**Synthesis of Porous Gas-Sensitive Materials for Ethanol Semiconductor Sensor**

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**Abstract.** As a result of the experiments, a nanocomposite with the composition of TEOS/60%SnO2 + 30%TiO2 + 10%CuO was selected as the gas-insensitive material for a semiconductor sensor selectively detecting ethanol from a gas mixture. The dependence of the sensor signal, developed on this composite, on the ethanol concentration over a wide range was studied. The obtained results showed that the signal in the mixture is linearly dependent on the ethanol concentration in the range from 0.25 to 2.00, with a proven margin of error within the relevant boundary.

**Keywords:** copper oxide, ethanol, gas-insensitive material, metal oxides, semiconductor sensor, sol-gel, tetraethoxysilane, tin oxide, titanium oxide.

**INTRODUCTION**

The sol-gel method is an effective technique for producing gas-sensitive nanocomposites with specific molecular structures and physicochemical properties [1]. The advantage of sol-gel synthesis for gas-sensitive materials lies in its ability to combine various fragments of initial organic and inorganic reagents at the molecular level in a solution. By changing the nature of the components introduced into the solution and modifying the conditions of the sol-gel synthesis process, it is possible to tailor the structure of the synthesized nanocomposites as desired. The convenience of the sol-gel synthesis lies in ensuring high purity of the materials obtained, distributing porosity across the surface, achieving molecular-level structural uniformity, synthesizing samples at low temperatures, and introducing multiple components in a single step [2].

The sol-gel synthesis of a sensitive material for the ethanol semiconductor sensor includes the stages of sol formation and its subsequent transition to a gel. The preparation process of the sensitive material consists of the following stages: preparation of a homogeneous sol solution, gelation, and drying.

For the preparation of modified gas-sensitive material suitable for ethanol semiconductor sensors, reagents of analytical grade purity (chemically pure and high-purity) were used, including tetraethoxysilane, metal salts, ethyl alcohol, and hydrochloric acid. The reaction mixtures were prepared by gradually adding pre-heated aqueous-alcoholic solutions of tetraethoxysilane to the dopant compounds and catalysts at 70 °C in a water bath, followed by slow mixing [3]. The gelation process was carried out by maintaining the sol in a closed fluoroplastic container at a room temperature of no less than 20 °C. After an interval of one day, the modified sols were coated onto glass substrates (glass tubes) pre-washed with alcohol and distilled water, and then heated in a drying oven at 60-80 °C for 30 minutes[4-9].

During the preparation of the initial sol, the acidic hydrolysis products of tetraethoxysilane were removed from the system by heat treatment, ensuring sufficiently high chemical purity of the final material. The processes occurring in the system during this hydrolysis have been thoroughly studied [10-11]. The hydrolysis of tetraethoxysilane proceeds according to the following scheme:

Si(OC2H5)4+4H2O→Si(OH)4+4C2H5OH→SiO2+2H2O+ C2H5OH (1)

Simultaneously with hydrolysis, the polycondensation process begins and proceeds in two directions.

First, the interaction of two silanol groups (oxolation) leads to the formation of a product with the release of water:

≡Si(OH) + ≡Si(OH) → ≡Si–O–Si≡ + H2O (2)

Second, the interaction of a silanol group with silicon alkoxide (alkoxolation) results in the formation of an alcohol molecule:

≡Si(OH) + C2H5OSi≡ → ≡Si–O–Si≡ + C2H5OH (3)

The polycondensation reaction then continues with the formation of siloxane bonds. The key factors influencing the reaction rate are pH value, the ratio of component concentrations, and temperature.

The viscosity of the film-forming solution is a crucial parameter affecting the quality of the coating obtained by the sol-gel method. Many film-forming solutions thicken over time, leading to a decrease in the quality of the synthesized coating. A sol is a suspension resulting from the hydrolysis and partial condensation of precursors (alkoxides and silicates), consisting of solid particles with sizes ranging from 1 nm to 1 μm. Each elementary particle consists of a disordered three-dimensional network of SiO2 tetrahedra. Gas-sensitive materials are formed by the condensation of gel-sol particles.

Hybrid composites combine organic and inorganic polymers and belong to a new and unique class of nanomaterials. Several studies are dedicated to the sol-gel synthesis of insoluble organo-inorganic composites involving TEOS (tetraethoxysilane). The resulting hybrid composites are solid, powder-like substances with specific surface areas and are thermally stable (230–330 °C), having porosities ranging from 0.8 to 34.7 m²/g.

