-gel method. The process of obtaining films, which was implemented as a whole, met the typical procedures for the deposition of semiconductor layers by this technology [1, 2, 4, 5]. The following chemical substances were used to form the sols: the precursor was tetraethyloxysilane $Si(OC_2H_5)_4$, and the solvent was a solution of ethyl alcohol in water. The chemical reaction was catalyzed by chloride acid. Zinc nitrate – $Zn(NO_3)_2 \cdot 6H_2O$ was used to dope the silicate matrix.

The sol preparation process was carried out in accordance to the typical steps for the sol-gel technology. At the first stage, an exchange reaction of tetraethyloxysilane with ethyl alcohol was carried out for 30 min at room temperature. The hydrolysis of the obtained esters was carried out by introducing into the resulting solution of distilled water in a ratio of 4: 1 and chloride acid (20…50 μl) as a catalyst. The process of chemical interaction was accompanied by vigorous stirring of the solution for 1 hour. Orthosilicate acid, which was synthesized and polycondensed during chemical processes, formed the main chain of the polymer sol molecule. Thus, it was the obtained solution of sol of orthosilicate acid with film-forming properties, which was the purpose of this stage of synthesis [1, 2, 4, 5]. At the same stage, the calculated the amount of dopant $Zn(NO_3)_2 \cdot 6H_2O$ – salt of zinc nitrate – was introduced into the solution. This made it possible to form a transparent silica sol solution of a given composition. The largest number of experiments on the synthesis of layers was carried out with sols of the following composition $50\,ZnO \cdot 50\,SiO_2$ wt. %.

Therefore, the obtaining sol solution was deposited on substrates that were previously prepared by chemical etching of their surface in acid. Glass was used as a substrate in the overwhelming set of experiments. This made it possible to minimize the influence of the crystallographic and mechanical properties of the substrate on the formation of final properties of the synthesized layers.

The necessary properties of the gel layer on the substrate surface were formed by centrifugation at the next stage of the process. The parameters that controlled this stage of the process were the time of sol deposition on the substrate, the number of revolutions, and the location of the substrate on the substrate holder during centrifugation. The ranges of variations of these parameters were found during preliminary evaluation experiments. The main quality criterion for conducting this stage of the process was the requirement to obtain continuous films of a given thickness. The found ranges of variation of the indicated parameters of this process were as follows: the prepared sol was aged for 2 hours, 50 μl of sol was applied to a horizontally placed substrate. Centrifugation was carried out for 2 min at 3600 rpm.

The final stage of the sol-gel process was the annealing of the formed films. At this stage, the solvent was removed both from the pores on the surface and from the volume of the film, the syneresis of the sol, chemical reactions of the decomposition of zinc nitrate and orthosilicate acid took place too. The complexity and multi-stage of physic-chemical processes occurring at this method of synthesis stimulated carry out the annealing in two stages. This allowed us to significantly improve the morphological quality of the surface of the films. The low-temperature annealing stage corresponded to a temperature of 80…90 °C. The temperature of the final annealing in the experiments was considered as an independent variable and its value varied in the range from 200 till 500 °C. A typical high-temperature annealing step for all samples was carried out for 10 min.

The phase composition of the synthesized layers was controlled by X-ray diffractometry measurements [5]. According to X-ray studies films obtained by the sol-gel method form a crystalline phase of zinc oxide with a wurtzite structure. A strong confirmation of the aforesaid was the clear diffraction peaks in the diffraction patterns, which corresponded to the reflection of X-ray radiation from planes with (100), (002), (101) crystallographic orientation.

2. SEM measurements. To analyze the surface morphology of the samples, a FEI Quanta FEG 250 scanning electron microscope (SEM) operated at 10 kV was used. SEM images were recorded in contact mode using a Si tip with a radius lower than 10 nm.

Typical SEM images of the surface of the synthesized ZnO layers are shown in Fig. 1 for various temperatures of final annealing.

