

Investigation of the vapor-sensitive properties of zinc oxide layers by impedance spectroscopy

S. S. Nalimova¹, I. E. Kononova¹, V. A. Moshnikov^{1,3}, D. Tz. Dimitrov^{2*}, N. V. Kaneva²,
L. K. Krasteva², S. A. Syuleyman², A. S. Bojinova², K. I. Papazova², A. Ts. Georgieva⁴

¹*Department of Micro- and Nanoelectronics, Saint-Petersburg State Electrotechnical University, Saint-Petersburg 197376, Russia*

²*Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, Sofia 1164, Bulgaria*

³*Department of Integrated Electronics, Peter the Great Saint-Petersburg Polytechnic University, Saint-Petersburg 195251, Russia*

⁴*Department of Materials Science & Engineering, University of Florida, Gainesville, FL 32611, USA*

Received November 4, 2015; Revised June 27, 2016

In the field of gas sensory research, metal oxide layers are used as sensitive elements of semiconductor adsorption gas sensors. In this work samples of ZnO were prepared by the sol-gel method with variation of the annealing temperature from 100 to 500 °C. The microstructure of the surface of the obtained samples was investigated by atomic force microscopy. The sensitivity of the samples to the vapors of acetone and ethanol was investigated by the method of impedance spectroscopy. For interpretation of the obtained results an electric equivalent R-CPE circuit was used. The ZnO sample produced by annealing at 300 °C exhibited maximum sensitivity to both vapors. Addition of Fe to the ZnO sample annealed at 500 °C led to an increase in the sensitivity to the vapors of acetone and ethanol due to the increased concentration of reducing vapor adsorption sites.

Keywords: Impedance spectroscopy, zinc oxide; gas sensors; sol-gel method.

INTRODUCTION

Various metal-oxide materials as SnO₂, ZnO, Fe₂O₃, WO₃, Co₃O₄, etc., are used as sensitive materials in metal-oxide semiconductor gas sensors. Their operating principle is based on increasing the sensitive element conductivity in the surface region as a result of sorption of the analyzed gas. Depending on the composition of the sensitive layer, the sensor reacts with different vapors and gases as C₂H₅OH, CO, CH₄, H₂, O₂, etc. The operating temperature is within the range from 200 °C to 500 °C.

Sensitive layers for gas sensors are based on a significant number of materials and technologies. In modern sensor technology gas-sensitive layers are prepared using metal oxides having electron conductivity, such as SnO₂, In₂O₃, ZnO, Fe₂O₃, CuO, TiO₂, WO₃ and Co₃O₄. The principle of operation, based on metal oxide layer semiconductor gas sensors [1–4], is the reversible change in the electrical properties during the charged oxygen species adsorption and desorption of reaction products as a result of the interaction with the molecules of reducing gases at elevated operating temperatures, usually within the range from 200 °C to 500 °C. In gas sensory research tin

dioxide is the most studied material [5]. However, ZnO is also suitable for use in this field due to the possibility to vary its resistance in a broad range, its high chemical stability, and low toxicity. Nowadays, a variety of methods is used for the preparation of nanostructured layers of ZnO, such as spray pyrolysis [6], chemical vapor deposition [7], magnetron sputtering [8], hydrothermal method [9], sol-gel technique [10–15]. The sol-gel method allows easy control over the structure of the obtained materials by varying the technological conditions of the process, such as the choice of solvent and precursor, the aging time of the sol, etc. For example, in [14], porous layers based on zinc oxide are produced by the sol-gel method and it is shown that the pore size depends on the concentration of zinc nitrate in solution.

The aim of this paper is to investigate the sensitivity of semiconductor nanomaterials based on ZnO prepared by the sol-gel method under the conditions of a gaseous medium in an alternating electric field.

EXPERIMENTAL

Four types of samples were obtained by the sol-gel method (Table 1).