**METHODS**

As of today, work is being carried out at Samarkand State University in the field of using nanocomposites and gas-insensitive materials based on them to create chemical sensors. The goal of this work is to obtain a nanocomposite material based on metal oxides for a semiconductor sensor detecting ethanol using the sol-gel technology method and to study its capabilities in the process of ethanol detection.

In our experiments, we used the sol-gel method to synthesize gas-sensitive materials based on metal oxides.

To date, methods such as X-ray diffraction, gas adsorption, electron microscopy, and IR spectroscopy have been widely used to study nanocomposites and gas-sensitive materials derived from them [5].

For mesoporous materials, atomic absorption analysis or X-ray fluorescence analysis can be employed to determine elements when working with inorganic substances. Since atomic absorption analysis is more suitable for analyzing solutions and composite materials are typically solid, X-ray and fluorescence analysis methods are commonly used in the analysis of composite materials.

**RESEARCH RESULTS**

In our experiments, we explored the possibility of creating composite gas-sensitive materials based on tetraethoxysilane (TEOS) and oxides of tin, titanium, and copper using the sol-gel method by hydrolyzing TEOS in an aqueous-alcoholic mixture.

During the experimental studies, tetraethoxysilane (TEOS) (C2H5O)4Si (TU 2637-059-44493179-0) was used as the initial compound for synthesizing gas-sensitive materials.

The synthesis of porous silica gel materials was carried out as described above. TEOS solutions were prepared in purified ethanol with a 1:30 molar ratio of TEOS to alcohol. The resulting mixture was stirred for 2 hours and then left at room temperature for another 2 hours. Afterward, a mixture of hydrochloric acid dissolved in distilled water and the corresponding salts was added to the TEOS solution in alcohol under continuous stirring. The homogenization of the initial component mixture was carried out at 25°C for 15 minutes using an automatic disperser UDN-P-2T.

The stability of the solution in the conducted experiments was studied in relation to the composition and ratios of the solution components. The effect of various factors on the speed of the synthesis process for sensitive films for ethanol sensors was investigated by monitoring the viscosity of the solution using viscometry.

The stability of the film-forming solutions was assessed by measuring their viscosity using a VPZh-2 glass viscometer (GOST 10028-81) with an internal capillary diameter of 0.9 mm. Measurements were conducted at a temperature of 25°C.

The composition of the initial mixture components is one of the key factors strongly influencing the stability of the solution. In all experiments, the TEOS-to-dopant molar ratio was maintained at 2:1. The stability of various dopant-containing solutions prepared under identical conditions varied depending on the dopant composition.

It was observed that the stability of dopant-containing solutions was significantly higher than that of dopant-free solutions. Moreover, the stability also depended on the composition of the salts used as dopants. Experiments revealed that the stability of sols with compositions TEOS/100% SnO₂, TEOS/75% SnO₂ + 25% TiO₂, and TEOS/60% SnO₂ + 30% TiO₂ + 10% CuO was 62, 75, and 110 hours, respectively (Figure 1).

The film-forming solution gains the ability to create coatings only after a specific period, which depends on the composition and ratio of the components.

**2,5**

**5,0**

**7,5**

**10,0**

Viscosity, sPa

**1** SiO2/100%SnO2

Duration of the experiment, hours

**25**

**50**

**75**

**100**

**125**

**150**

**12,5**

**2** SiO2/75%SnO2 +25%TiO2

**3-**SiO2/60%SnO2 +30%TiO2+10%CuO

**1**

**2**

**3**

**FIGURE 1.** The dependence of the stability of the film-forming solution on the composition of the initial mixture

From the results presented in Figure 1, two distinct regions can be identified in terms of the kinematic viscosity over the aging time of the solution, which aligns with the data in the literature. The first region, almost parallel to the abscissa axis, is hypothesized to correspond to the hydrolysis of silicon alkoxide and the condensation reactions of monomers into dimers. The second region, with a steeply increasing curve, corresponds to the progression of polycondensation processes.

Effect of pH on Solution Stability: to study the effect of pH on solution stability and the porous structure of the gas-sensitive material for ethanol, solutions with different pH values were prepared. The composition of the components corresponded entirely to the composition and synthesis method of the initial materials described earlier, with the exception of the acid concentration.