The composition of the initial sol: $50\,ZnO \cdot 50\,SiO_2$ wt. %. The top photos show the image acquisition modes and their linear scale.

The obtained SEM images of the film surface were used to calculate the multifractal (MF) spectra of both the surface area and the volumes of nanoforms that were formed during the synthesis of the layers [6–10].

The reliability of the conclusions about the existence of relationships between the parameters of the MF spectra and the synthesis conditions requires an assessment of the accuracy for the final results for the parameters of the MF spectra. Reliability estimates performed in the work showed that the greatest error in the final values of the parameters of the MF spectrum is connected with the contrast of the resulting image, which depends, first of all, on the magnification factors of the obtained image.

To evaluate the effect of this error on the calculated parameters of the MF spectra, we used surface images obtained with different magnifications. The variation range of the increase factors in the SEM method varied from 10^5 till $2 \cdot 10^4$. The performed calculations of the parameters of the MF spectra, performed for the same sample, but with a different magnification factor, made it possible to find quantitative values for the most probable error of their finding. Thus the obtained estimates of the error in determining the MF parameters are shown in Fig. 2, 3, where the main results of quantitative image processing are presented.

Experience with MF spectra has shown that the final calculations of MF parameters also differ somewhat for the same sample when varying the position of the photographic sample over the layer surface. Calculations of the parameters of the MF spectra for different regions on the surface of the same sample showed that their numerical values differ from each other by less than 1…3 rel. %. Therefore, according to the estimates made, it can be argued that the main uncertainty in the numerical processing of surface relief data is created by the contrast of the resulting image, which depends primarily on the magnification of the microscope. This allowed for further analysis to use the image acquisition mode with a gain of 10^5 and to maintain it constant for all photographs taken.

The obtained SEM images of the film surface were used to calculate the MF spectra of both the surface area and the volumes of nanoforms that were formed during the synthesis of the layers.

3. MFA implementation features. To calculate the MF spectra of the surface area and volumes of the relief-forming nanoforms, the procedures described in detail in [6, 7] were used. The method of coarse partitions was realized when the MF spectra parameters were calculated in accordance with the procedure typical for this analysis method [6, 7, 12–15]. In this case, a statistical sum was formed for a cell of a given size: $Z(q,K) = \sum_{i=1}^{K} \nu_i^q$, where K is the index of the maximum value for the normalized length of the cube edge l_i used at the current step in the method of coarse partitions, q is the increasing number in the MF analysis. Naturally, when calculating the MF spectra of the surface area or volume of the relief-forming layer, either the area of the layer surface element or the volume of the relief-forming part of the surface were chosen as the base measure set.

The related surface area $\nu_{S,i}$ and related volume $\nu_{V,i}$ contained in a given box were considered as a measure of this box: $\nu_{S,i} = S_i / S$; $\nu_{V,i} = V_i / V$ where S_i and V_i – are the elementary surface area and the volume of contained in the i box correspondingly; S and V – are the total area and the volume correspondingly, which were obtained from spatial video images.

Calculations of generalized statistical sums for the indicated geometric parameters of the surface of the layers synthesized by the sol-gel method show that, depending on the chosen values of "k", they are a collection of points that are grouped along straight lines. This is significant evidence of the presence of fractal symmetry in the system for its selected geometric parameters. The calculation of linear regression parameters between the indicated system parameters was carried out using the least squares method for each of the selected values of the number. The data on linear regression coefficients were used to calculate all the functions necessary for conducting MF analysis [12–15]. All the components of the MF analysis and functions are calculated by numerical methods.

