

Article

The Analysis of the ZnO/Por-Si Hierarchical Surface by Studying Fractal Properties with High Accuracy and the Behavior of the EPR Spectra Components in the Ordering of Structure

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Abstract: A hierarchical surface that includes objects with different sizes, as a result of creating local fields, initiates a large number of effects. Micropores in the composition of macropores, as well as nanoclusters of the substance, were detected by scanning electron and atomic force microscopies on the surface of ZnO/Por-Si samples. An identical fractal dimension for all levels of the hierarchy was determined for these structures, which is associated with the same response to external excitation. Photoluminescence studies have shown the presence of localized levels in the band gap, with the probability of capturing both electrons and holes, which ensures charge transitions between energy bands. Decomposition of the electron paramagnetic resonance (EPR) signal into components made it possible to determine the manifestations of various types of interaction between paramagnetic particles, including the hyperfine structure of the spectrum. The ordering of the structure of the substance as a result of sequential annealing in the range from 300 to 500 °C was revealed in the EPR spectrum. This fact, as well as photo- and gas sensitivity for all types of samples studied, confirms the prospects of using these structures as sensors.

Keywords: surface nanostructures; fractal dimension; neural network; localized energy states; components of EPR signal; doublet EPR signal

1. Introduction

Composite materials based on ordered arrays of nanoparticles have many relevant applications. They are used for the creation of fluorescent devices, storage of ultra-high-density information, sensors and others. For this purpose, the method of synthesis based on the direct formation of nanostructures in the volume of the matrix during its chemical modification is suitable. In such cases, the presence of voids (pores) in the matrix structure, which act as solid-phase nanoreactors, is necessary to limit the reaction area.

This approach eliminates the disadvantages of methods for obtaining free nanoparticles in colloidal nanoreactors with subsequent incorporation into an inert matrix [1]. Moreover, it is possible to directly control the size and properties of nanoparticles at the stage of formation.

Hierarchical architecture allows the creation of materials with a wide range of characteristics within a single technological platform, controlling the composition and structure at hierarchical levels. Such materials are organized by incorporating small-scale elements into larger ones. At the same time, various manifestations of effects are possible at different hierarchical levels with many functional purposes.

The main mechanism of formation of hierarchical nanomaterials is self-assembly [2,3]. The essence consists in the synthesis of the initial building blocks with fixed dimensions and shape with their further integration. Hierarchical self-assembly can be multilevel when integrated blocks serve as the initial elements of larger formations. The restructuring of the internal structure, taking into account the processes occurring in porous materials (oxidation, diffusion of components, Frenkel effects, etc.), leads to a unique design on a nanoscale with a given degree of structural perfection, the required profiles of doping materials, etc.

Porous silicon (Por-Si) with several levels of hierarchy is a promising material for sensors [4]. The variety of sizes of structures, including particles with uncompensated charges, determines sensitivity to a wide range of influences. During the synthesis of Por-Si, a multiphase structure of crystalline, amorphous and polycrystalline silicon is formed. Further complication of the structure by depositing thin layers to the developed surface makes it possible to enhance some parameters. For example, graphene-decorated porous silicon demonstrated increased sensitivity to low ppm H_2 at room temperature compared to the initial por-Si [5]. Such a complex structure determines the selectivity and multitasking of the sensor.

The formation of zinc oxide layers on the surface of porous silicon increases the energy stability and intensity of photoluminescence. A wide energy range, high bond energy and mechanical and thermal stability at room temperature make zinc oxide attractive for possible applications in electronics [6]. Based on its pyroelectric and piezoelectric characteristics, ZnO can be used as a sensor and an energy generator [7]. There are many different structures of zinc oxide that determine a variety of properties [8–11]. The deposition of zinc oxide to the surface of porous silicon with several levels of hierarchy leads to an expansion of the variety of structures obtained.

The growth of structures and their roughening is a complex nonlinear process [12]. It is assumed that as a result of the formation of thin films, the morphology of the surface changes in the form of a statistically self-similar structure. The study [13] shows the correlation of the deposition angle and grain size of ZnO thin films obtained by the atomic beam sputtering method with the fractal dimension. In [14], the dependence of the gas sensitivity of SnO_2 films on the fractal dimension of the structures was shown.

The application of neural networks to count the number of research objects in determining fractal parameters can significantly increase the accuracy of the analysis. The ability to learn is one of the main advantages of such systems over traditional algorithms. During the learning process, the neural network is able to identify complex dependencies between input and output data, as well as perform generalization. This means returning the correct result based on data that were missing from the training sample, as well as incomplete or “noisy”, partially distorted data in the case of successful network training. This is important because during nonequilibrium processes of growth of the porous structure, the formation of incomplete pore boundaries is possible. Therefore, it is difficult to count the number of such objects for the subsequent determination of fractal parameters.

The accuracy of determining the level of fractality of the surface depends on the correct identification of the object of study in the microscopic image. Recognition of images is a difficult area of research because most objects contain elements in a wide range of intra-class variability. The study of multiscale organization in the colorimetric structure of images is necessary to determine the level of its complexity [15–18].

A neural network created and trained to classify images identifies the class of the object and returns its name and the probability of this prediction. In addition, it defines the coordinates of the object and its shape on the image. It is also possible to detect

multiple objects on the image and their bounding boxes. Many different neural network architectures have been developed for these purposes. However, the YOLO network uses a single platform to solve all these tasks.

The formation of self-similar structures is associated with a certain mechanism of interaction of particles with uncompensated charge—paramagnetic centers (PMCs). Spatial directions of energy migration through the donor subsystem become prevalent in this process. PMCs and surface nanocrystals are the centers of adsorption, growth of matter and diffusion processes. The balance between the physical and chemical processes occurring on these active particles determines the flow of currents on the sensor material.

The Pb PMC is an important component of the degradation processes of silicon structures. The difficulty of detecting such particles lies in their low concentration and possible diamagnetic environment [19]. It is known that during the formation of porous silicon, the concentration of broken bonds on its surface and, accordingly, the intensity of the EPR signal increase. In this case, PMCs can be formed at the boundaries of pores and their walls, which affects the variety of *g*-factors, constants of fine and hyperfine splitting of EPR lines. During the formation of silicon with several levels of hierarchy and the subsequent deposition of thin layers of metal oxide on it, the diversity is further expanded.

Determining the characteristics of the EPR signal during the formation of a multi-component cluster system in a porous structure is a difficult task. The spin states of a paramagnetic ion can be affected by various nuclear magnetic moments of nearby atoms. An increase in the covalent component of the chemical bond enhances this influence. The interaction can be based on the impact of numerous identical nuclei during the formation of clusters. Since the nuclear and total magnetic moments of the nearest ions are quantized, the unpaired electron of the paramagnetic center will be in several local fields depending on the mutual orientation of the nuclear moment and the external magnetic field. As a result, each line in the EPR spectrum will be split into several. Thus, the super hyperfine structure of the spectrum is manifested.

The nature of sensory properties is particularly related to the trapping of charges on paramagnetic centers. The concentration of such particles increases in hierarchically developed objects. Structures with similar parameters can have the same types of PMCs in their composition, with the identical mechanism for capturing and transferring charges. In this case, the hierarchical surface is comparable to memory elements, consisting of large elements, including smaller ones. The interaction between paramagnetic centers of certain types can be the basis of the process of charge transfer between structures of various hierarchical levels.

New surface magnetic states—nanometric spin switches—can arise in nanoscale systems [20]. The principle of their operation is based on highly localized and controlled magnetization. These devices are used in quantum computing or small magnetic storage devices and sensors. The emergence of controlled surface quantum states is due to a delicate balance between the chemical and physical interactions of nanoparticles, which depends on the mechanisms of their growth and passivation.

The study of surface-active structures and the mechanisms of passage of excitation waves of various nature through them, including the interaction of particles with an uncompensated charge, is a promising area of research. At the same time, the dependence of the sensor response on the level of ordering of the particles of matter is known. If the structure is regular, the exciting signal moves over the surface of the sample along a short path at a given speed [21]. It is interesting to study the characteristics of the sensor material with several levels of hierarchy and various fractal parameters.

1.1. Goal

Investigation of the evolution of paramagnetic particles during the formation of the ZnO/PS surface with several levels of hierarchy and the study of the distribution of structures using fractal analysis with increased accuracy to determine the characteristics of sensory properties.

1.2. The Novelty of the Research

Spectral manifestations of PMCs localized at different levels of the surface hierarchy were studied and separated by the EPR method. Features of the transformation of PMCs as a result of sequential annealing during the formation of energetically stable structures are determined. The transfer of an exciting signal through structures with such properties leads to the lowest energy losses.

The accuracy of fractal analysis was increased using a neural network. This affects the determination of the properties of materials for detecting short-lived exciting signals with low energy, which lose significant energy moving along the surface of the sample. Moreover, the relationship between ZnO/PS structures formed at different levels of the hierarchy was determined by the identity of their fractal properties.

To compare the results of our work with others, the following literature review was conducted.

The aggregation of nanoparticles during the formation of a fractal structure, which significantly affects their electronic properties, was shown in [22]. Therefore, it is interesting to study the changes in the EPR spectra of nanoparticles during their synthesis. The consideration was limited to the dipole–dipole interaction of the electron spins in this work. Probably, the investigation of various types of interaction would determine in more detail the features of the formation of aggregates in the fractal structure.

The difference in the magnetic properties of materials in magnetic separation processes has a wide range of applications. This is of great importance for the metallurgical industry. Study of the motion of particles deposited in a liquid under the action of gravity near a magnetized cylinder of finite length revealed the possibility of using this geometry for spatial separation of diamagnetic particles and analysis of their distribution by magnetic properties [23]. However, the behavior of particles in local electromagnetic fields of surface nanostructures with different sizes is also of interest. Hierarchical samples create interconnected fields formed by multiple objects.

Over the years, the ability of plasma treatment to significantly change the wettability of polymers has been demonstrated [24–31]. The superhydrophobic properties of flexible surfaces with fractal properties under this influence were shown in [25,26,28]. In this regard, it is important to quantify the effective surface area of the material in determining the improvement in the properties of the sample. Incomplete understanding of the formation of nanostructures after plasma treatment limits the possibility of studying the relationship between nanoscale changes and macroscopic properties. In particular, the question of the mechanisms of changing the fractal properties of the surface under the influence of plasma remains open. Probably, an increase in the accuracy of fractal analysis will allow determining in detail the fractal parameters and the effect of plasma treatment on changes in the properties of the substance.

2. Materials and Methods

2.1. Synthesis of Porous Silicon

In order to create the por-Si layers, monocrystalline silicon was electrochemically anodically etched in an electrolyte obtained from an aqueous solution of hydrogen fluoride, supplemented with isopropyl alcohol. The ground side of the silicon wafer was chosen for etching due to the presence of regular formations. These rough structures served as the basis for obtaining a macroporous surface structure. The characteristics of the initial monocrystalline silicon material: mark—KEF-4.5 (n-Si (111)), resistivity 4.5 ohms/cm, doping impurity—P. Before the electrochemical etching procedure, silicon wafers were cleaned by exposure in acetone, isopropyl alcohol and distilled water in an ultrasonic bath (UZ Sapphire). The following reagents were used to synthesize the electrolyte: hydrogen fluoride 45.00%, GOST 10484-78, CAS: 7664-39-3, isopropyl alcohol SSPIRT-9805.F01080, GOST 9805-84, CAS: 67-63-0, distilled water.

The etching direction (111) in the silicon structure was chosen for the following reasons.