**2,5**

**10,0**

**7,5**

**1.рН=0,1**

**2.рН=0,5**

**3.рН=1,0**

**4.рН=1,5 моль**

**5,0**

Viscosity, sPa

**0**

**25**

**1**

**4**

**3**

**2**

**75**

**65**

**100**

Duration of the experiment, hours

**FIGURE 2.** The dependence of the stability of the film-forming mixture on the pH value of the solution

A laboratory pH meter with a measurement error of ±0.05 was used to control the pH. The stability of the solutions was investigated depending on the pH of the mixtures obtained with dopants based on tin and titanium salts (Figure 2).

The pH value in the solution was varied from 0.1 to 1.50. A pH meter was used to monitor the initial pH of the solution. Figure 2 shows the graph of kinematic viscosity changes of the solution over its aging time for different pH values of 0.1, 0.5, 1.0, and 1.5. From the graph, it is evident that the stability of the solution is significantly dependent on its pH value.

The curve depicting the relationship between the kinematic viscosity and aging time can be divided into two parts, consistent with the data in the literature. The section almost parallel to the abscissa axis is hypothesized to correspond to the hydrolysis of silicon alkoxide and the condensation reactions of monomers into dimers. The steeply rising section of the curve corresponds to the progression of polycondensation processes.

Observations:Sols formed at pH ~0.50–1.0 are the most resistant to gelation. At lower (pH = 0.1) and higher (pH = 1.50) pH values, the gelation rate increases. These results align with findings reported by other researchers. The minimal viscosity and its relative change for silicic acid sol occur at pH ~0.50 due to minimal sol particle charge in this range. Electrophoretic measurements show that for a solution with an H₂O/TEOS = 20 ratio: Sol particles have a positive charge (H⁺) at pH < 1. Sol particles have a negative charge (OH⁻) at pH > 1.5.

Therefore, the isoelectric point (IEP) of the sol corresponds to the pH range of 0.5 to 1.0. The position of the IEP depends on various factors, but the minimal viscosity curves are observed in this range, likely due to the minimal charge on the sol particles.

Above IEP (pH > 1): The condensation reaction proceeds via a base-catalyzed mechanism, and the rate of condensation is proportional to [OH⁻].

Below IEP (pH < 1): The reaction follows an acid-catalyzed mechanism, and the condensation rate is proportional to [H⁺].

In acidic environments, hydrolysis occurs at a higher rate than condensation, resulting in a weakly cross-linked gel. In alkaline environments, the opposite occurs, producing a highly cross-linked gel containing colloidal aggregates.

The surface morphology of gas-sensitive film samples synthesized and thermally treated at various pH values based on TEOS, tin, titanium, and copper oxides was examined. The surface structure depends on the pH value, influencing the final material properties.

The conducted studies show that the pH value and the H₂O/TEOS ratio significantly affect the stability of the solution, the relative rates of hydrolysis and condensation reactions, and the structure of the resulting material. These key parameters determine the porosity, structure, and application areas of the material.

Effect of pH on Material Structure

Acidic medium (pH < 1): Silica gel with predominantly microporous and mesoporous structures is formed. The hydrolysis process occurs at a high rate, resulting in weakly branched polymer structures.

Alkaline medium (pH > 1.5): dense silica gel with pore sizes of 2 nm or larger and highly branched structures is formed. Condensation dominates over hydrolysis.

Effect of H₂O/TEOS Ratio: the H₂O/TEOS ratio significantly influences the hydrolysis rate and the resulting structure:

Low water ratios (H₂O/TEOS = 10–15); Produces dense gels with low porosity; High solution stability; Medium water ratios (H₂O/TEOS = 20–25)Leads to: the formation of colloidal particles.

Optimal stability. High water ratios (H₂O/TEOS = 30–35): results in porous materials but reduces solution stability.