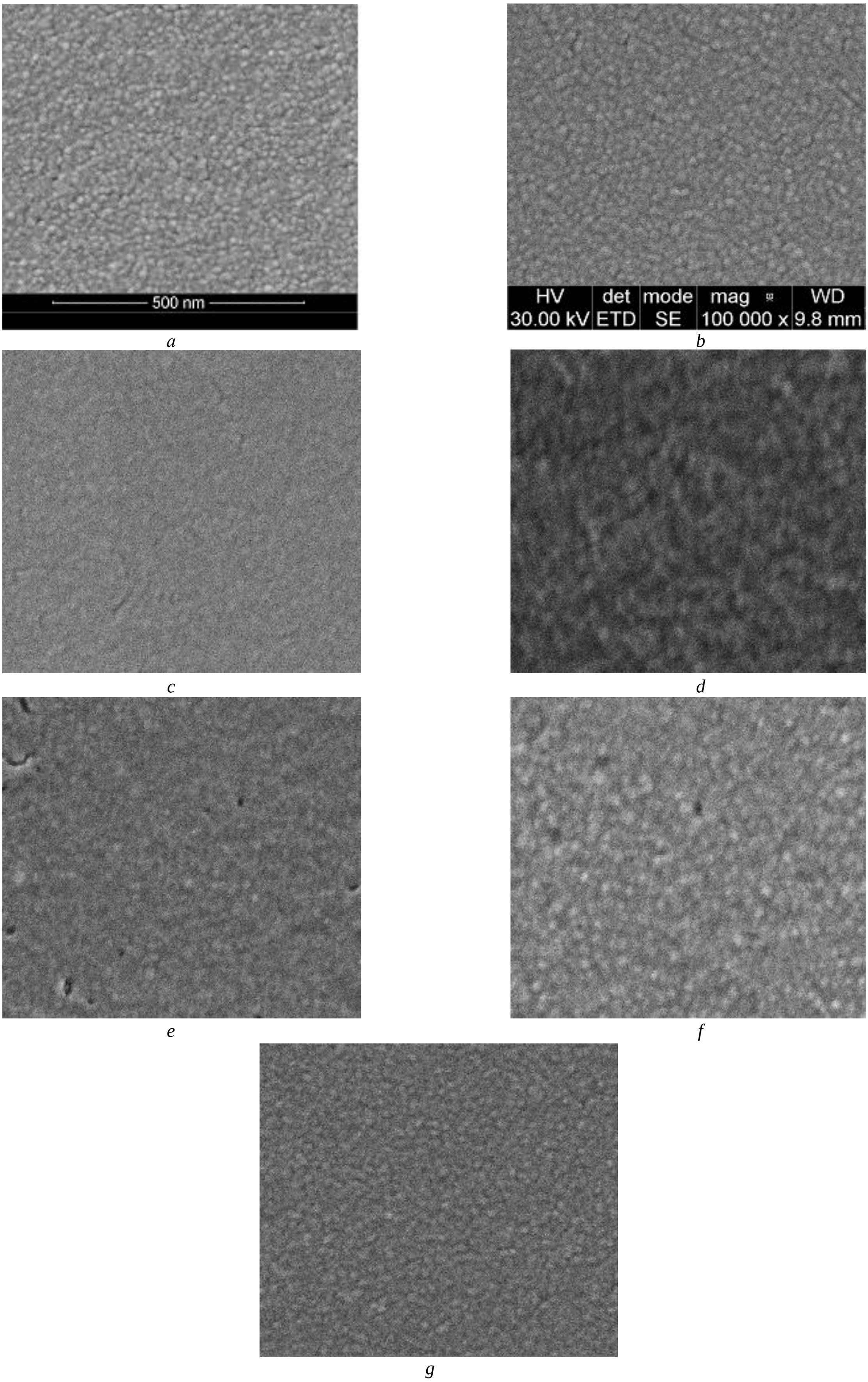

Fig. 1. SEM images of ZnO layers synthesized on glass substrates. Temperature of final anneal are the fol-low: *a* – 200 °C; *b* – 250 °C; *c* – 300 °C; *d* – 350 °C; *e* – 400 °C; *f* – 450 °C; *g* – 500 °C for 10 min