The rate of chemical reaction of a liquid etchant and a solid is minimal in the direction (111), since in the plane perpendicular to orientation, (111) is the maximum density of silicon atoms. Therefore, the formation of pores occurs in the direction at an angle to the applied field. In this case, the etching front moves slowly deeper into the substrate. At the same time, a significant part of the energy of the etching process is spent on etching the formed quantum filaments, which leads to their fragmentation and, accordingly, to an increase in the number of smaller clusters. Therefore, the PL intensity of por-Si samples obtained on substrates with orientation (111) increases both with increasing etching time and with enhancing anode current density.

A single-chamber electrochemical cell was used for electrochemical etching of silicon. A glass-carbon crucible, chemically resistant to electrolytes, was used as the cathode electrode. The galvanostatic mode was applied to the etching process. The porous silicon obtained as a result of electrochemical etching was washed in isopropyl alcohol and distilled water. The implementation of these processes on the surface of macroporous silicon led to the formation of a micro-meso porous layer of complex composition. In order to remove this layer, the samples were chemically kept in a 20% aqueous solution of hydrogen fluoride for 1–2 min. Immediately after that, the samples were used for the deposition of ZnO layers on their surface.

The anodizing current density (J_A) is an important technological parameter in the synthesis of porous silicon by electrochemical etching of silicon. To obtain pores with different sizes, J_A decreased from 80 mA/cm² to 40 mA/cm² within 10 min. In this case, the processes of formation of porous channels in the directions of easiest etching and force lines compete. Low anodizing current densities allow the formation of a porous layer with a “tree” type structure, and the direction of the pore channels is determined by the substrate.

2.2. Synthesis and Deposition of a ZnO Coating on a Substrate

2.2.1. Sol-Gel Method

Due to the simplicity and effectiveness of the effect on the growth of structures, the sol-gel method was used to form a film-forming solution. The rationale for using this method is as follows. Dispersed systems are mainly formed from two or more phases with a highly developed interface between them. Obviously, such systems are a group of heterogeneous systems in which one or more phases are in an ultradispersed (or nanodispersed) state. In dispersed systems, one of the phases forms a continuous dispersion medium, in the volume of which the dispersed phase is distributed in the form of small particles (crystals, filaments, films, plates, nanotubes, droplets, pores). Since the dispersed phase can be in three aggregate states, their combination mainly results in 9 different types of dispersed systems. This diversity provides a large number of particles with various properties that are interesting for research.

The sol solution was synthesized by mixing 0.1 M zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) with 9 mL isopropanol ($\text{C}_3\text{H}_7\text{OH}$) as a solvent and 1 mL monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$) as a stabilizing agent. Within an hour after preparing the solutions, ZnO films were deposited on the substrate.

The nucleation conditions of ZnO particles are key parameters in obtaining structures with certain stable properties, especially on a highly developed surface. For this purpose, the spin-coating method was applied when rotating the substrate at a speed of ~3400 rpm for 1 min. Thus, a layer was formed on the surface, which was held by surface tension forces. The remaining particles of the solution were removed by rotating the substrate. Further, the samples were dried at a temperature of 130 °C, and then annealed at a temperature of 450 °C (1 h) to obtain stable ZnO nuclei. This approach of sequential heat treatment led to a homogeneous growth of ZnO on the entire surface of porous silicon.

2.2.2. Deposition of the ZnO Film Layers

Liquid solutions were sprayed on the surface of the heating element using a pneumatic airbrush. The distance between the airbrush nozzle and the substrates ranged between 20

and 30 cm. The flow rate of the sprayed solution was most uniform when the pressure was 1.4 bar. When the substrate temperature varied from 350 to 400 °C, the solvent evaporated before the aerosol droplets deposited on the surface. In this case, zinc oxide films particles with a polycrystalline (spherical and hexagonal cell) structure were formed. As a result of the deposition of layers on a hierarchical porous surface, crystallites with different sizes were formed at the boundaries of various pores. The deposition of 20 and 25 layers of ZnO was due to the assumption of homogeneous formation of ZnO at the boundaries of macropores under these synthesis conditions.

2.3. Characterization Methods

The morphology of the macroporous level of the surface hierarchy was studied using a scanning electron microscope JSM-6490LA (JEOL, Akishima, Japan). The JSM-6490LA has an analytical working distance of 10 mm, take-off angle of 35° and a high resolution of 3.0 nm.

The atomic force microscope was used to study the micro and nanoscale surface morphology (AFM) JSPM-5200 (JEOL, Akishima, Japan). The depth of the vacuum was 10^{-6} mm Hg. AFM AC scanning mode, 13-minute image scanning speed, and NSC35/AIBS probe brands were used.

Optical microscopic studies were carried out on a POLAM R-312 microscope (Lomo, Saint Petersburg, Russia).

The “Gwiddion” program, version 2.64 (Brno, Czech Republic) was used to obtain three-dimensional images of surface structures and to distribute structures by height.

An EPR spectrometer JES-FA200 (JEOL, Akishima, Japan) was used to study the paramagnetic properties. Measurements were made at ~9.4 GHz (X-Band) and ~35 GHz (Q-Band). Microwave frequency stability: $\sim 10^{-6}$. Sensitivity = $7 \times 10^9/10^{-4}$ Tl. The resolution was 2.35 μ T. The output power ranged from 200 mW to 0.1 μ W, with a Q-factor of 18,000.

Identical settings were used to analyze the nature of the EPR signal saturation. At the same time, microwave radiation power was changed from 1 to 12 mW (sample with 20 layers of ZnO ($m = 5.2$ mg), sample with 25 layers of ZnO ($m = 7.4$ mg)).

Photoluminescence studies were carried out using a spectrophotometer Cary Eclipse (Agilent, Santa Clara, CA, USA) in the range from 200 to 800 nm. The PL spectra of the samples were measured at room temperature (the wavelength of the exciting radiation was 320 nm). The spectral width of the slit in this device varied from 0.5 to 2.4 nm. A deuterium lamp was employed as the radiation source for UV measurements, while a tungsten-halogen lamp was used for visible measurements.

The level of fractality of the studied surface was determined in several stages. SEM images with macroporous and microporous areas of surface (two levels of hierarchy) were studied using the YOLOv8 neural network. To do this, the scale of the SEM images was consistently changed during the shooting process. Next, the neural network was trained to count the number of objects (pores) in order to reduce the error. After that, the fractal dimension was determined based on the calculated number of pores using the following formula:

$$N(\delta) \sim \delta^{-D} \quad (1)$$

where N is the number of objects, δ is the scale, and D is the fractal dimension of the image.

The logarithmic transformation of this law allows us to obtain a linear dependence and a graph with a slope of D . Thus, the dimension of fractality can be estimated by the gradient of the graph $\ln N(\delta)$ relative to $\ln \delta$, given by the following expression:

$$D = -\lim_{\delta \rightarrow 0} \frac{\ln N(\delta)}{\ln \delta} \quad (2)$$

The fractal properties of surface areas with nanoclusters located between micropores, due to their complex and irregular shape, were investigated by the “Box-counting” method.

To do this, a square grid was superimposed on the AFM image. Next, the number of cells in which the elements of the object were present was calculated. After that, the cells sizes decreased, and they were counted again. Further, the fractal dimension was calculated by the formula described above.

Electrical resistance measurements were performed on the TRM-0.1/100i device (JSC Telecom—STV, Russia, Zelenograd). A change in resistance was observed under the influence of water vapor (0.5 mL) and ethyl alcohol vapor (0.5 mL) on the surface of the sample. The measurement is based on the determination of magnetic field energy losses due to eddy currents occurring in the material. An alternating magnetic field is created by the inductance coil of the sensor located at the end of the measuring probe. The inductance coil of the sensor and capacitors located on the computing board of the measuring probe form a resonant circuit. When the measured material comes into contact with the magnetic field of the sensor, the Q-factor of this circuit decreases, which causes a decrease in the amplitude of vibrations in the circuit. The amplifier circuit with a tracking bridge, assembled on a computer board, maintains the oscillation amplitude constant, but as a result, the voltage drop on the ballast resistor increases. The change in the value of the voltage on this resistor is proportional to the value of the electrical resistivity at a given point of the plate. Next, this voltage is supplied to the amplifier board. Then, the amplified signal is sent to the control board, where it is converted into a digital code and translated into the value of the electrical resistivity in ohms*sm.

Annealing of the structures was carried out for a sample with 25 layers of ZnO (the largest number of layers), in an air atmosphere, at temperatures of 300 °C, 400 °C, and 500 °C, for 30 min at each temperature. This range is associated with the removal of OH groups from the porous structure at various temperatures above 100 °C. The annealing process took place sequentially in order to study the gradual transformation of the structure of paramagnetic centers, including their surroundings. The choice of an annealing atmosphere is associated with the intensive formation of oxygen vacancies in this environment.

3. Results

3.1. Investigation of Surface Morphology

The surfaces of the samples were studied sequentially from larger to smaller objects. Obtaining SEM images at an angle to the horizontal axis of the samples without zinc oxide (initial sample) determined a macroporous structure with basically the same deepenings (Figure 1a,b). The development of the macropore relief occurred at the grinding sites of silicon wafers (Figure 1a–c). The further etching process with a decrease in the anodizing current density (from 80 mA/cm² to 40 mA/cm²) led to the formation of micropores between and inside the macropores. All these irregularities are points of growth of structures during the deposition of thin layers of zinc oxide.

The identity of the surface structure was also noticeable at different scales of consideration (Figure 1a,b). The following image shows the stepped structure of the walls of the macropores (Figure 2).

A detailed study of the chipping of the por-Si sample showed the formation of more than two layers of different textures (pore diameter, porosity) (Figure 3). The following layers could be distinguished in depth from the surface to the substrate:

- a layer with a high level of porosity, near the surface (d_1),
- next, a layer of lower porosity (d_2)
- a low-porous layer (d_3) located in the depth of the sample near the substrate.

The movement of charges through the jumping conduction mechanism will occur most intensively on the surface due to its highest level of development.

The surface of the sample with 20 layers of ZnO had a morphology similar to that of the initial sample. However, the degree of development of the pore boundaries increased (Figure 4). This indicates the formation of islands of zinc oxide, rather than a continuous layer, as a result of depositing a given number of layers. Figure 4b shows the location of

crystallites of different heights and sizes at the boundaries of macropores for a sample with 20 layers of ZnO.

