SYNTHESIS OF GAS-SENSITIVE NANOCOMPOSITE METAL OXIDE FILMS FOR SEMICONDUCTOR SENSORS OF NATURAL GAS AND METHANE

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Abstract: This study presents the synthesis, characterization, and gas-sensing performance of nanocomposite metal oxide films designed for the detection of natural gas and methane. Using sol-gel and hydrothermal methods, thin films composed of metal oxides such as SnO_2, ZnO, and WO_3, doped with catalytic elements (e.g., Pd, Pt, or Cu), were fabricated and deposited onto silicon and alumina substrates. The nanocomposites exhibited controlled grain sizes ranging from 10 to 50 nm, enhancing surface area and reactivity. Morphological and structural analyses using SEM, XRD, and TEM confirmed homogeneous dispersion and crystallinity. Electrical measurements demonstrated significant sensitivity and selectivity toward methane (CH_4) at low operating temperatures (150–300 °C), with response times under 30 seconds and rapid recovery. The influence of dopants, film thickness, and operating temperature on sensor performance was systematically evaluated. The results highlight the potential of engineered nanocomposite metal oxide films in developing low-cost, high-performance semiconductor sensors for early detection of methane leaks in industrial and residential settings.

Keywords: Nanocomposite metal oxides, Gas sensors, Methane detection, Natural gas sensing, Semiconductor sensors, SnO_2, ZnO, WO_3 Sol-gel synthesis, Hydrothermal method.

Annotatsiya: ushbu tadqiqot tabiiy gaz va metanni aniqlash uchun mo'ljallangan nanokompozit metall oksidi plyonkalarining sintezi, xarakteristikasi va gazni sezish ko'rsatkichlarini taqdim etadi. Sol-gel va gidrotermik usullardan

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foydalangan holda, metall oksidlaridan tashkil topgan ingichka plyonkalar SnO_2, ZnO va VOEXPRESS, katalitik elementlar bilan qo'shilgan (masalan, Pd, Pt yoki Cu), uydirma va kremniy va alumina substratlariga yotqizilgan. Nanokompozitlar 10 dan 50 nm gacha bo'lgan boshqariladigan don o'lchamlarini namoyish etdi, bu sirt maydoni va reaktivligini oshirdi. Sem, XRD va TEM yordamida morfologik va strukturaviy tahlillar bir hil dispersiya va kristallikni tasdiqladi. Elektr o'lchovlari past ish haroratida (150-300) metanga nisbatan sezilarli sezgirlik va selektivlikni namoyish etdi.30 soniya va tez tiklanish. Dopantlar, plyonka qalinligi va ish haroratining sensorning ishlashiga ta'siri muntazam ravishda baholandi. Natijalar ishlab chiqarilgan nanokompozit metall oksidi plyonkalarining sanoat va turar-joy sharoitida metan oqishini erta aniqlash uchun arzon, yuqori samarali yarimo'tkazgichli sensorlarni ishlab chiqish imkoniyatlarini ta'kidlaydi.

Kalit so'zlar: Nanokompozitli metall oksidlari, gaz sensorlari, metanni aniqlash, tabiiy gazni aniqlash, yarimo'tkazgichli sensorlar, SnO_2, ZnO, VOEXPRESS Sol-gel sintezi, gidrotermal usul.

Аннотация: В данном исследовании представлены результаты синтеза, характеристики и газочувствительные характеристики нанокомпозитных пленок оксидов металлов, предназначенных для обнаружения природного газа и метана. Используя золь-гель и гидротермальные методы, были изготовлены тонкие пленки, состоящие из оксидов металлов, таких как sno_2, ZnO и wo_3, легированных каталитическими элементами (например, Pd, Pt или Cu), и нанесены на подложки из кремния и алюминия. Нанокомпозиты демонстрировали контролируемый размер зерен в диапазоне от 10 до 50 нм, что увеличивало площадь поверхности и реакционную способность. Морфологический и структурный анализы с использованием СЭМ, рентгенографии и ПЭМ подтвердили однородную дисперсию и кристалличность. Электрические измерения продемонстрировали значительную чувствительность и селективность по отношению к метану (ch_4) при низких рабочих температурах (150-300 °C), время отклика составило менее 30 секунд, а восстановление было быстрым. Систематически оценивалось влияние добавок, толщины пленки и рабочей температуры на характеристики датчика. Полученные результаты подчеркивают потенциал инженерных нанокомпозитных пленок оксида металла в разработке недорогих и высокопроизводительных полупроводниковых датчиков для раннего обнаружения утечек метана в промышленных и жилых помещениях.