The approach described above made it possible to calculate the MF spectra and parameters for the areas and volumes of surface forms both for the images shown in Fig. 1 and for similar images of the layer surfaces for (CdO–ZnO) solid solutions. As in [6–9], the most informative MF parameters describing the spatial characteristics of the surface structure were selected Renyi's numbers $D_{S,q=0}$, $D_{V,q=0}$ and ordering parameters: $\Delta_{S,q=80} = D_{S,q=1} - D_{S,q=80}$; $\Delta_{V,q=80} = D_{V,q=1} - D_{V,q=80}$ (the degree of fractal symmetry breaking). In the designation of the MF spectra parameters their double indexation is used. This is necessary because according to the subsequent analysis, the MF parameters obtained in the work will be used both for surface areas and for volumes of surface forms formed on the surface of the layers.

Results and discussions. The calculations showed that the characteristic functions of the MFA $\tau(q)$, $f(\alpha)$, $D(q)$ in accordance with [12–15]) for the distribution of the surface area and volumes of nanoforms of the layers obtained by the sol-gel method correspond to their canonical forms. This means that the sequences of Renyi's numbers $D_S(q)$, $D_V(q)$ are decreasing and the corresponding $f(\alpha)$ functions have a characteristic maximum. It should be noted as in [12–15], that when processing SEM images of the surface of films deposited at different temperatures, no result was obtained to ensure the obtaining of the so-called pseudo-spectrum [9]. This result once again confirms the importance of the stage of the correct formation of the initial data or, which is the same, the generation of the initial measure in the implementation of the MFA [6, 7, 12–15].

The obtained quantitative data on the MF parameters for the distributions of volumes and surface areas of nanoforms allow a comparative quantitative analysis of the influence of the synthesis temperature of the ZnO films on the geometric parameters of surface nanoforms. The set of such relationships between the Renyi's numbers D_{S0}, D_{V0}, ordering parameters Δ_V, Δ_S and the temperature on the sub-

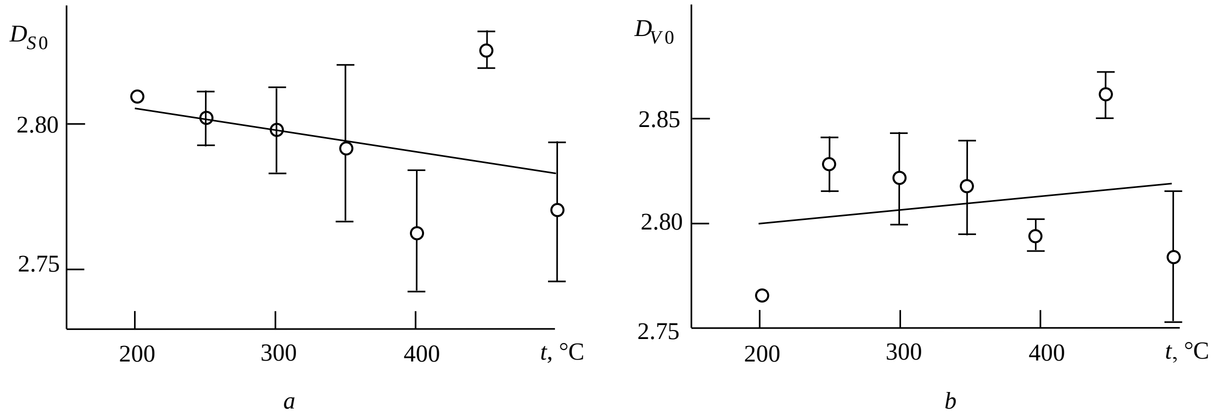

Fig. 2. Dependences of the Renyi′s numbers for surface area D_{S0} (*a*) and volumes of nanoforms D_{V0} (*b*) on the temperature of the synthesis of ZnO layers by the sol-gel method