* To whom all correspondence should be sent:
E-mail: dimitrov2001@yahoo.com

Table 1. Conditions of preparation of sols and corresponding samples

Type of sample	Composition of sample	Used precursors	Annealing temperature, °C
I			100
II	ZnO	Zn(CH ₃ COO) ₂ ·2H ₂ O	300
III			500
IV	ZnO-Fe	Zn(CH ₃ COO) ₂ ·2H ₂ O, Fe(NO ₃) ₃ ·9H ₂ O	500

Table 2. Parameter values of relaxators in air and in the presence of reactant gases

Type of sample	Atmosphere	f _{max} , kHz	τ, μsec	R, kOhm	R _{air} /R _{gas}	A _{air} /A _{gas}
I	Air atmosphere	11.233	14.17	434.1		
	In the presence of acetone vapor	486.26	0.33	15.7	27.6	3.1
	In the presence of ethanol vapor	46.416	3.43	125.4	3.5	1.5
II	Air atmosphere	5.094	31.24	1100		
	In the presence of acetone vapor	162.975	0.98	50.9	21.6	2.0
	In the presence of ethanol vapor	34.305	4.64	218.4	5.0	1.7
III	Air atmosphere	6.734	23.63	955		
	In the presence of acetone vapor	22.051	7.22	248	3.9	1.1
	In the presence of ethanol vapor	19.630	8.11	278	3.4	1.1
IV	Air atmosphere	2.656	59.92	1150.7		
	In the presence of acetone vapor	57.224	2.78	140.7	8.2	3.3
	In the presence of ethanol vapor	26.561	5.99	273.3	4.2	2.9

Table 3. Sensitivity of the sample in an alternating electric field to acetone and ethanol vapors

Sample type	Atmosphere	maxS _{Re}	f, Hz	maxS _{Im}	f, Hz
I		25.8	1384	536.0	2984
II	In the presence of acetone vapor	30.9	5995	9457.7	6734
III		3.8	1149.8	15.3	1385
IV		7.9	2257	126.8	1707
I	In the presence of ethanol vapor	3.3	1233	15.5	1385
II		4.7	1520	35.8	1592
III		3.2	1098	12.4	1123
IV		4.1	1707	22.2	1831

The first three types of samples were produced from sols and Zn(CH₃COO)₂·2H₂O precursor [16, 17]; for the fourth type of samples, Zn(CH₃COO)₂·2H₂O was used as a precursor and Fe(NO₃)₃·9H₂O was subsequently added [18]. Precursors were dissolved in 2-methoxyethanol. Monoethanolamine was added as a surfactant. For the fourth type of sample the mole fraction of iron nitrate in the film was chosen to be 0.5 %. All films were annealed for 1 h at fixed temperatures, as listed in Table. 1. The film thickness was kept about 1.5 μm.

The microstructure of the surface of zinc oxide layers, prepared by the sol-gel method, was investigated using atomic force microscopy (NTEGRA Thermo, NT-MDT) in semi-contact mode [19, 20].

Investigation of the electrical properties of the produced samples was performed by the method of impedance spectroscopy [21], which was a tool for investigation of electrical properties on the

interface based on the study of the influence of an electrical field with variable frequency.

Measurement of the frequency dependence of the module of complex resistivity and phase shift angle between current and voltage in the capacitor circuit was carried out in the frequency range from 100 Hz to 500 kHz. The experiment was carried out in a laboratory installation [22], providing opportunities for investigation of samples by the method of impedance spectroscopy under changing gas environment (in an air atmosphere, in the presence of vapors of ethanol and acetone at a concentration of 1000 ppm at the temperature of measurement of 300 °C).

For processing of impedance spectroscopy experimental data, the complex plane method was used. As a complex number, the impedance is represented as the dependence of the imaginary component as a function of the real one (Nyquist plot).

RESULTS

The results of the investigation of the surface morphology of the samples, produced by variation of the annealing temperature and the composition of the material, are shown in Figures 1 and 2. It was found that increasing the annealing temperature from 100 °C to 300 °C resulted in an increase in the average particle size from 10 to 100 nm and during annealing at a temperature of 500 °C aggregation of nanoparticles into larger objects of elongated shape occurred.

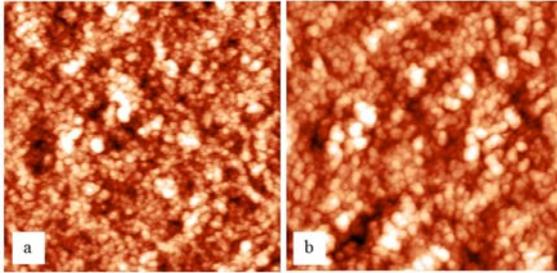


Fig. 1 a

Fig. 1 b

Fig. 1. AFM images of zinc oxide layers, prepared by the sol-gel method at various annealing temperatures: a - 100°C; b - 300°C. Scan size area of $10 \times 10 \mu\text{m}^2$.