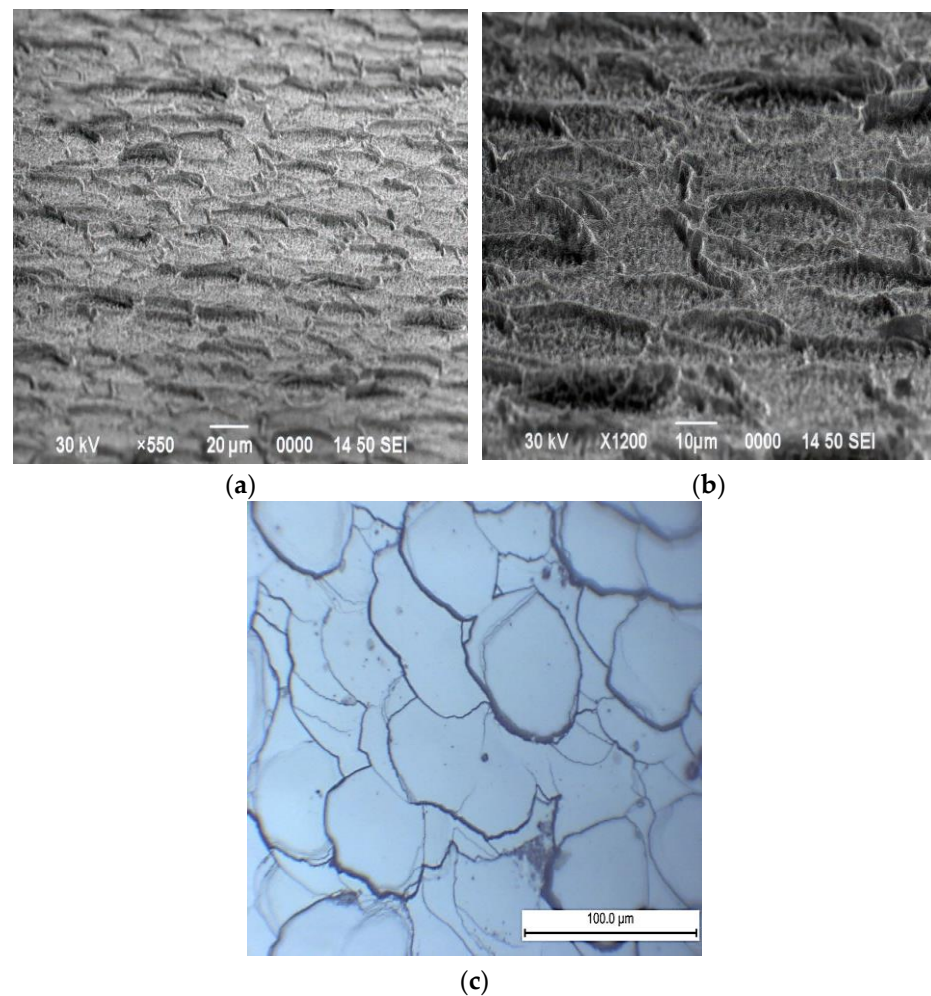


Figure 1. Images of the sample surface without depositing ZnO layers: (a) SEM image taken at an angle of 12° to the horizontal axis, at magnification $\times 550$, (b) SEM image taken at an angle of 12° to the horizontal axis, at magnification $\times 1200$, (c) Optical microscope image of the surface of ground side of a silicon wafer.

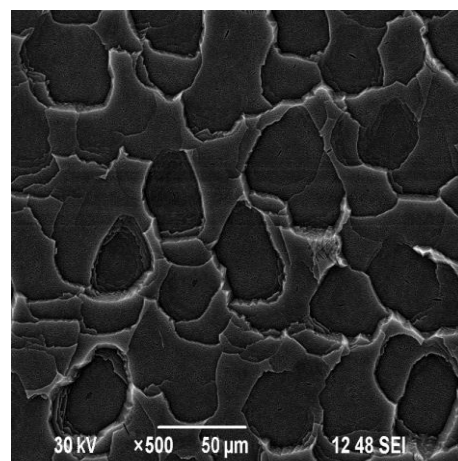


Figure 2. SEM image of a sample without depositing ZnO, taken vertically to the surface.

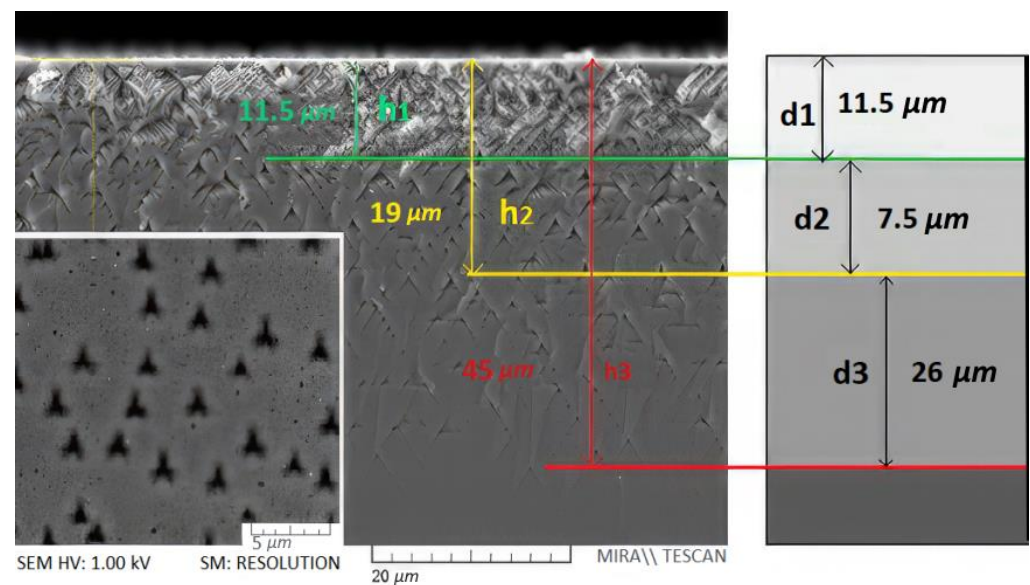


Figure 3. Schematic representation of the structure of the porous layer of the sample without depositing ZnO layers.

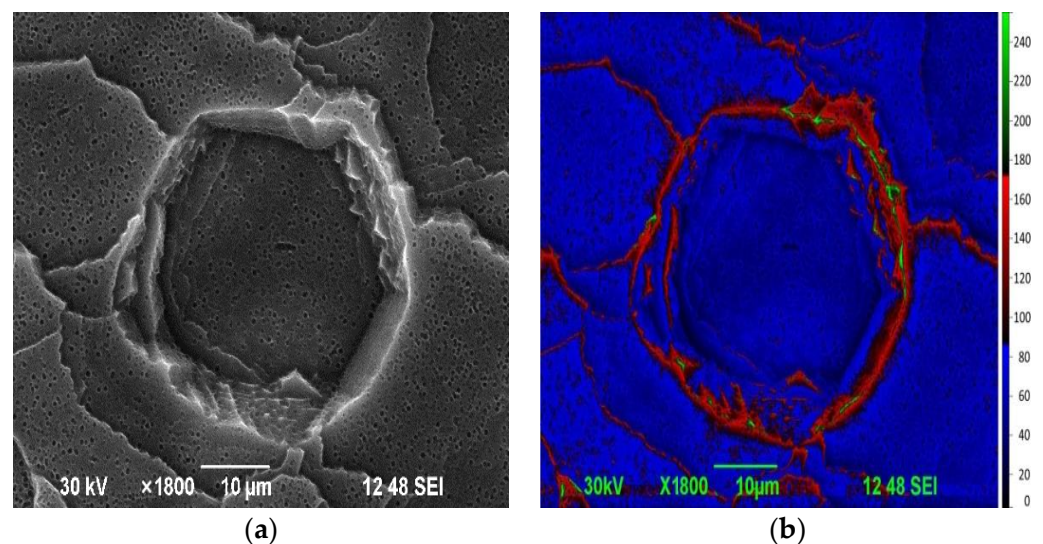


Figure 4. (a) SEM image of a macropore of a sample with 20 layers of ZnO; (b) The height distribution of structures at the boundary of macropores of a sample with 20 layers of ZnO, obtained by the Gwyddion program v2.64.

In contrast, the boundaries of the macropores were more ordered for a sample with 25 ZnO layers (Figure 5). Therefore, such a number of zinc oxide layers is sufficient to obtain a thin layer with a homogeneous structure on a porous surface.

The structure of the sample surface, with 25 layers of zinc oxide, had three hierarchical levels (Figure 6). Figure 6a shows a macroporous relief uniformly distributed over the surface. Micropores are formed inside the macropores (Figure 6b,c), and nanoclusters are synthesized between the micropores (Figure 6d).

The synthesis of nanoclusters between micropores makes it possible to localize charges and efficiently transfer them along levels in the band gap (Figure 7). This reduces the response time of the sensor based on these structures.

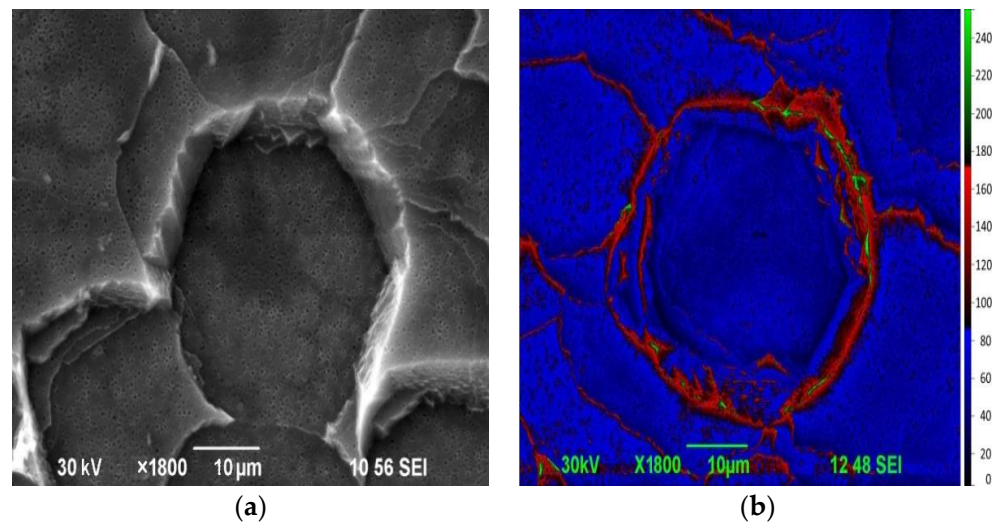


Figure 5. (a) SEM image of a macropore of a sample with 25 layers of ZnO; (b) The height distribution of structures at the boundary of macropores of a sample with 25 layers of ZnO, obtained by the Gwyddion program v2.64.

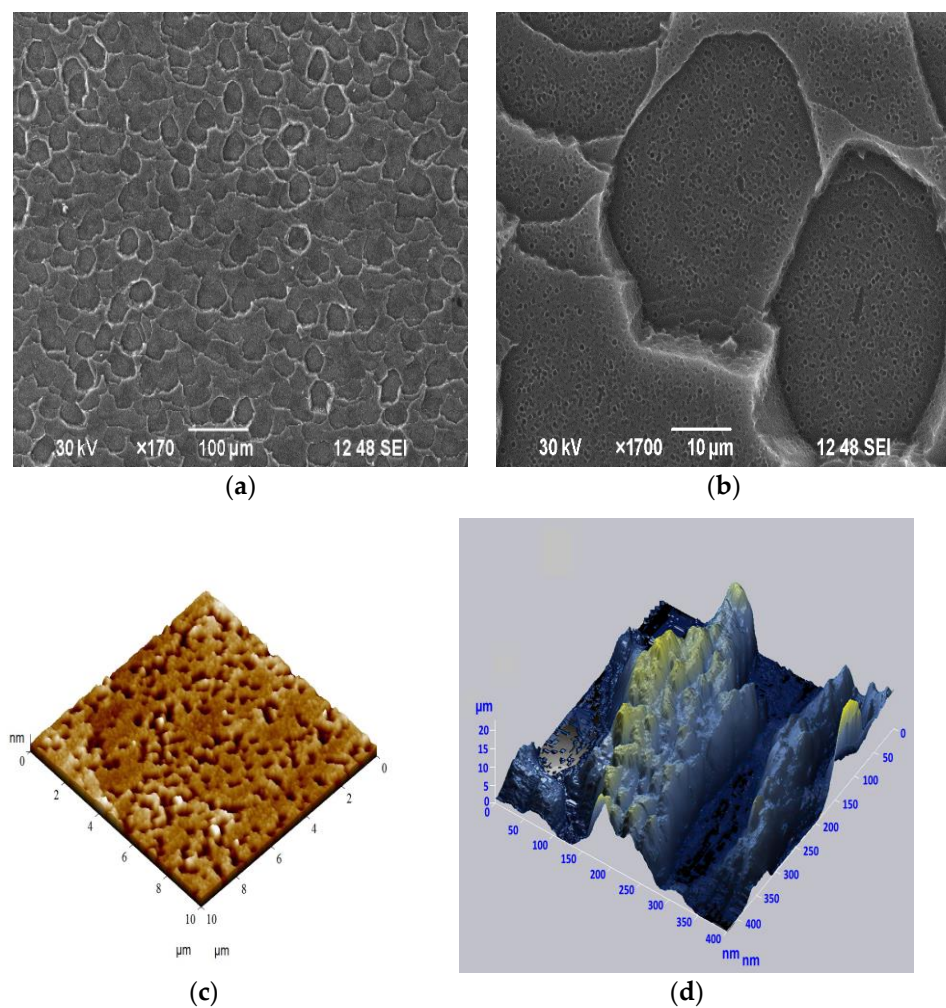


Figure 6. Microscopy images of the sample with 25 ZnO layers: (a) SEM image of the macroporous structure of the sample; (b) SEM image of the surface inside the macro pores; (c) AFM image of the microporous structure of the sample; (d) AFM image of the structure of nanocrystals formed between micropores, transformed in the Gwyddion program v2.64.