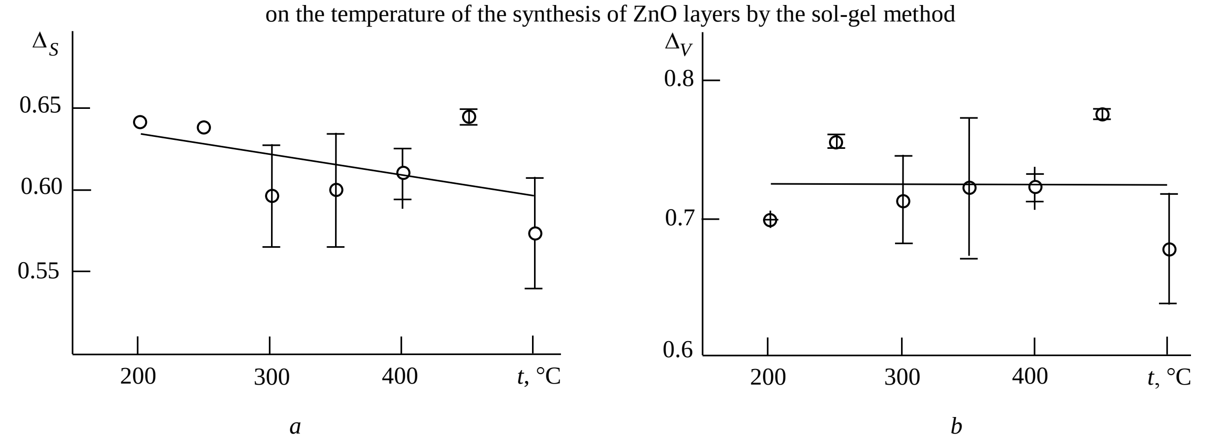

Fig. 3. Dependences of fractal ordering parameters for surface area Δ_S (*a*) and volumes of nanoforms Δ_V (*b*) on the temperature of the synthesis of ZnO layers by the solgel method

strate is shown in Fig. 2, 3 for the constant time of the synthesis process. Straight lines on the correlation dependencies are drawn by the least squares method applied to each set of experimental data. The values of our estimates of the accuracy of finding the values of the corresponding MF surface parameters, which are made in accordance with the above considerations, are also presented there.

The data in Fig. 2, 3 demonstrate the existence of stable relationships between the MF parameters and the temperature of the process of layer synthesis for both the distribution of the surface area of nanoforms and their volumes. It proves that it is precisely the values of the MF parameters that quantitatively tracked and described the differences in the surface structure between samples of the same composition, but formed at different temperatures. This quantitative result is confirmed by the visual analysis of images in Fig. 1. Therefore, the graph shows that the crystallite sizes on the surface of the layers increase slightly, which ensures the appearance on the layer surface of a larger proportion of areas with a flat surface.

The data in Fig. 2, 3 quantitatively show that with increasing annealing temperature the space dimension of the surface area of the polycrystalline film (number D_{S0}) decreases, approaching the number "two", and the corresponding parameter for their volumes (number D_{V0}) increases, approaching "three". Such a course of the considered dependences reflects the tendency of the system to form flat surfaces faster with increasing temperature on the substrate when the rate of surface reactions increases.

Fig. 3 shows the data on the ordering parameters Δ for the surface area and volumes of nanoforms that form on the surface of the ZnO layer at various synthesis temperatures. The data in Fig. 3 show a stable tendency of the system to decrease the width of its MF spectrum with increasing growth temperature. Such a course of the considered dependence reflects the desire of the system to form "monofractal" structures on the surface, which are characterized by a decrease in the fractal ordering parameters and a compression of the spectrum of Renyi's numbers. Thus, it can be argued that the obtained data on the MF parameters of the system quantitatively confirmed that an increase in the temperature of the synthesis of layers in the indicated range leads to an increase in planarity of the obtained layers.