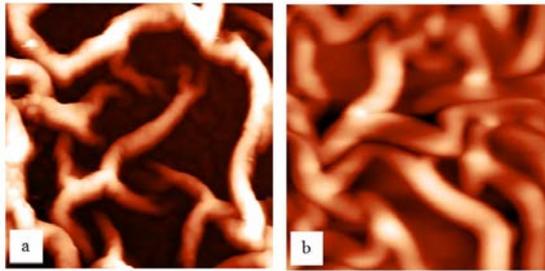


Fig. 2 a

Fig. 2 b

Fig. 2. AFM images of layers, prepared by the sol-gel method at annealing temperature of 500°C: a - ZnO; b - ZnO with the addition of Fe. Scan size area of $10 \times 10 \mu\text{m}^2$.

The investigations of the frequency dependence of the real $\text{Re}Z$ and the imaginary $\text{Im}Z$ components of the complex impedance were performed by plotting it in semi-logarithmic coordinates for an atmosphere of air and vapors of ethanol and acetone at a detection temperature of 300 °C. As an illustrative example, in Fig. 3 the frequency dependence of both, $\text{Re}Z$ (Fig. 3a) and $\text{Im}Z$ (Fig. 3b) components is shown in an air atmosphere and in the presence of vapors of acetone and ethanol for a sample of III type. On the plot of the reactive component of the complex impedance, (shown in Fig. 3b), a relaxation maximum is observed satisfying the condition $\omega\tau = 1$, where ω is the angular frequency for the maximum value of the reactive component of complex impedance (relaxation maximum point on the hodograph of the

impedance), τ is the relaxation time of polarization (characteristic charge accumulation time). The value of the characteristic charge accumulation time is inversely proportional to the angular frequency ($\tau = 1/\omega = 1/2\pi f_{\text{max}}$, where f_{max} - frequency corresponding to the position of the relaxation maximum).

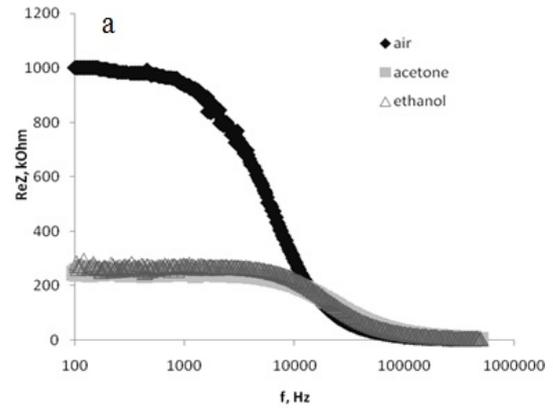


Fig. 3 a

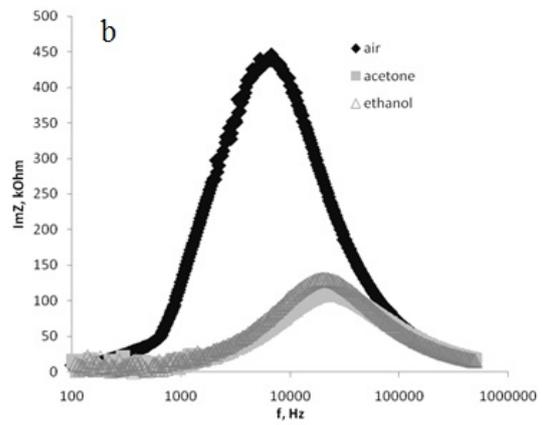


Fig. 3 b

Fig. 3. The frequency dependence of the components of the complex impedance of the sample of type III: a - real component; b - imaginary component.

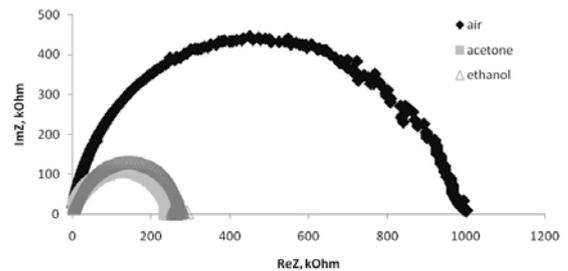


Fig. 4

Fig. 4. Nyquist diagrams for the sample of type III.

A Nyquist diagram in air and in the presence of reducing gas vapors for the sample of type III is shown in Fig. 4. It reveals that the center of the semicircle in the detection of gas shifts to higher frequencies. This is due to the shift of the relaxation maximum in the frequency dependence of the reactive component of the impedance at higher frequencies.