**TABLE 1.** Solution Stability and H₂O/TEOS Ratio

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| № | Н2О/ TEOS ratio | Solution stability, hours | | |
| ±Δх | S | Sr\*102 |
| 1 | 5 | 15,2±0,2 | 0,16 | 1,0 |
| 2 | 10 | 22,9±0,3 | 0,24 | 1,0 |
| 3 | 15 | 39,0±0,7 | 0,56 | 1,4 |
| 4 | 20 | 68,6±0,8 | 0,64 | 0,9 |
| 5 | 25 | 71,7±0,5 | 0,40 | 0,5 |
| 6 | 30 | 63,6±0,6 | 0,48 | 0,7 |
| 7 | 35 | 41,9±0,6 | 0,48 | 1,1 |

Based on the data presented in the table, the stability of the solution depending on the water content passes through a maximum at H₂O/TEOS ratios of 20 to 25 mol per 1 mol of TEOS. Gas-sensitive materials obtained from solutions with H₂O/TEOS ratios of 20 and 25 were thermally treated at 120°C, 350°C, and 550°C, with each treatment lasting 30 minutes.

Observations: 1. Gas Sensitivity: the change in resistance of gas-sensitive materials in a gas-air mixture containing 0.1% ethanol showed similar values for H₂O/TEOS ratios of 20 to 25, ranging from 68.6 to 71.7. This indicates that films obtained with these ratios have comparable micropore volumes.

2. Microstructure: films formed at stoichiometric H₂O/TEOS values (20–25) and lower ratios exhibited notable porosity. The resistance of films in an atmosphere with 0.1% ethanol was 147 Ohms, supporting the formation of porous structures at these ratios.

Dopants and Gas-Sensitive Films: metal oxides were used as dopants due to their environmental safety, stability, and cost-effectiveness. Gas-sensitive nanocomposite films were synthesized based on titanium oxide and modifiers such as tin, cadmium, zinc, molybdenum, and copper oxides. The most suitable material composition for ethanol detection was TEOS/60%SnO₂ + 30%TiO₂ + 10%CuO. Electrical conductivity changes under ethanol exposure were studied to evaluate its potential as a gas-sensitive material.

Sensor Dynamics: the time required for the sensor to reach its maximum signal and return to its initial value under ethanol exposure characterizes its dynamic response. Results of dynamic indicators for ethanol detection (ethanol concentration: 500 mg/m³) are presented in Table 2.

**TABLE 2.** Dynamic Indicators of the Ethanol Sensor

|  |  |  |
| --- | --- | --- |
| GSF composition | Sensor detection time (τdet or τ09), sec | Sensor recovery time (τrec or τ01), sec |
| ТЭОС/100%SnO2 | 27 | 43 |
| ТЭОС/75%SnO2+25% TiO2 | 23 | 35 |
| ТЭОС/60%SnO2+30%TiO2+10%CuO | 12 | 21 |

Films synthesized with the selected composition exhibit high sensitivity to ethanol and favorable dynamic response characteristics.

The combination of SnO₂, TiO₂, and CuO provides optimal electrical and structural properties for gas sensor applications.

This research demonstrates the potential for developing efficient and cost-effective gas-sensitive materials based on nanocomposite films.

The minimum time required to reach the highest signal value for the sensor based on TEOS/60%SnO₂ + 30%TiO₂ + 10%CuO is 12 seconds. The recovery time for all gas-sensitive materials containing SnO₂, TiO₂, and CuO is in the range of 21 to 43 seconds.

The main absolute and relative error values for the ethanol detection process using a semiconductor sensor based on TEOS/60%SnO₂ + 30%TiO₂ + 10%CuO within a concentration range of 0-2.50% are presented in Table 4.

**TABLE 3.** Main Absolute and Relative Error Values of Ethanol Detection Process in a Semiconductor Sensor Based on TEOS/60%SnO₂ + 30%TiO₂ + 10%CuO in the Concentration Range of 0-2.50% (Temperature: 325°C, n=5, p=0.95)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| № | Added ethanol,  vol. % | Found alcohol, vol. % | The detected value of the error | |
| Main absolute error (Δ) | Main relative error (ϒ) |
| 1 | 0,25 | 0,24 | 0,01 | 0,5 |
| 2 | 0,50 | 0,49 | 0,01 | 0,5 |
| 3 | 0,75 | 0,74 | 0,01 | 0,5 |
| 4 | 1,00 | 1,02 | 0,02 | 1,0 |
| 5 | 1.25 | 1,27 | 0,02 | 1,0 |
| 6 | 1,50 | 1,49 | 0,01 | 0,5 |
| 7 | 1,75 | 1,73 | 0,02 | 1,0 |
| 8 | 2,00 | 2,03 | 0,03 | 1,5 |

These results demonstrate the accuracy and reliability of the sensor in detecting ethanol within the given concentration range.