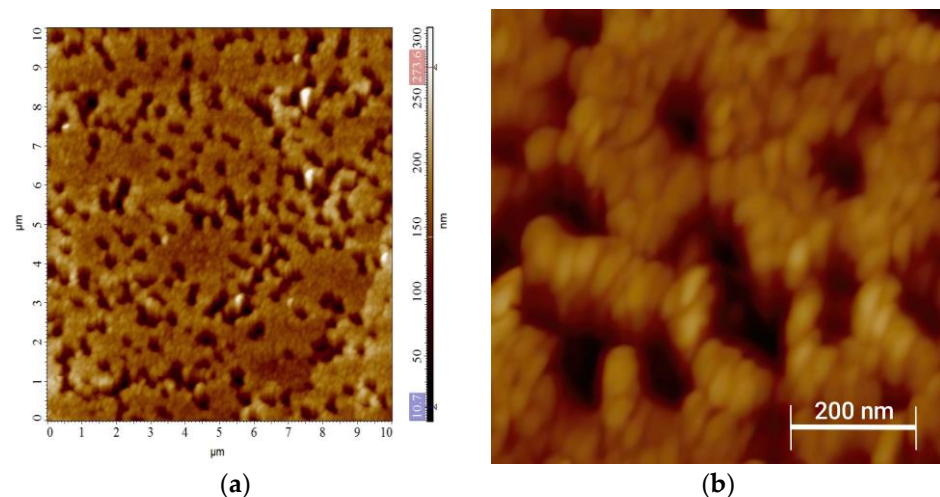


Figure 7. AFM images of the microporous structure of the sample with 25 layers of ZnO: (a) $10 \times 10 \mu\text{m}$, (b) 200 nm resolution.

The effect of polarization in the formation of crystallites is interesting. The induction of opposite charges occurs at the boundaries of closely located nanostructures. As a result, mutual electrostatic attraction arises, affecting the diffusion of processes and the density of the final structure.

The crystallinity of the structures revealed by the X-ray diffraction method was proved in [32]. At the same time, the study of the invariance properties of the formed multistage surface when changing the scale is interesting.

3.2. Study of the Fractal Properties of the Surface

The process of obtaining a hierarchical surface by pore formation of silicon and subsequent deposition of ZnO layers on it is nonequilibrium. The sizes and shapes of the formed objects vary depending on the synthesis conditions. Consideration of such objects when changing the scale determines the properties in their different parts.

Fractal dimension is an important characteristic reflecting the complexity and degree of disorder of the porous structure of the material. In this work, the study of fractal properties is due to the probable invariance of sensor characteristics based on these structures with respect to scale changes.

Application of the “Box-counting” method in our previous research [32] made it possible to clearly determine the presence of fractal properties of the surface of ZnO/Por-Si structures. However, it was not possible to accurately calculate the fractal dimension and any additional data. In common methods for determining the fractality of “Box counting” and “Triangulation”, a grid with a square or triangular cell is superimposed on the image of the object of study [32–37]. During the measurement, the cell sizes change, while the image scale remains constant. In this study, the neural network counted the number of pores on the SEM images, with successive changes in their scale. Taking into account the process of training the neural network and absence of human work, the measurement error is significantly reduced. In this research, neural networks were used for the first time to study the level of fractality of the surface of hierarchical porous objects.

Pores with at least half of the boundaries visible were the objects of the study. This choice was due to the highest concentration of particles with broken bonds and the most intense formation of ZnO at the pore boundaries.

Figure 8a shows the results of a study of the fractal properties of a sample with 25 ZnO layers for the first level of the hierarchy (macropores). The dimension of fractality in this case was $D = 1.95$.

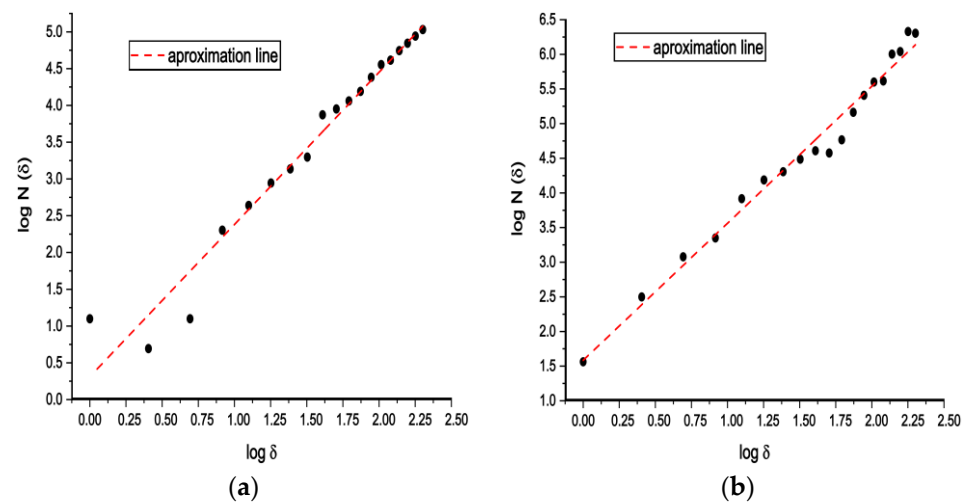


Figure 8. Dependence of the logarithm of the number of pores $N(\delta)$ on the scale δ for (a) macroporous level of surface hierarchy, (b) microporous level of surface hierarchy.

The determination of the level of fractality ($D = 1.96$) for the second level of the surface hierarchy (micropores) is presented in Figure 8b. The relationship between the macro and micro levels of the hierarchy is proved by the presence of the same fractal dimension.

The calculation of the number of pores using YOLOv8 neural network showed an accuracy of 92%, which confirms the high efficiency of this model for automated analysis of porous structure (Figure 9).

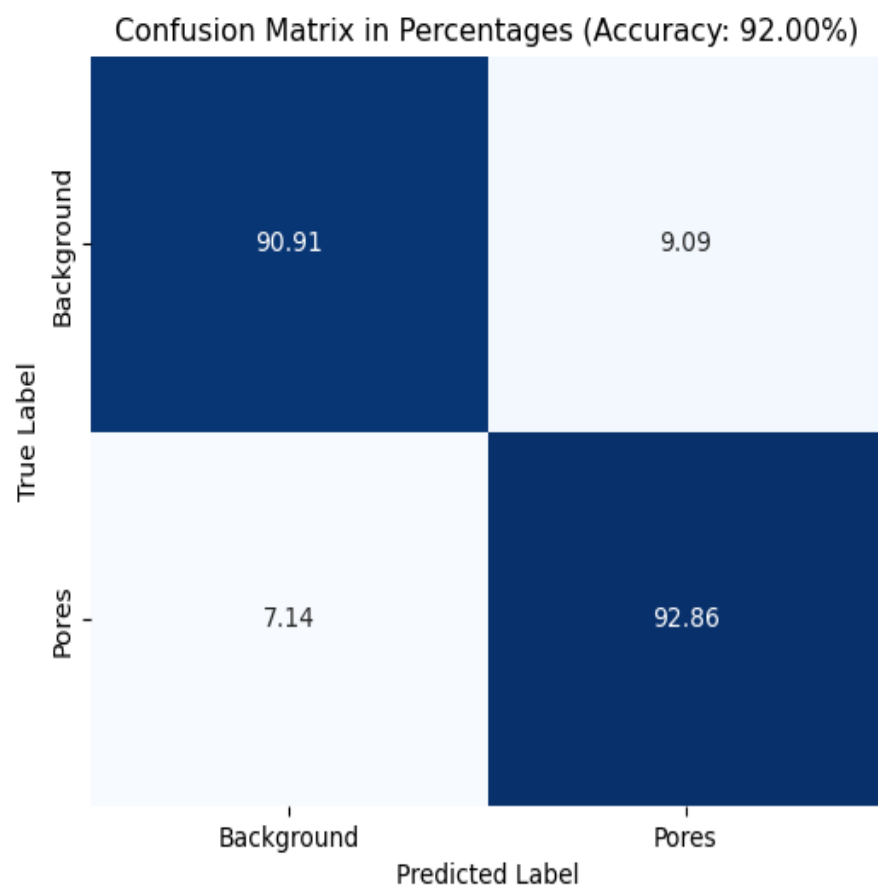


Figure 9. A percentage error matrix for determining the number of pores of porous silicon using YOLOv8 neural network.

The requirements for such accuracy are due to the following reasons. The size and structure of objects in systems with multiple levels of hierarchy may vary when the scale of consideration changes. At the same time, the concentration of particles with broken bonds at the boundaries of structures is different. Consequently, the exciting signal has different energy losses during the transition from one hierarchical level to another. However, for low-energy exciting signals, this difference is significant. Therefore, the precise determination of the invariance of the surface with respect to the change in scale, which in turn determines the invariance of the concentration of particles with broken bonds, plays an important role for short-lived and low-energy exciting signals.

To study the third level of the hierarchy associated with nanoclusters located between micropores, the “Box counting” method was used (Figure 10). The calculation showed a fractal dimension equal to 1.9.

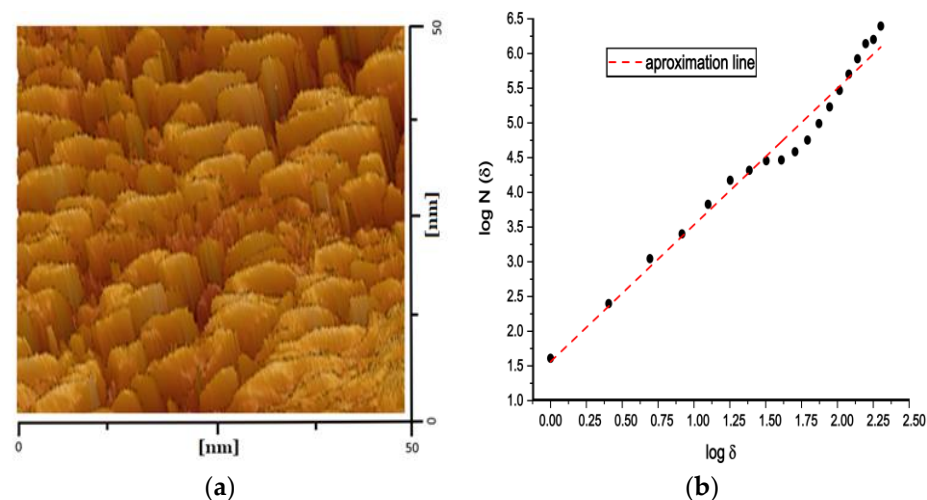


Figure 10. (a) AFM image of nanoclusters located between micropores; (b) Dependence of the logarithm of the number of pores $N(\delta)$ on the scale δ for nanoscale level of surface hierarchy.