Impedance spectroscopy data obtained in this work are interpreted in terms of "equivalent electrical circuit". To describe the resistive-capacitive properties of the materials in the equivalent circuit the constant phase element (CPE) was used due to the fact that the centers of the semicircles on the complex plane are lying below the x-axis. The choice of the equivalent circuit elements was due to the fact that the samples are characterized by a set of relaxation times. The impedance of a constant phase element is described

by the formula: $Z = 1/A(j\omega)^n$, where A is the factor of proportionality, n is the exponential index indicating the phase deviation within the range $-1 \leq n \leq 1$, ω is the angular frequency, j is the imaginary unit. The pre-exponential frequency-independent factor has the dimension of capacitance. It was revealed that the value of the exponential index in air and in the presence of reactant gases is 0.82 – 0.99.

The spectroscopic data were interpreted by using LabVIEW media with a parallel R – CPE chain, where R is the resistance of the relaxator. The R – CPE chain is associated with the region characterizing the grain boundary of zinc oxide particles.

The value of the sensitivity toward reducing gases at a temperature of 300 °C in the detection frequency range from 100 Hz to 500 kHz was calculated in two ways: by the real component: $S_{Re} = ReZ_{air}/ReZ_{gas}$, where ReZ_{air} is the real component of the complex impedance in air, ReZ_{gas} is the real component of the impedance in the presence of reactant gas; and by the imaginary component: $S_{Im} = ImZ_{air}/ImZ_{gas}$, where ImZ_{air} is the imaginary component of the complex impedance in air, ImZ_{gas} is the imaginary component of the impedance in the presence of reactant gas.

The influence of annealing temperature and added iron to the gas sensing properties of nanomaterials is discussed in details in the next section.

DISCUSSIONS

It was revealed that the relaxation time, associated with the contact area of the particles (grain boundaries), was very sensitive to changes in the environment and resulted in a 3.4 - 42.9 fold decrease depending on the annealing temperature of the samples (Table 2). It was established that with an increase in annealing temperature of the samples from 100 °C (I type samples) to 500 °C (III type sample) the characteristic charge accumulation time increases 1.7 times in air, 21.8 times in the presence of acetone vapor, and 2.4 times in the presence of ethanol vapor (Table 2).

It is shown that on adding iron (IV type samples) to samples annealed at 500 °C (III type samples), the characteristic charge accumulation time increases 2.5 times in air, while it decreases 2.6 times and 1.4 times in the presence of vapors of acetone and ethanol, respectively (Table 2).

In this way it was revealed that for the samples, produced in the presence of reducing reactant vapors the value of the frequency-independent pre-exponential factor (the minimal and maximal values of A_{air}/A_{gas}) decreases 1.1-3.3 times, while the resistance of the grain boundaries of the particles (R_{air}/R_{gas}) - 3.1-27.6 times, calculated for all samples (Table. 2). The reasons for the decreasing values are considered to be the combined effect of the reduction of the charge depletion region at the grain boundary, the modulation of current flow channels and the recharge of surface states.

It was revealed that the maximum sensitivity is observed for type II samples annealed at 300 °C. The sensitivity of this type of samples towards acetone vapor was 30.9 at a frequency of 5995 Hz by the real component of the complex impedance and 9457.7 by the calculated imaginary component at a frequency of 6734 Hz. The sensitivity was lower towards ethanol vapor, but still significant. It was 4.7 by the real component of the complex impedance at the frequency of 1520 Hz and 35.8 by the imaginary component at a frequency of 1592 Hz (Table 3).

It was established that adding of iron (IV type samples) to the samples annealed at 500 °C (III type samples) increased the sensitivity to ethanol vapor by a factor of 1.3, evaluated by the real component of the complex impedance and by a factor of 1.8 calculated by the imaginary component. At the same time, the sensitivity to acetone vapor evaluated by the real component of the complex impedance increased by a factor of 2.1 and by a factor of 8.3 calculated by the imaginary component (Table 3). This result could be

explained by means of the model of interaction of reducing gases with metal oxides developed by our team [23].

According to our model, the increase in gas sensitivity can be achieved by using multicomponent metal oxides as sensor materials. This is done by careful selection of oxide components, taking into account their redox and acid-base properties. The effect of increasing the sensitivity of the composite materials based on ZnO-Fe₂O₃ to the vapors of acetone and ethyl alcohol in comparison with Fe₂O₃ and ZnO alone, was investigated experimentally in our work [24]. It was confirmed beyond any doubt that increasing of the concentration of reducing vapor adsorption sites (metal cations and acid OH-groups) on the surface of the composite material is responsible for the increase in sensitivity.