According to the state standard, the allowable errors are as follows: main absolute error: Δ = ±0.25; Main relative error: ϒ = ±5.0.

From the table, the results obtained at a temperature of 325°C show that within the concentration range of 0.25–2.00%, the signal, which is dependent on the ethanol concentration in the mixture, follows a linear relationship and falls within the specified error limits.

**CONCLUSION**

Thus, based on the results of the conducted experiments, the gas-sensitive material for the semiconductor sensor selectively detecting ethanol from a gas mixture was selected as a nanocomposite with the composition TEOS/60%SnO₂ + 30%TiO₂ + 10%CuO. The sensor, developed on this composite, was found to have a signal dependent on the ethanol concentration within a wide range of concentrations. Gas sensors based on the SnO₂ + 30%TiO₂ + 10%CuO nanocomposite film demonstrated high sensitivity to ethanol. The results obtained at a temperature of 325°C, within the range of 0.25–2.00%, show a linear relationship between the signal and the ethanol concentration in the mixture, confirming the accuracy of the measurements within the acceptable error limits.

**REFERENCES**

1. Verezhnikov, V. N., Sedykh, V. A., Shabanova, N. A., Sergeeva, M. N., & Bederkin, M. S. (2008). Effect of dispersity and drying mode of silica on deformation-strength properties of latex films. Russian Journal of Applied Chemistry, 81(4), 682–686. <https://doi.org/10.1134/s1070427208040228>
2. Shabanova, N. A., & Sergeeva, M. N. (2011). Aggregative stability and structure formation in binary mixtures of synthetic latex and silica hydrosol. Russian Journal of Applied Chemistry, 84(8), 1422–1425. <https://doi.org/10.1134/s1070427211080222>
3. Yarullin, A. F., Kuznetsova, L. E., Yarullina, A. F., & Stoyanov, O. V. (2013). Electrophysical properties of oligomer-polymer complexes based on heat-resistant oligoaryleneamines. Polymer Science Series D, 6(2), 109–115. <https://doi.org/10.1134/s1995421213020172>
4. Eshkabilova, M., Abdurakhmanov, I. E., Muradova, Z., Abdurakhmanov, E., & Abdurakhmanova, Z. (2022). Development of selective gas sensors using nanomaterials obtained by sol-gel process. Journal of Physics Conference Series, 2388(1), 012155. <https://doi.org/10.1088/1742-6596/2388/1/012155>
5. Nikonorov, N., Ivanov, S., Dubrovin, V., & Ignatiev, A. (2017). New Photo-Thermo-Refractive Glasses for Holographic Optical Elements: Properties and Applications. In InTech eBooks. <https://doi.org/10.5772/66116>
6. Abdurakhmanov, E., Sidikova, K. G., Muradova, Z. B., & Abdurakhmanova, Z. E. (2021). Development of a selective carbon monoxide sensor. IOP Conference Series Earth and Environmental Science, 839(4), 042078. <https://doi.org/10.1088/1755-1315/839/4/042078>
7. Anuchkin, S. N. (2020). Interaction of exogenous refractory nanoparticles of Al2O3 and MgAl2O4 with nonferrous metal impurities in iron melts. IOP Conference Series Materials Science and Engineering, 848(1), 012005. <https://doi.org/10.1088/1757-899x/848/1/012005>
8. Filin, S., Rogalin, V., & Kaplunov, I. (2023). Methods of stabilization of halogenated hydrocarbons during automated physico-chemical cleaning of metal-optics. Procedia Structural Integrity, 50, 91–99. <https://doi.org/10.1016/j.prostr.2023.10.026>
9. Mazalova, V. L., Soldatov, A. V., Adam, S., Yakovlev, A., Möller, T., & Johnston, R. L. (2009). Small copper clusters in AR shells: A study of Local structure. The Journal of Physical Chemistry C, 113(21), 9086–9091. <https://doi.org/10.1021/jp809401r>
10. Madkour, L. H. (2019). Introduction to Nanotechnology (NT) and Nanomaterials (NMS). In Advanced structured materials (pp. 1–47). <https://doi.org/10.1007/978-3-030-21621-4_1>
11. Domingos, R. F., Tufenkji, N., & Wilkinson, K. J. (2009). Aggregation of titanium dioxide nanoparticles: role of a fulvic acid. Environmental Science & Technology, 43(5), 1282–1286. <https://doi.org/10.1021/es8023594>