Thus, for three levels of the hierarchy of these samples, the surface structure remains invariant with respect to scaling. This leads to the same speed of movement of the exciting signal, which is due to the identity of the structure in different parts of the sample surface. And this, in turn, proves the same distribution of particles with broken bonds, which primarily interact with external excitation. The combination of these factors affects the sensory characteristics of the material.

The presence of voids evenly distributed over the surface of the sample and a decrease in the density of the substance with an increase in the scale of consideration determine the type of mass fractal. At the same time, pores of different sizes are formed in hierarchical material with such fractality. Therefore, after ZnO is deposited on a porous surface, a variety of crystals are synthesized. In this case, photoluminescence (PL) emission occurs at different wavelengths. Thus, the presence of fractality of this type of hierarchical material broadens the spectrum of photosensitivity and photoluminescence. Thus, this analysis supports the high prospect of creating a sensor based on these structures.

The ordering of the structure of matter leads to the formation of energy bands. Photoluminescence studies make it possible to identify interband transitions.

3.3. Photoluminescence Studies

The features of radiation recombination in structures are important for the study of light-emitting particles. In this case, it is possible to determine their energy levels in the band gap, which significantly affects the understanding of charge and energy transfer mechanisms.

The complex structure of the PL spectrum is noticeable for a sample of porous silicon without ZnO (Figure 11). This is due to the heterogeneity of the material composition as a result of silicon etching.

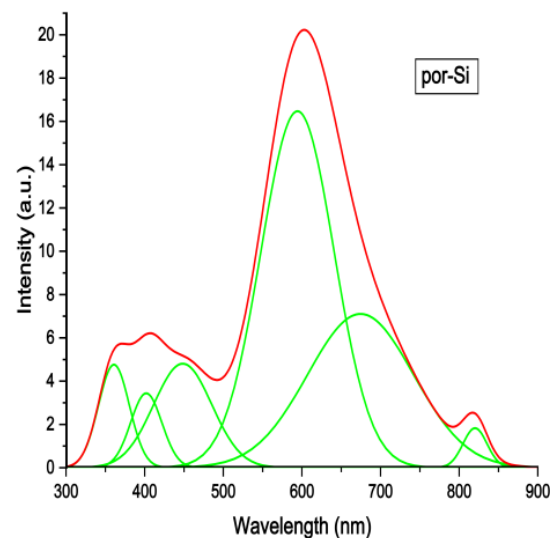


Figure 11. The photoluminescence spectrum, decomposed by Gaussian for a sample of porous silicon without ZnO.

Two PL emission bands are mainly detected in various forms of zinc oxide: a short-wavelength band near the absorption edge of the crystal, and a broad long-wavelength band, the maximum of which is in the green part of the spectrum. The nature of the second band is associated with the radiative recombination of charges on various types of nanostructures: films with different grain sizes, nanocrystals, nanorods, nanoneedles, polycrystals, etc. An important type of defect in this case are particles based on charges trapped on oxygen or zinc vacancies [38–40]. A change in their structure leads to a variation in the position of the energy level in the band gap [41–43].

The following are the types of particles based on oxygen vacancies depending on the charge 0, +1 and +2, which correspond to V_0^0 , V_0^+ and V_0^{2+} particles. Neutral (V_0^0) and dual-charge (V_0^{2+}) are stable to thermal effects. On the contrary, the V_0^+ centers are unstable to this influence. As a result of this influence, they are transformed into V_0^0 centers by capturing electrons from the conduction band [44].

At the same time, different types of particles can be in the structure of various nanoobjects. V_0^{2+} is mainly located at the grain boundaries of nanostructures, and V_0^0 is in volume of the material. According to [45], the V_0^0 vacancy level is located 0.86 eV below the bottom of the conduction band, and the V_0^{2+} vacancy level is 1.16 eV above the top of the valence band.

The spectrum comparing the PL intensities of samples of the initial porous silicon and with the deposition of 20 and 25 layers of ZnO is presented in [32].

The decomposition of the spectrum into components in the green part for samples with zinc oxide reveals signals with maxima at about 514 nm and 568–588 nm (Figure 12). Parameters of the photoluminescence signal decomposed into components for a sample with ZnO layers are shown in Tables 1 and 2. Their nature is related to the presence of ZnO nanocrystals [44]: hole recombination at V_0^+ centers in the volume of the material is responsible for the peak at 514 nm, and electronic transitions to V_0^{2+} centers in the depleted region of the material are responsible for the peak at 568 nm. The shift of these peaks to the long-wavelength region of the spectrum for a sample with 25 ZnO layers occurs due to a higher ordering of the structure.

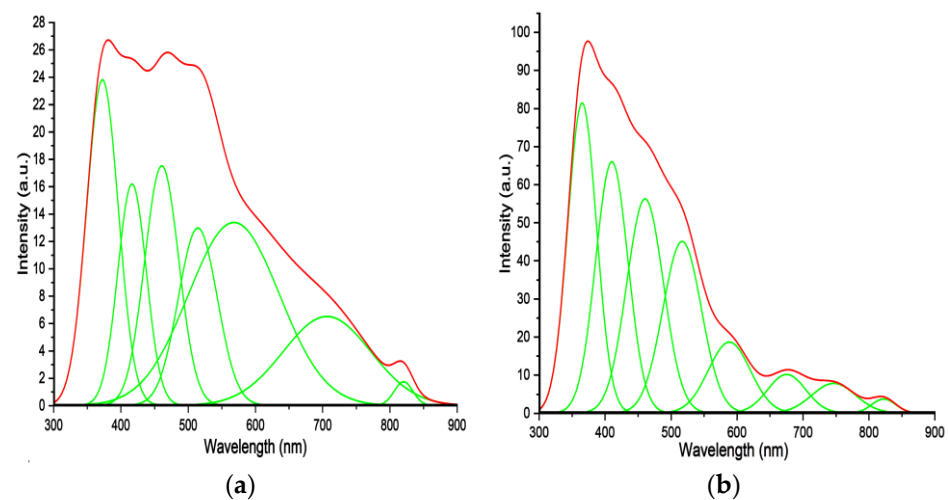


Figure 12. Photoluminescence spectrum decomposed into Gaussians for a sample: (a) with 20 layers of ZnO, (b) with 25 layers of ZnO.

Table 1. Parameters of the photoluminescence signal decomposed into components for a sample with 20 layers of ZnO.

Peak Index	Peak Type	Peak Area by Integrating Data	FWHM	Max Height	Peak Gravity Center (nm)	Peak Area by Integrating Data (%)
1	Gaussian	1404.63429	55.45643	23.81948	372.52117	18.18912
2	Gaussian	861.00573	49.94219	16.19594	416.54235	11.14947
3	Gaussian	1115.64625	59.819	17.52085	460.72678	14.44691
4	Gaussian	943.80171	68.31489	12.97876	514.36612	12.22163
5	Gaussian	2274.32267	159.61148	13.38667	568.06421	29.45103
6	Gaussian	1062.00582	153.31764	6.51692	706.38661	13.7523
7	Gaussian	60.97181	32.89116	1.74148	820.30619	0.78955

Table 2. Parameters of the photoluminescence signal decomposed into components for a sample with 25 layers of ZnO.

Peak Index	Peak Type	Peak Area by Integrating Data	FWHM	Max Height	Peak Gravity Center (nm)	Peak Area by Integrating Data (%)
1	Gaussian	4443.54601	51.3345	81.43342	365.12158	23.63743
2	Gaussian	4065.32884	57.84383	66.02494	410.1776	21.62551
3	Gaussian	3927.57602	65.56325	56.27712	460.60109	20.89273
4	Gaussian	3308.54433	68.89699	45.11329	516.80328	17.59979
5	Gaussian	1489.78852	74.92078	18.68057	588.37295	7.92493
6	Gaussian	740.36261	68.237	10.19277	675.30738	3.93836
7	Gaussian	652.47072	78.11686	7.84666	746.67008	3.47082

At the same time, the presence and growth of several peaks in the spectrum with an increase in the number of ZnO layers determines various mechanisms of photosensitivity (Figure 13). This expands the application areas of sensors based on these structures.

Peaks in the long-wavelength region of the spectrum (from 600 nm) have low intensity and are associated with radiative recombination in porous silicon structures [46–48] (Figure 12).

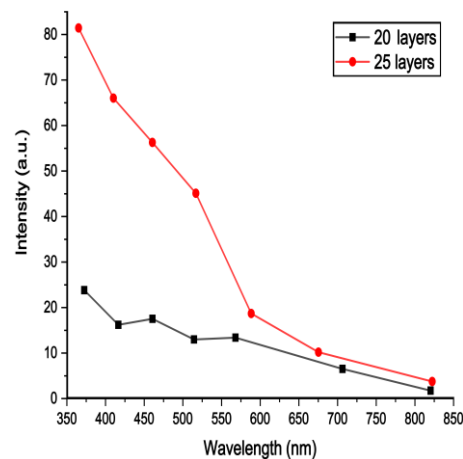


Figure 13. The comparison of photoluminescence peak intensities for samples with 20 and 25 ZnO layers.

Thus, localized energy levels were formed in the band gap as a result of sample synthesis. In this case, it is possible to capture both electrons and holes, which ensures a gradual transfer of charges between energy bands.

The main defects in these studies are vacancies, the concentration of which is highest on the surface of the sample. Therefore, the most intense charge transfer occurs along the energy levels of surface structures.

3.4. Mechanisms of Formation of Energy Levels in the Band Gap

Despite a certain number of particles involved in the processes of radiation recombination, there are many mechanisms of their formation.

In the case of a defect with a positive charge relative to the crystal lattice (for example, an anionic vacancy), the electron energy on the particles adjacent to the anionic vacancy will be reduced. This can lead to the creation of a local level at a certain depth below the conduction band. The transition of an electron from the conduction band to such a level leads to a decrease in their energy (the energy difference is transferred to the lattice and converted into heat). The reverse transition to the conduction band is possible by transferring the lost energy to the electron (due to thermal fluctuations or photon absorption).

In the presence of a negative charge of the defect relative to the lattice, a local level is formed above the top of the valence band (trap for holes).

The formation of energy levels in the band gap significantly affects the resistance of structures. A description of these studies is provided in the next section.

3.5. Investigation of the Dependence of Electrical Resistance of Samples on the Effects of the Vapors of Water and Alcohol

The influence of various exciting factors on a substance changes its electrophysical characteristics. At the same time, the effects appearing at the nanoscale of the surface structure are particularly interesting.

Based on the chosen manufacturing method, the composition of the electrolyte, and the characteristics of the silicon substrate, the porosity of the silicon layers may vary significantly. The porosity level affects various characteristics of the substance.

In the vicinity of the pores, areas depleted of charge carriers are formed. The electrophysical properties vary depending on the distribution of these areas. A material with a high level of porosity is a surface consisting of silicon nanocrystals of different sizes, in a matrix of complex composition. Their presence determines the occurrence of quantum-confinement effects. Localization of charges in nanocrystals leads to a significant increase in resistivity.