It is possible to control the surface morphology or, equivalently, the parameters of the surface microrelief by introducing another isomorphic component into the material. The introduction of cadmium into the initial growth system, which was accompanied by the synthesis of the $(\mathrm{CdO})_x(\mathrm{ZnO})_{1-x}$ solid solution, allowed us to evaluate the effect of the third component on the state of the surface of the grown layer. The process of obtaining the specified solid solution was consistent with the technology described above. The only difference was the change in the concentration of the $\mathrm{Zn}(\mathrm{NO_3})_2$ dopant by the required fraction of $\mathrm{Cd}(\mathrm{NO_3})_2$. The technique for obtaining SEM images and calculating the parameters of the MF spectrum remained the same. To solve this problem, the largest number of experiments on the synthesis of layers was carried out with a sol of the following composition $20\mathrm{CdO}\cdot 30\mathrm{ZnO}\cdot 50\mathrm{SiO_2}$ wt. %.

The data on the dependences of the Renyi's numbers and the disordering parameters on the synthesis temperature for layers obtained from sols of the indicated composition are presented in Fig. 4, 5. On the same figures, dashed lines for comparison represent the averaged functional dependences for similar data describing the surfaces of the layers of the ZnO system.

As expected, the values of the Renyi's numbers and the fractal ordering parameters for the layers of the solid solution, in general, turn out to be large in value or remain practically close to their counterparts for the binary system. Such a course of the dependence under consideration, apparently, is a direct consequence of the appearance in ZnO–CdO solid solutions of excess mixing entropy, which is characteristic of mixtures of substances. The appearance of the configuration component of the entropy of mixing is reflected in the values of the Renyi's numbers, whose interrelations with various components of the entropy of the system are known [6]. Therefore, the experimental data on the Renyi's numbers obtained for solid solutions should be considered as confirmation of the theoretical relationship between the Renyi's numbers and the configuration component of the entropy of the system.

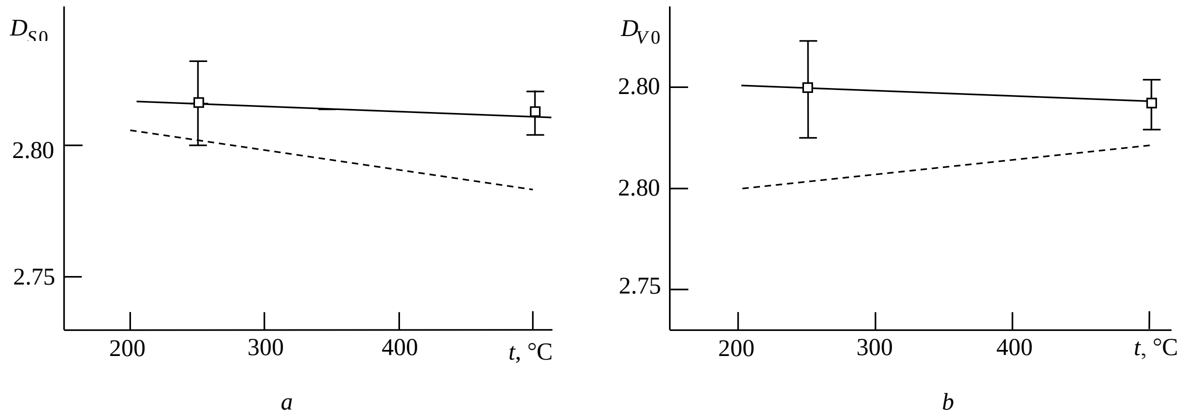

Fig. 4. Dependences of the Renyi's numbers for surface area D_{S0} (*a*) and volumes of nanoforms D_{V0} (*b*) on the temperature of layer synthesis in the ZnO–CdO system by the sol-gel method. The composition of the initial sol: 20 CdO • 30ZnO • 50 SiO_2 wt. %. The dashed lines correspond to similar data for the layers in the ZnO system

