Investigation of the correlation between gas-sensitive properties and fractal dimension of nanostructured ZnO/ZnO\(<\text{Cu, Fe}>\) films obtained by the sol-gel method

N D Yakushova\(^1\), I A Pronin\(^1\), I A Averin\(^1\), A A Karmanov\(^1\), V A Moshnikov\(^{1,2}\) and D Tz Dimitrov\(^3\)

\(^1\) Department of Nano- and Microelectronics, Penza State University, 440026, Penza, Russia
\(^2\) Department of Micro- and Nanoelectronics, Saint-Petersburg Electrotechnical University “LETI”, 197376, Saint-Petersburg, Russia
\(^3\) Department of General and Inorganic Chemistry, University of Sofia, Sofia 1164, Bulgaria

E-mail: pronin_i90@mail.ru

Abstract. Correlations between gas sensitive properties and fractal dimension of nanostructured ZnO/ZnO\(<\text{Cu, Fe}>\) films obtained by the sol-gel method are established. The thickness of the films and their fractal dimension were determined by the number of dives in the sol of the upper zinc oxide film, alloyed with metal cations. It was found out that in all cases larger values of the fractal dimension correspond to lower values of the gas sensitivity.

1. Introduction

Gas-sensitive sensors appeared in 1970s as ceramic pressed samples of \(n\)-type oxide powders with a built-in heater. Then, sensors created by microelectronics technology on the basis of thin films were developed. As an alternative to the traditional methods of manufacturing sensor elements, a sol-gel method is used, the essential advantage of which is the possibility for achieving high homogeneity of synthesized materials, which greatly simplified the technology for obtaining nanostructured composites based on semiconductor oxides. The films obtained by sol-gel method have a developed relief, which leads to a significant increase of actual area of interaction with the gas phase, as well as the contact area between the lower and upper layers of the structure. This fact leads to a change of the characteristics of the gas sensor, which are not always explainable with the help of simple model representations of a thin continuous layer that do not take into account the nanorelief of contact surfaces, as well as features of transference phenomena. Therefore, it is important to evaluate the properties of the nanostructured surface of the films for the purpose of predicting the instrument parameters. The difficulty of numerical estimation of the nanorelief is in the strong dependence of the results on the scale of the measurements; therefore, a fractal approach is applied in the work, the results of which are invariant with respect to the scale. Thus, the purpose of the research was to investigate the correlation dependences between the fractal dimension of the surface of ZnO/ZnO\(<\text{Cu, Fe}>\) samples and their gas sensitive properties. The methods for manufacturing and study of samples are considered in detail in [1].
2. Calculation and discussion of results

The fractal dimension of the material was calculated using film surface images obtained by a scanning electron microscope. There are many ways of extracting the value of fractal dimension $D$ from the image: “perimeter – area”; “area – volume of ratios”; variation, etc. [2]. Accordingly, the values of the fractal dimensions obtained by different methods also differ. In the research, $D$ calculation for each sample was carried out by two methods: “perimeter – area” and approximations of a two-dimensional mass fractal.

The algorithm for calculating the fractal dimension of films by AFM and SEM images by the “perimeter – area” method is reduced to the following (figure 1):

1. Forming a contour image of the relief by cutting the film with the plane parallel to the plane of sample. Three contour images were obtained for each image, with subsequent averaging of the fractal dimension.

2. Covering the contour image of the surface with squares of $\delta \times \delta$ size of the variable side length, with subsequent counting the number of squares $N_s$, proportional to the area $S$, of the contours. Dimensions of $\delta$ in all cases are chosen in such a way that the surface behaves as a fractal object, which corresponds to a local approximation in the definition of fractal dimension.

3. Selecting the perimeter of each contour in the image.

4. Covering the resulting image with squares of $\delta \times \delta$ size with a variable side length and subsequent calculation of the number of squares $N_p$, proportional to the perimeter $P$, of the contours.

5. Replication of operations 1 – 4 for other $\delta$ values.

![Figure 1](image)

*Figure 1.* An algorithm for fractal dimension calculation by the “perimeter – area” method.

Since there is a relation $S(f) \sim [P(f)]^{2/D}$, then in the double logarithmic coordinates the tangent of the slope angle of this function characterizes the fractal dimension $D$ [3]. The calculated values of the fractal dimension of the contour are related with the fractal dimension of the surface $D_f$ by the following simple relation [4]: $D_f = D + 1$.

The method for fractal dimension calculation in terms of the mass two-dimensional fractal approximation is based on the approximation of a two-dimensional mass fractal aggregate. Since the technology for producing gas-sensitive films has layer-by-bivariate symmetry, then the scaling factors along the axis perpendicular to the substrate plane are strongly smoothed. This leads to the applicability of the two-dimensional mass fractal approximation. In this case, the fractal dimension is close to the Hausdorff-Besicovitch dimensionality. In this method, the calculation of the fractal dimensionality $D_k$ was carried out by slope ratio of the direct function $\ln(N_{fl}) = f(\ln(\delta))$.

To calculate the fractal dimension, ZnO-Me samples were made, the upper layer of which was formed by one, two and three dives in the sol. Figure 2, for example, shows morphology images of ZnO-Cu and ZnO-Fe film surfaces obtained by scanning electron microscopy. It is seen from the Figure, the results obtained by the two methods correlate with each other. In all cases, there is a decrease in fractal dimension with the increasing number of layers during the formation of the film. In general, this indicates that the surface becomes smoother. The obtained result can be related with improvement of the crystalline structure of the material, which is most likely due to the fact that the substrate for each subsequent layer is the previous one, which is substantially more porous and developed than the crystalline substrate $\text{Al}_2\text{O}_3$. The effect of improving the crystalline structure of ZnO using porous substrates is described in [5]. Figure 3 shows the obtained results for ZnO-Cu samples.
Figure 2. SEM images of ZnO-Cu (a) and ZnO-Fe (b) film surfaces formed by one dive in the sol.

Figure 3. Dependence of the surface fractal dimension of ZnO-Cu films on the dives number in the sol, calculated by the “perimeter – area” method (a) and in the mass surface fractal approximation (b).

Figure 4 shows the results for calculating the fractal dimension for samples of ZnO-Fe series. Based on the results shown in figures 3 and 4, the following conclusions can be drawn: the fractal dimension of ZnO-Fe composition films in all cases is larger than the analogous composition of ZnO-Cu. This conclusion is in accordance with the difference in the radii of modifier cations and Zn$^{2+}$. In the case of ZnO-Fe, the difference in radii is large, which leads to substantial distortions of the crystal lattice, the appearance of mechanical stresses and, as a consequence, to more developed and defective surface; as in the case of ZnO-Cu samples, the surface fractal dimension in ZnO-Fe decreases with increasing number of film layers. This effect, apparently, is also due to an improvement in the crystallinity of the material during the formation of films on a porous substrate.

Figure 4. Dependence of the surface fractal dimension of ZnO-Fe films on the number of dives in the sol calculated by the “perimeter – area” method (a) and in the mass surface fractal approximation (b).
3. Conclusions
Thus, the correlations between gas sensitive properties and fractal dimension of nanostructured ZnO/ZnO <Cu, Fe> films obtained by the sol-gel method are established. It was found out that in all cases larger values of the fractal dimension correspond to lower values of the gas sensitivity.

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