There is a noticeable increase in resistance after gas injection for all types of samples. This change is especially noticeable for uncoated samples compared to samples with zinc

oxide synthesis. This is due to passivation of the porous silicon surface as a result of deposition of ZnO layers.

A significant increase in resistance under the influence of water vapor may be due to the characteristics of the particles (Figure 14). The size of water molecules is smaller in comparison with alcohol molecules. Therefore, the level of penetration of water particles into the channels between the nanostructures and passivation of the porous surface is high.

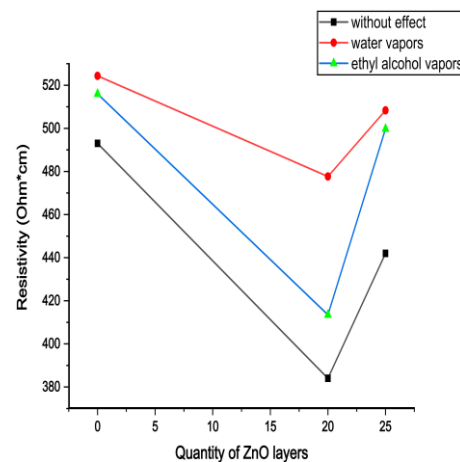


Figure 14. The dependence of the resistance of the samples on the number of deposited layers of ZnO.

The resistance of the initial monocrystalline silicon plate KEF-4.5 (n-Si (111)) was $4.5 \text{ ohms} \times \text{cm}$. As a result of pore formation, the resistance increased and amounted to $493 \text{ ohms} \times \text{cm}$. After the water vapor was injected, the value of resistance increased to $524.3 \text{ ohms} \times \text{cm}$, and after the alcohol vapor was injected, it reached $516 \text{ ohms} \times \text{cm}$.

The resistance of the initial monocrystalline silicon plate changed to $384 \text{ ohms} \times \text{cm}$ after deposition of 20 layers of ZnO. Under the influence of water vapor, the resistance value increased to $477.6667 \text{ ohms} \times \text{cm}$, and under the influence of alcohol vapor, it reached $413.5 \text{ ohms} \times \text{cm}$.

The formation of 25 ZnO layers led to an increase in resistance, to $442 \text{ ohms} \times \text{cm}$. After the water vapor was injected, the resistance value increased to $508.333 \text{ ohms} \times \text{cm}$, and after the alcohol vapor was injected, it reached $499.75 \text{ ohms} \times \text{cm}$.

The electrical characteristics of sensor materials are usually described using the following paradigm. The subsurface region is formed by a charge-depleted layer with a thickness equal to the Debye length. The formation of a surface gas-sensitive layer of the grains, the size of which is less than the Debye length, leads to a high sensitivity of the structures. This is due to the propagation of electric fields through the surface layer deep into the structure of the sample. Based on the presence of regularly distributed nanocrystals over the studied surface, the sensitivity of this material is high.

As mentioned above, one basis for changing the resistance of structures is the capture of charges on paramagnetic centers. At the same time, various types of interaction are possible. The following is a section describing research in this area.

3.6. EPR Spectroscopy Studies

The gradual synthesis of individual crystallites, clusters and multilevel nanostructures occurs during the creation of complex hierarchical systems. This requires energy consumption and certain conditions for the ordering of particles [6].

The transformation of the EPR spectra of a porous silicon (n-type) sample with 25 homogeneously formed layers of zinc oxide under various conditions of thermal annealing and signal registration has been studied.

EPR spectra were recorded in the range of the magnetic field, where spectral manifestations were given by paramagnetic centers of an electronic nature (in the range between the 3rd and 4th lines of the Mn(2+) standard).

Two groups of lines were found in the left and right parts of the spectrum—two quasi-symmetric doublets (Figure 15). In the center of the spectrum, under certain registration conditions, a signal appeared, the parameters of which changed with a sequential increase in microwave power. The spectrum was decomposed into components for a detailed study of their behavior and belonging to individual signals.

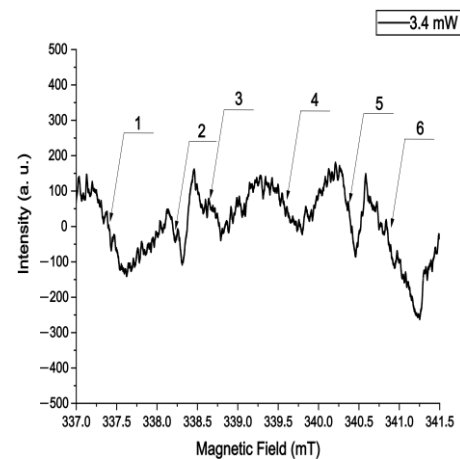


Figure 15. EPR spectrum of the sample with 25 ZnO layers before annealing.

The parameters of the components were selected in the process of repeatedly comparing the spectra when changing various recording conditions (Table 3).

Table 3. Parameters of the doublet signal components at microwave powers of 2.2 mW and 3.4 mW.

The Power of the Microwave Radiation, mW	Part of Spectrum	Nº of Component	Magnetic Field, mT	g-Factor	Width of Line, mT	Signal Amplitude, A, a.u.
2.2	Left doublet	1	337.248	2.00093	0.52	915
		2	338.253	1.99499	0.16	660
	Middle	3	338.474	1.99368	0.43	655
		4	339.585	1.98759	0.25	525
	Right doublet	5	340.350	1.98264	0.18	1090
		6	340.830	1.97985	0.60	1310
3.4	Left doublet	1	337.399	2.00005	0.43	1090
		2	338.250	1.99501	0.16	715
	Middle	3	338.490	1.99267	0.38	780
		4	339.610	1.98706	0.44	700
	Right doublet	5	340.369	1.98270	0.20	1085
		6	340.745	1.97985	0.66	1944

During the preliminary study of the EPR spectra obtained under various signal recording conditions, the following main conclusions were drawn:

- The positions of the doublet lines of the EPR spectrum are symmetrical relative to the center of the spectral scan.

- The symmetry of the spectrum, expressed in the difference in width and amplitude of its components, can be caused for the following reasons. Firstly, it is possible to overlap more than two signals with different parameters. Secondly, this may be due to structural features, local coordination of paramagnetic particles and other properties of PMCs.

The purpose of this analysis is to study the characteristics of the relationship between the fluctuations of the distinguished spectral manifestations and the nature of paramagnetic centers.

The doublet on the right side of the spectrum, in comparison with the left, was characterized by a higher signal amplitude (Figure 16). The components of this doublet were signals with axial symmetry and g-factor anisotropy. A significant increase in signal intensity was noticeable as a result of a change in microwave power from 1 to 7.4 mW (Table 4). At the same time, the left doublet included a component that behaved individually.

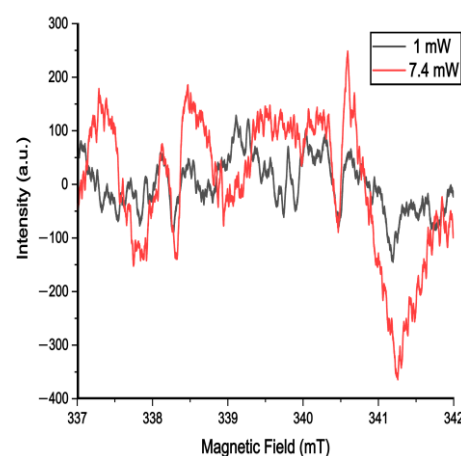


Figure 16. Comparison of EPR spectra for extreme points at signal saturation ($P_1 = 1$ mW, $P_2 = 7.4$ mW).

Table 4. Parameters of the sixth component of the doublet signal at microwave capacities of 1 mW and 7.4 mW.

Microwave Power, mW	Magnetic Field, mT	g-Factor	Width of Line, ΔH mT	Intensity of Signal (a.u.)
7.4	340.54	1.97959	0.67	458
1.0	340.59	1.97951	0.57	150

Figure 17 shows changes in the parameters of the components of the right doublet, which vary depending on the change in the power of microwave radiation. There is a noticeable difference in the rate of change in the amplitudes and widths of the components of this signal.

The presence of obvious kinks in the spectrum can be explained by the influence of another PMC with different relaxation parameters in the microwave saturation process. For some mechanisms, such a relationship is based on the exchange of charges. Under the influence of the excitation of an external field, energy is transferred through these interconnections, which affect sensory characteristics.

The fourth component, in the center of the scan, has the lowest intensity and complex structure (Figure 18). These signals, with g-factors of 1.98951 and 1.98687, obtained by subtracting the spectra of the uncoated sample (5.8 mW–5.4 mW), can be referred to broken Si-O-O bonds in silicon oxide.

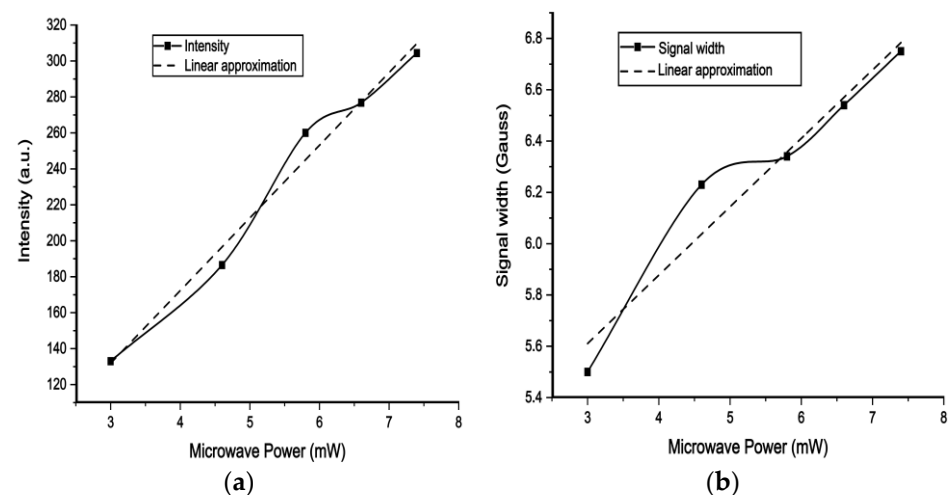


Figure 17. Changing the signal parameters for the components of the right doublet at microwave powers from 3.4 to 6.6 mW: (a) changing the signal intensity from microwave power; (b) changing the signal width from microwave power.

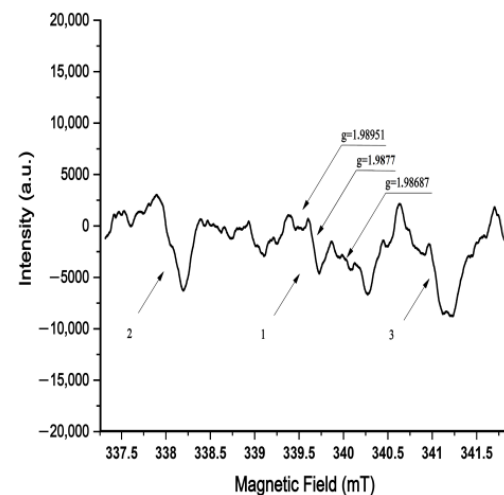


Figure 18. The EPR spectrum for the sample without ZnO deposition, obtained by subtracting the spectra at 5.8 mW and 5.4 mW: 1—signal in the middle of the magnetic field sweep, 2—left doublet signal, 3—right doublet signal.

The value of the g -factor of the electronic center signal is shifted from $g = 2$ in accordance with the symmetry and intensity of the local fields. This is due to the following process of the influence of the zinc particle field on the energy level of Si-O-O bonds. When an electron-hole pair and an electron interact, taking into account the difference in the energy levels of the particle, the g -factor of the electron decreases from 2.