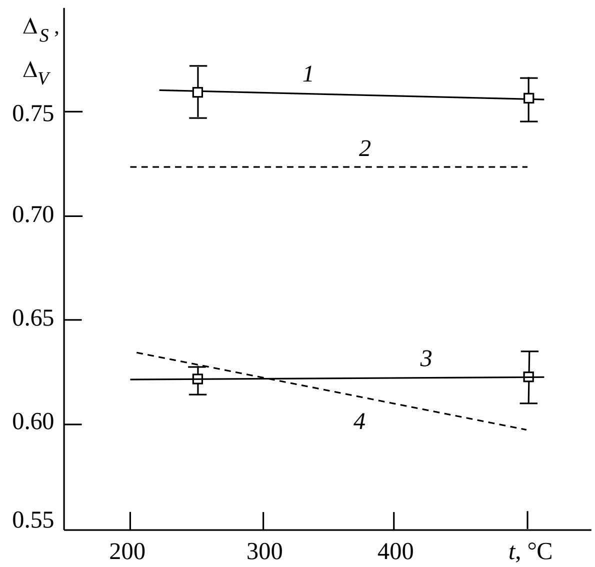

Fig. 5. Dependences of the fractal ordering parameters for the volumes of nanoforms Δ_V (*1, 2*) and for their surface area Δ_S (*3, 4*) on the temperature of layer synthesis in the ZnO–CdO system by the sol-gel method. The dashed lines (*2, 4*) correspond to similar data for ZnO layers

The effect of fractal structure on the surface energy of the layer. The obtained MF data should be used on the fractal parametrization of film surfaces to implement an attempt to thermodynamically describe the energy state of a surface having a fractal relief. In [7], using a formal approach, it was shown that the chemical potential of the surface of the layer is connected with its geometric (fractal) characteristics by the expression:

$$\mu^S = dG_S^{\text{ex}} / dn = (\alpha \cdot M / \rho) B, \qquad (1)$$

where dG_S^{ex} is the variation of Gibbs free excess energy due to the appearance of the interface by the dS area, α is the specific surface energy of the interface; dn – a change on the number of moles of a substance due to a change in its volume dV; ρ, M – density and molecular weight of solid phase; $B = \dfrac{N_S D_{S0}}{N_V D_{V0} l^{(D_{V0} - D_{S0})}}$ – coefficient depending on surface geometry (geometric coefficient); N_S and N_V – coefficients that take into account the dimensions of the corresponding parameters in theoretical dependencies: $S = N_S l^{D_{S0}}$; $V = N_V l^{D_{V0}}$.

The results on the Renyi's numbers for the surface area and volumes of nanoforms allow us to quantitatively analyze the effect of the fractal structure of the surface on the value of its surface energy. Naturally, this analysis will be performed with respect to the geometric coefficient, since it is the parameter that contains data on the fractal characteristics of the surface, and it is its form that should determine the main trends in the thermodynamic behavior of the considered parameter of the system.

Fig. 6 shows the results of calculating the dependence of the coefficient *B* on the characteristic linear size of the fractal structure for various temperatures of the synthesis of the ZnO layer. These data were obtained by direct substitution of the values of Renyi's numbers for the surface area and volumes of nanoforms in the formula (1).

The fundamentally important result on the behavior of the geometric coefficient B should be recognized as follows. Indeed, according to the calculations, the effect of the fractal structure of the surface begins to increase significantly only at very small

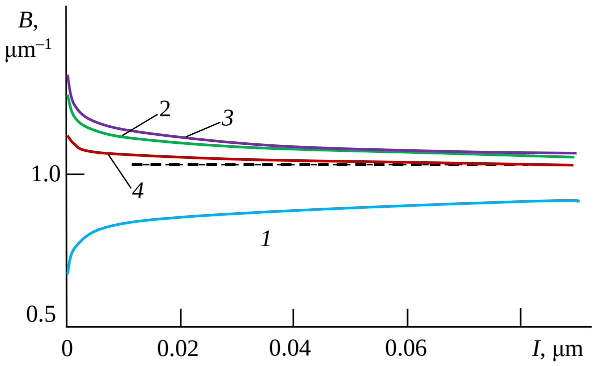

Fig. 6. Dependence of the geometric factor *B* on the characteristic size of the fractal formation *l* on the surface of the ZnO layers obtained by the sol-gel method at various synthesis temperatures: *1* – *t* = 200 °C; *2* – *t* = 300 °C; *3* – *t* = 350 °C; *4* – *t* = 450 °C