In summary, the observed dependence of the properties of samples of type I, II, III, based on pure zinc oxide gas-sensitive layer, as a function of annealing temperature could be explained by their specific morphological and structural characteristics. For the sample of type I the annealing temperature of 100 °C is not sufficient for the formation of the crystal structure of zinc oxide and complete evaporation of the organic components of the initial solutions. For the sample of type II the annealing temperature of 300 °C causes formation of zinc oxide particles of a size about 100 nm. For the sample of type III the annealing temperature of 500 °C causes association of the particles in micrometer-sized objects. This causes a reduction of the surface area available for surface-vapor interaction.

CONCLUSIONS

The gas-sensitive properties of samples based on zinc oxide were investigated by impedance spectroscopy at a detection temperature of 300 °C. It is revealed that during vapor detection the center of the semicircle at the Nyquist diagrams shifts to the higher frequencies region.

The data obtained by spectroscopic measurement were interpreted by using parallel R – CPE - chains. Those R – CPE - chains are associated with the region which characterizes the grain boundaries of zinc oxide particles. It was found that the values of the exponential index, the relaxation time, the pre-exponential frequency-independent factor and the resistance of the grain boundaries of the particles are very sensitive to the changes in air conditions.

It is shown that the sample of pure ZnO annealed at 300 °C has the maximum sensitivity

values to acetone and ethanol vapors. That fact is explained by the smaller particle size and structural perfection of the zinc oxide layers obtained in these synthesis conditions. It was found that the sensitivity values of ZnO samples with added Fe annealed at 500 °C to both acetone and ethanol vapors are higher than those of pure ZnO. This can be associated with complementary redox and acid-base properties of ZnO and Fe₂O₃.

Acknowledgements: Researchers from Sofia University are thankful to Beyond Everest project FP7-REGPOT-2011-1 for financial support. Russian researchers express their gratitude to the grant of Russian Science Fund (project №14-15-00324).

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ИЗСЛЕДВАНЕ НА ИЗМЕРЕНИ ПО МЕТОДА НА ИМПЕДАНСНА СПЕКТРОСКОПИЯ НА ЧУВСТВИТЕЛНИТЕ КЪМ ИЗПАРЕНИЯ СВОЙСТВА НА СЛОЕВЕ ОТ ЦИНКОВ ОКСИД

С. С. Налимова¹, И. Е. Кононова¹, В. А. Мошников^{1,3}, Д. Ц. Димитров^{2*}, Н. В. Кънева², Л. К. Кръстева², Ш. А. Сюлейман², А. С. Божинова², К. И. Папазова², А. Ц. Георгиева⁴

¹Катедра по Микро- и Наноелектроника, Санкт-Петербургски Държавен Електротехнически Университет, Санкт-Петербург 197376, Русия

²Лаборатория по Наука и Технология на Наночастици, Катедра по Обща и Неорганична Химия, Факултет по Химия и Фармация, Софийски Университет, София 1164, България

³Катедра по Интегрирана Електроника, Санкт-Петербургски Политехнически Университет на името на Петър Велики, Санкт-Петербург 195251, Русия

⁴Катедра Материалознание & Инженеринг, Университет на Флорида, Гейнсвил, ФЛ 32611, САЩ

Получена на 4 ноември, 2014 г.; ревизирана на 27 юни, 2016 г.

(Резюме)

В областта на газ-сензорните изследвания метални оксидни слоеве се използват като чувствителни елементи на полупроводниковите адсорбционни газови датчици. В тази работа проби от ZnO са получени чрез зол-гелен метод с промяна на температурата на отгряване от 100 до 500 °С. Микроструктурата на повърхността на получените проби е изследвана чрез атомно-силов микроскоп. Чувствителността на пробите към изпарения на ацетон и етанол се изследва по метода на импедансна спектроскопия. За интерпретация на получените резултати е използвана електрическа еквивалентна R-CPE схема. Пробата от ZnO, получена чрез отгряване при 300 °С проявява максимална чувствителност към изпаренията на двата органични разтворителя. Добавянето на Fe към ZnO пробата, отгрята при температура от 500 °С води до увеличаване на чувствителността към изпаренията на ацетон и етанол. Причината за това е увеличаването на концентрацията на адсорбционните центрове за редукторните газове, каквато функция изпълняват изпаренията от етанол и ацетон.