The fourth component has an uneven saturation character with a sequential increase in microwave power (Figure 19). This is due to the overlap of signals from the PM centers, which belong to different levels of the hierarchical structure.

The saturation of the fourth component for a sample with 25 ZnO layers differs from the uncoated sample and reflects differences in charge relaxation time (Figure 20).

The homogeneous saturation for a sample without deposition of ZnO (curve 2) is manifested due to the dipole-dipole interaction inside clusters on a silicon substrate.

It is interesting to consider the structure of the PMCs and the behavior of spectral components under various thermal influences, which differ from the conditions of sample synthesis.

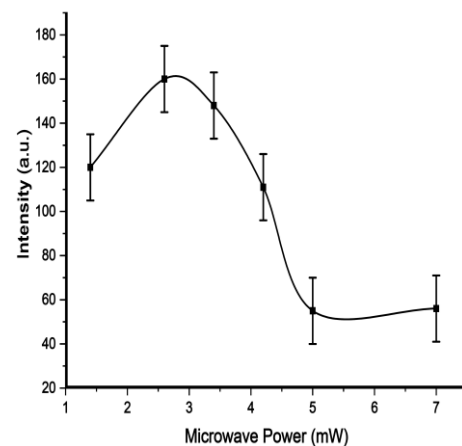


Figure 19. The dependence of the intensity of the fourth component of the spectrum on the sequential increase in microwave power for a sample with 25 ZnO layers.

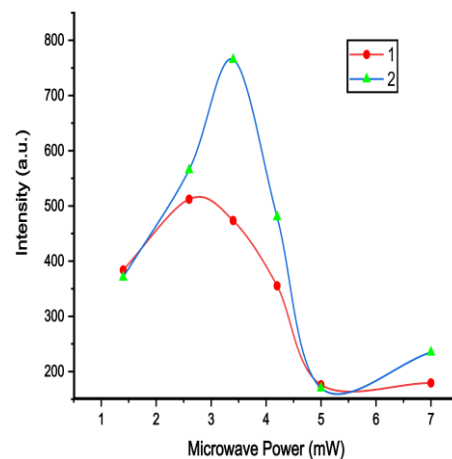


Figure 20. Comparison of the dependences of the intensity of the fourth component of the spectrum on the sequential increase in microwave power for samples: 1—25 layers of ZnO, 2—without deposition ZnO.

3.7. EPR Studies After Annealing of Structures

A change in the environment of the paramagnetic center and its energy stability occurs during the heat treatment of the substance. The kinetics of the PMC transformation are determined by sequential annealing at increasing temperatures. The effect of thermal annealing on the change in the components of the EPR signals in the temperature range (300–500 °C) has been studied.

The 2nd and 3rd components of the signal were considered as a single signal in these studies, based on the proximity of their values (Table 3). At the same time, the 4th component before annealing became 3rd, the 5th component became 4th, and the 6th component became 5th.

Paramagnetic centers influencing each other, probably through hyperfine interactions, are responsible for the components of the right doublet after annealing at 300 °C and 400 °C (Figure 21a,b). In this case, the manifestation of super hyperfine interactions is possible. This is expressed in the broadening of the fifth component and an increase in its intensity. The amplitude-opposite changes of the 4th and 5th components in this annealing mode are of particular interest.

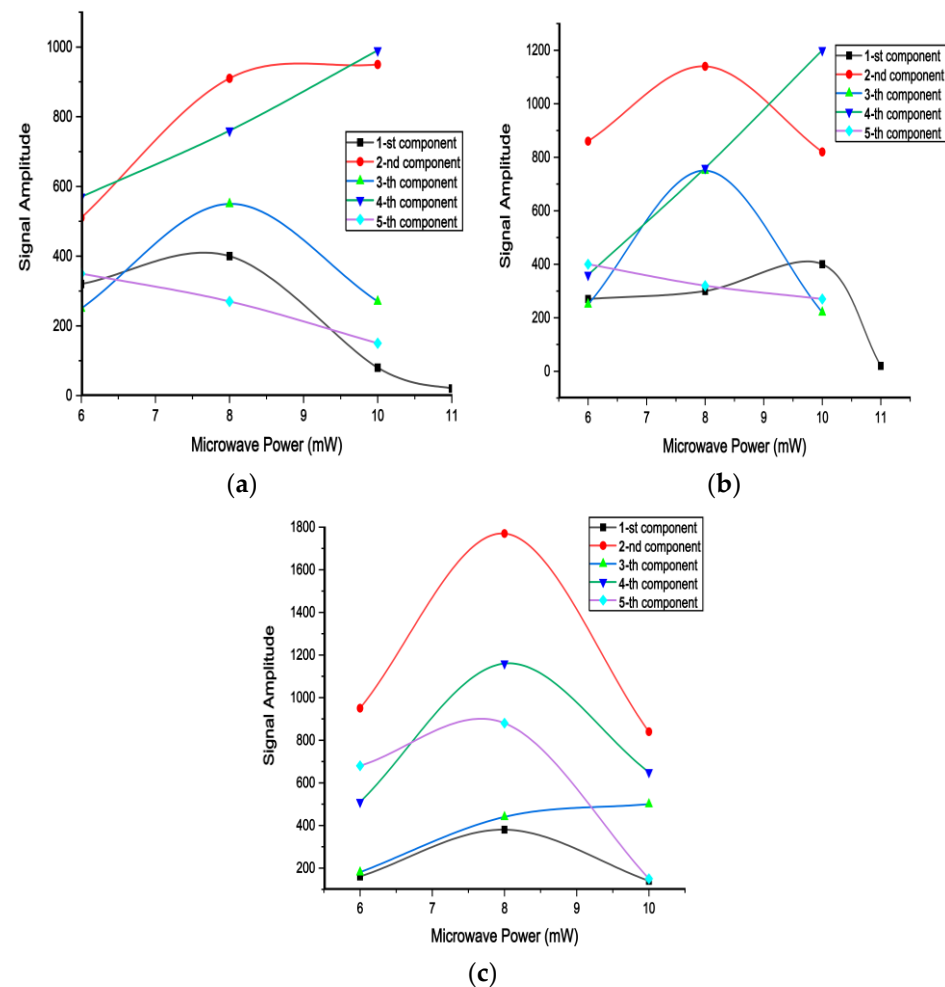


Figure 21. EPR spectrum decomposed into components for a sample with 25 ZnO layers: (a) after annealing at 300 °C, (b) after annealing at 400 °C, (c) after annealing at 500 °C.

An increase in the intensities of the 3rd and 4th components in the range up to 8 mW, after heating at 300 °C, is probably due to the process of changing the local environment of the PMC. Energy transfer through phonons (stress relief) was stimulated by heating in the range of 200–300 °C. In this case, the local symmetry is restored, and then the structure is stabilized during subsequent cooling. At the same time, it is possible to preserve the broken bonds as the Pb paramagnetic center of Si-SiO₂ bonds.

The behavior of the components, after annealing at 500 °C, under the influence of gradually increasing microwave radiation power (6–11 mW) is similar (Figure 21c). This indicates that an energetically stable state has been achieved, and transitions between magnetic sublevels occur uniformly.

The results of the analysis of the effect of heat treatment during the transformation of the EPR spectra of ZnO/Por-Si structures made it possible to determine the dependencies important for the development of mechanisms for the formation of material properties in future studies.

4. Conclusions

The developed morphology of the surface of the synthesized ZnO/Por-Si structures, including three levels of hierarchy, was revealed. The pore walls play a key role in the formation of ZnO, based on the high concentration of particles with broken bonds on them. The presence of nanoclusters of the substance allows the possibility of charge transfer on localized states between energy bands. Increasing the accuracy of counting the number of pores using a neural network made it possible to determine the identity of the

fractal dimension for all levels of the surface hierarchy. The probability of radiative charge transitions from the valence and conduction band levels to localized levels in the band gap has been determined by photoluminescence. A gradual increase in the microwave power (from 1 mW to 10 mW) and the decomposition of the EPR signal into components led to the effective determination of the difference in parameters between the doublet signals. Annealing at 300 °C and 400 °C led to the manifestation of a hyperfine interaction between paramagnetic centers associated with the components of the right doublet. Sequential annealing at 300 °C, 400 °C and 500 °C led to an ordered structure of the PMCs, manifested in a similar increase in the components of the EPR spectrum. Studies of photoluminescence, as well as the sensitivity of samples to water and alcohol vapors, have shown a significant reaction to changes in resistance. Thus, the formation of three levels of the surface hierarchy with the same fractal dimension, energy levels in the band gap for the charge transition and the ordered structure of the PMCs allows the use of ZnO/Por-Si structures as an effective sensory material.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

List of Abbreviations

ZnO	zinc oxide
SnO ₂	tin oxide
PMCs	paramagnetic centers
EPR	Electron paramagnetic resonance
por-Si	porous silicon
SEM	scanning electron microscope
PL	photoluminescence
Mn	manganese
Si	silicon
SiO ₂	silicon oxide

List of Symbols (Nomenclature)

kV	kilovolt
μm	micrometer
°C	degree Celsius
mA/cm ²	milliampere per square centimeter
eV	electron volt
nm	nanometer
mW	milliwatt
mT	milliTesla
a.u.	arbitrary unit

References

1. Bagraev, N.T.; Bouravleuv, A.D.; Klyachkin, L.E.; Malyarenko, A.M.; Gehlhoff, W.; Romanov, Y.I.; Rykov, S.A. Local tunnelling spectroscopy of silicon nanostructures. *Semiconductors* **2005**, *39*, 716–728. [[CrossRef](#)]
2. Gong, C.; Sun, S.; Zhang, Y.; Sun, L.; Su, Z.; Wu, A.; Wei, G. Hierarchical nanomaterials via biomolecular self-assembly and bioinspiration for energy and environmental applications. *Nanoscale* **2019**, *11*, 4147–4182. [[CrossRef](#)] [[PubMed](#)]