values of the characteristic dimensions of the structure. This is a region of linear dimensions less than 0.01 μm. For the same conditions, calculations using an expression $B \approx 1/l$ that takes into account the energy of formation of a spherical interface suggest an extremely sharp increase in the surface energy of the system [6–7]. Such a situation with an extremely sharp increase in the fraction of surface energy in the overall energy balance of the system still seems unlikely.

It is noteworthy that according to the results of calculations with relatively large linear dimensions of the structure (*l* more than 0.02 μm) the coefficient *B* taking into account the fractal structure of the surface practically ceases to depend on the latter. This means that the contribution to the total energy of the solid phase due to the fractal structure with significant linear dimensions of its elements will create only a small additive to the total phase energy.

Attention should be paid to the anomalous behavior of the dependence of the geometric coefficient on the characteristic size of the fractal structure for a temperature of 200 °C (curve *1* in Fig. 6). If, for curves *2*–*4*, the result expected from theoretical positions is observed, according to which, with a decrease in size and, accordingly, curvature of their interfaces, the energy of the system should increase, then this curve assumes the opposite effect. This situation was manifested due to the fact that, according to the estimates obtained, at the lowest synthesis temperature, the Renyi's number for the surface area turned out to be large in terms of the Renyi's number for their volumes. This situation changed the sign of the exponent in the analyzed dependence (1) and led to a decrease in the contribution of fractal geometry to the surface energy of the system. Physically, this ratio between the indicated Renyi's numbers corresponds to the existence of a very curved and pored surface with an increased area, which was formed at a super low temperature of layer synthesis.

Conclusion.

1. The conditions for obtaining high-quality layers of ZnO and ZnO–CdO systems by the sol-gel method at various temperatures of final annealing were found and implemented. The surface of the synthesized layers was studied by the SME method depending on the temperature of their final formation.

2. Multifractal analysis is applied to processing SEM images of the surface of the obtained layers deposited by the sol-gel method. The MF spectra from surface areas and volumes of relief-forming nanoforms formed on their surface were calculated and analyzed. The dependences of the MF spectral parameters on the surface area and on the volumes of nanoforms on the layer surface on the temperature of their final annealing are found.

3. The analysis of the relationships between the Renyi's numbers, the fractal disordering parameter and the synthesis temperature of the layers quantitatively confirms the fact that with an increase in the annealing temperature from 200 to 500 °C a more planar surface is formed with a higher degree of fractal symmetry of the geometric parameters of nanoforms. The latter quantitatively reflects the fact of obtaining layers with increased structural perfection with increasing temperatures of their final annealing in the indicated temperature range.

4. The found MF parameters of the surface relief were used to evaluate the contribution of fractal geometry to the surface energy of the layers. It is shown that taking into account the fractal geometry of the surface of the layers of ZnO and CdO–ZnO systems leads to a relatively weak dependence of the surface energy on the characteristic linear sizes of surface nanoforms.

Authors' contribution

Wojciech Sadowski, statement of a scientific problem, general guidance, discussion of results.
Pavel P. Moskvin, statement of a scientific problem, general guidance on the mathematical support of the problem, discussion of the results.
Vyacheslav B. Kryzhanivskyy, mathematical and software problems.
Galyna V. Skyba, performing experiments on the synthesis of semiconductor nano layers, discussion of the results.
Oleksandr I. Prylypko, software for multifractal analysis of spatial forms.

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