3. Zhu, Y.; Inada, H.; Hartschuh, A.; Shi, L.; Della Pia, A.; Costantini, G.; Mocuta, C. Self-assembly of Nanostructures. *Encycl. Nanotechnol.* **2012**, 2371–2382. [[CrossRef](#)]
4. Baran, N.; Gebavi, H.; Mikac, L.; Ristić, D.; Gotić, M.; Ali Syed, K.; Ivanda, M. Sensing Properties of Oxidized Nanostructured Silicon Surface on Vaporized Molecules. *Sensors* **2019**, *19*, 119. [[CrossRef](#)]
5. Eom, N.S.A.; Cho, H.-B.; Song, Y.; Lee, W.; Sekino, T.; Cho, Y.-H. Room-Temperature H₂ Gas Sensing Characterization of Graphene-Doped Porous Silicon via a Facile Solution Dropping Method. *Sensors* **2017**, *17*, 2750. [[CrossRef](#)]
6. Kołodziejczak-Radzimska, A.; Jesionowski, T. Zinc Oxide—From Synthesis to Application: A Review. *Materials* **2014**, *7*, 2833–2881. [[CrossRef](#)]
7. Chaari, M.; Matoussi, A. Electrical conduction and dielectric studies of ZnO pellets. *Phys. B Condens. Matter* **2012**, *407*, 3441–3447. [[CrossRef](#)]
8. Frade, T.; Jorge, M.E.M.; Gomes, A. One-dimensional ZnO nanostructured films: Effect of oxide nanoparticles. *Mater. Lett.* **2012**, *82*, 13–15. [[CrossRef](#)]
9. Nikoobakht, B.; Wang, X.; Herzing, A.; Shi, J. Scalable synthesis and device integration of self-registered one-dimensional zinc oxide nanostructures and related materials. *Chem. Soc. Rev.* **2013**, *42*, 342–365. [[CrossRef](#)]
10. Cui, J. Zinc oxide nanowires. *Mater. Charact.* **2012**, *64*, 43–52. [[CrossRef](#)]
11. Xu, T.; Ji, P.; He, M.; Li, J. Growth and structure of pure ZnO micro/nanocombs. *J. Nanomater.* **2012**, *2012*, 797935. [[CrossRef](#)]
12. Ghosh, K.; Pandey, R.K. Assessment of fractal and multifractal features of sol-gel spin coated ZnO thin film surface. *Mater. Res. Express* **2019**, *6*, 086454. [[CrossRef](#)]
13. Yadav, R.P.; Agarwal, D.C.; Kumar, M.; Rajput, P.; Tomar, D.S.; Pandey, S.N.; Priya, P.K.; Mittal, A.K. Effect of angle of deposition on the Fractal properties of ZnO thin film surface. *Appl. Surf. Sci.* **2017**, *416*, 51–58. [[CrossRef](#)]
14. Chen, Z.; Pan, D.; Zhao, B.; Ding, G.; Jiao, Z.; Wu, M.; Shek, C.-H.; Wu, L.C.M.; Lai, J.K.L. Insight on Fractal Assessment Strategies for Tin Dioxide Thin Films. *ACS Nano* **2010**, *4*, 1202–1208. [[CrossRef](#)]
15. Nandhini, S.; Easwaramoorthy, D.; Abinands, R. An extensive review on recent evolutions in object detection algorithms. *Int. J. Emerg. Trends Eng. Res.* **2020**, *8*, 3766–3776. [[CrossRef](#)]
16. Uthayakumar, R.; Easwaramoorthy, D. Generalized fractal dimensions in the recognition of Noise Free Images. In Proceedings of the Third International Conference on Computing, Communication and Networking Technologies (ICCCNT'12), Coimbatore, India, 26–28 July 2012; pp. 1–5. [[CrossRef](#)]
17. Uthayakumar, R.; Easwaramoorthy, D. Multifractal Analysis in Denoising of Color Images. In Proceedings of the International Conference on Emerging Trends in Science, Engineering and Technology, Tiruchirappalli, India, 13–14 December 2012; pp. 228–234. [[CrossRef](#)]
18. Eliahim Jeevaraj, P.S.; Shanmugavadivu, P.; Easwaramoorthy, D. Fuzzy Cut Set-Based Filter for Fixed-Value Impulse Noise Reduction. *Adv. Algebra Anal. Trends Math.* **2018**, *1*, 205–213. [[CrossRef](#)]
19. Georgobiani, V.A.; Gonchar, K.A.; Zvereva, E.A.; Osminkina, L.A. Porous Silicon Nanowire Arrays for Reversible Optical Gas Sensing. *Phys. Status Solidi (A)* **2017**, *215*, 1700565. [[CrossRef](#)]
20. Marin, D.; Gerbaud, G.; Margeat, O.; Ziarelli, F.; Ferrer, F.; Ouari, O.; Campos, A.; Bertaina, S.; Savoyant, A. Magnetic functionalization of ZnO nanoparticles surfaces via optically generated methyl radicals. *J. Chem. Phys.* **2023**, *158*, 184704. [[CrossRef](#)]
21. Bobkov, A.; Luchinin, V.; Moshnikov, V.; Nalimova, S.; Spivak, Y. Impedance Spectroscopy of Hierarchical Porous Nanomaterials Based on por-Si, por-Si Incorporated by Ni and Metal Oxides for Gas Sensors. *Sensors* **2022**, *22*, 1530. [[CrossRef](#)]
22. Roldughin, V.I.; Dolotov, S.V. Electron Paramagnetic Resonance in Fractal Aggregates of Metal Nanoparticles. *Colloid J.* **2004**, *66*, 381–383. [[CrossRef](#)]
23. Zholud', A.; Kashevskii, B. Dia- and paramagnetophoresis of microparticles near a short magnetized cylinder. *J. Eng. Phys. Thermophys.* **2010**, *83*, 554–559. [[CrossRef](#)]
24. Roman, H.E.; Cesura, F.; Maryam, R.; Levchenko, I.; Alexander, K.; Riccardi, C. The fractal geometry of polymeric materials surfaces: Surface area and fractal length scales. *Soft Matter* **2024**, *20*, 3082–3096. [[CrossRef](#)] [[PubMed](#)]
25. Jiang, G.; Hu, J.; Chen, L. Preparation of a Flexible Superhydrophobic Surface and Its Wetting Mechanism Based on Fractal Theory. *Langmuir* **2020**, *36*, 8435–8443. [[CrossRef](#)] [[PubMed](#)]
26. Zhang, W.; Wang, D.; Sun, Z.; Song, J.; Deng, X. Robust superhydrophobicity: Mechanisms and strategies. *Chem. Soc. Rev.* **2021**, *50*, 4031–4061. [[CrossRef](#)] [[PubMed](#)]
27. Brito, C.; Butt, H.J.; Giacomello, A. Chemical physics of controlled wettability and super surfaces. *J. Chem. Phys.* **2023**, *159*, 150402. [[CrossRef](#)]
28. Piferi, C.; Bazaka, K.; D'Aversa, D.L.; Di Girolamo, R.; De Rosa, C.; Roman, H.E.; Levchenko, I. Hydrophilicity and Hydrophobicity Control of Plasma-Treated Surfaces via Fractal Parameters. *Adv. Mater. Interfaces* **2021**, *8*, 2100724. [[CrossRef](#)]
29. Wang, X.; Bi, L.; Han, W.; Zhang, X. Single-scattering properties of encapsulated fractal black carbon particles computed using the invariant imbedding T-matrix method and deep learning approaches. *J. Geophys. Res. Atmos.* **2023**, *128*, e2023JD039568. [[CrossRef](#)]
30. Liang, X.M.; Wang, G.F. A friction model of fractal rough surfaces accounting for size dependence at nanoscale. *Acta Mech.* **2022**, *233*, 69–81. [[CrossRef](#)]
31. Watzele, S.; Hauenstein, P.; Liang, Y.; Xue, S.; Fichtner, J.; Garlyyev, B.; Bandarenka, A.S. Determination of Electroactive Surface Area of Ni-, Co-, Fe-, and Ir-Based Oxide Electrocatalysts. *ACS Catal.* **2019**, *9*, 9222–9230. [[CrossRef](#)]

32. Murzalinov, D.; Seredavina, T.; Kemelbekova, A.; Spivak, Y.; Moshnikov, V.; Mukhamedshina, D.; Mit', K.; Ussipov, N.; Dmitriyeva, E.; Zhantuarov, S.; et al. Investigation of Surface Nanoclusters and Paramagnetic Centers of ZnO/por-Si Structures as the Basis of Sensory Properties. *Processes* **2023**, *11*, 3332. [\[CrossRef\]](#)
33. Madhuri, A.; Jena, S.; Dutta, S.; Swain, B.P. Evolution of Electroless Cu/Cu x O Nanostructured Thin Films: Study of Surface Fractal, Tuning Band Gap and Electronic Structure. *Arab. J. Sci. Eng.* **2024**, 1–12. [\[CrossRef\]](#)
34. Shrivastava, S.C.; Shrivastava, R.; Priyanka. Comparative analysis of fractal dimension of CdS, CdZnS and CdZnS: Ce thin films. *Indian J. Phys.* **2023**, *97*, 757–765. [\[CrossRef\]](#)
35. Mwema, F.M.; Akinlabi, E.T.; Oladijo, O.P. Fractal analysis of thin films surfaces: A brief overview. *Adv. Mater. Sci. Eng.* **2020**, 251–263. [\[CrossRef\]](#)
36. Wu, M.; Wang, W.; Shi, D.; Song, Z.; Li, M.; Luo, Y. Improved box-counting methods to directly estimate the fractal dimension of a rough surface. *Measurement* **2021**, *177*, 109303. [\[CrossRef\]](#)
37. Alevizos, P.D.; Vrahatis, M.N. Optimal dynamic box-counting algorithm. *Int. J. Bifurc. Chaos* **2010**, *20*, 4067–4077. [\[CrossRef\]](#)
38. Gurylev, V.; Perng, T.P. Defect engineering of ZnO: Review on oxygen and zinc vacancies. *J. Eur. Ceram. Soc.* **2021**, *41*, 4977–4996. [\[CrossRef\]](#)
39. Orudzhev, F.; Muslimov, A.; Selimov, D.; Gulakhmedov, R.R.; Lavrikov, A.; Kanevsky, V.; Gasimov, R.; Krasnova, V.; Sobola, D. Oxygen Vacancies and Surface Wettability: Key Factors in Activating and Enhancing the Solar Photocatalytic Activity of ZnO Tetrapods. *Int. J. Mol. Sci.* **2023**, *24*, 16338. [\[CrossRef\]](#)
40. Chen, H.; Gu, S.; Tang, K.; Zhu, S.; Zhu, Z.; Ye, J.; Zhang, R.; Zheng, Y. Origins of green band emission in high-temperature annealed N-doped ZnO. *J. Lumin.* **2011**, *131*, 1189–1192. [\[CrossRef\]](#)
41. Paudel, T.; Lambrecht, W. First-principles calculation of the O vacancy in ZnO: A self-consistent gap-corrected approach. *Phys. Rev. B* **2008**, *77*, 205202. [\[CrossRef\]](#)
42. Vlasenko, L.S. Magnetic Resonance Studies of Intrinsic Defects in ZnO: Oxygen Vacancy. *Appl. Magn. Reson.* **2010**, *39*, 103–111. [\[CrossRef\]](#)
43. Vempati, S.; Mitra, J.; Dawson, P. One-step synthesis of ZnO nanosheets: A blue-white fluorophore. *Nanoscale Res. Lett.* **2012**, *7*, 470. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Janotti, A.; Van de Walle, C.G. Fundamentals of zinc oxide as a semiconductor. *Rep. Prog. Phys.* **2009**, *72*, 126501. [\[CrossRef\]](#)
45. Ye, J.D.; Gu, S.L.; Qin, F.; Zhu, S.M.; Liu, S.M.; Zhou, X.; Liu, W.; Hu, L.Q.; Zhang, R.; Shi, Y.; et al. Correlation between green luminescence and morphology evolution of ZnO films. *Appl. Phys. A* **2005**, *81*, 759–762. [\[CrossRef\]](#)
46. Suhaimi, M.F.; Rusop, M.; Abdullah, S. Porosity and thickness effect of porous silicon layer on photoluminescence spectra. In Proceedings of the 2013 International Conference on Technology, Informatics, Management, Engineering and Environment, Bandung, Indonesia, 23–26 June 2013; pp. 115–118. [\[CrossRef\]](#)
47. Pastukhov, A.I.; Belorus, A.O.; Spivak, Y.M.; Moshnikov, V.A. Investigation of the photoluminescence of porous silicon layers obtained under various technological conditions. *J. Phys. Conf. Ser.* **2018**, *1038*, 012048. [\[CrossRef\]](#)
48. Cho, B.; Jin, S.; Lee, B.Y.; Hwang, M.; Kim, H.C.; Sohn, H. Investigation of photoluminescence efficiency of n-type porous silicon by controlling of etching times and applied current densities. *Microelectron. Eng.* **2012**, *89*, 92–96. [\[CrossRef\]](#)

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