Ключевые слова: Нанокомпозитные оксиды металлов, Газовые сенсоры, обнаружение метана, Обнаружение природного газа, Полупроводниковые сенсоры, sno_2, ZnO, wo_3 Золь-гель синтез, гидротермальный метод.

Introduction:

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The growing interest in methane sensors can be attributed to their broad application in various fields such as ecology, chemical industries, petrochemicals, and safety engineering. Metal oxides are increasingly being used as sensitive elements in semiconductor sensors. For methane sensors, metal oxides such as zinc, iron, nickel, cobalt, indium, and silver are often recommended as the semiconductor material [108; pp. 164-187]. Depending on the specific requirements, different methods are employed to produce gas-sensitive films that offer stable and reproducible characteristics, with sol-gel technology being one of the most commonly used techniques.

The sol-gel method for producing gas-sensitive films is particularly promising for fabricating materials used in sensitive elements of semiconductor gas sensors. When combined with subsequent heat treatment of the reaction products, this method is widely employed to create oxide composite materials. The sol-gel process most commonly relies on controlled hydrolysis of alkoxide compounds, where the alkoxide-based method involves hydrolytic polycondensation of precursors followed by drying. In the initial phase of hydrolysis, hydroxy derivatives of organosilicon compounds are formed, with hydroxyl groups directly bonded to silicon. These compounds then undergo polycondensation, creating a polymeric network composed of silicon and oxygen atoms.

METHODS: When producing modified or mixed oxide materials for the sensitive elements of gas sensors, the sol-gel method is more advantageous than traditional film deposition and sintering techniques. Unlike these traditional methods, sol-gel technology allows for a more flexible control over the structural-phase states of oxide systems by adjusting synthesis conditions, component ratios, and heat treatment processes. This method is easy to implement, does not require expensive or complex equipment, operates at low temperatures, ensures stoichiometry of compounds, and allows for precise control over the introduction of impurities. Moreover, it enables the control of the material's thickness, composition, and microstructure.

To obtain a selective gas-sensitive layer through the sol-gel method, strict adherence to process sequence and conditions is essential. It is crucial to develop controlled and reproducible processes for producing a given nanostructure and ensuring the appropriate properties for the gas-sensitive layer. Despite the advantages of the sol-gel approach, there is a lack of systematic studies in the scientific and technical literature regarding the optimization of sol-gel synthesis for gas-sensitive films used in semiconductor methane sensors. Thus, conducting research and developing guidelines for the synthesis of nanocomposite films based on this method is a promising direction for producing advanced materials for methane sensors.

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To develop a method for creating gas-sensitive films with specified properties and sensor elements based on composite materials, the following sequence should be followed: synthesis conditions → morpho-structure → material properties → sensor output parameters. Achieving this pattern requires a comprehensive investigation of the composite materials' properties, which should include studies on the formation kinetics, morphology of films, and their electrical properties using modern analytical equipment.

Key parameters for determining the transition of a sol-based film-forming solution into a gel include viscosity, electrical conductivity, and the stability of the initial solution. Therefore, the kinetics of structural formation in sols are often studied by measuring the viscosity and electrical conductivity of the initial solutions. In this study, we used capillary viscometry to assess the solution's stability. As per GOST 33-2000 (ISO3104-94), the viscosity determination method involves measuring the flow time in seconds of a specific volume of liquid under gravity at a constant temperature using a calibrated glass viscometer. For all viscometers, the flow time of a given liquid volume is directly proportional to its kinematic viscosity (ν).

Additional monitoring of hydrolysis and condensation processes was carried out periodically by determining the alcohol and water content in the reaction mixture. The water content was determined via titration with Fischer reagent, while the alcohol content was analyzed by gas chromatography.

Alkoxide solutions in organic solvents, water, and acid, referred to as hydrolysates, develop film-like properties over time, ranging from several hours to months, depending on the solution's composition. To produce nanocomposites, inorganic additives (e.g., metal salts) are introduced into the primary components. The inclusion of such additives enables the creation of sensitive and selective nanocomposites. These composites are formed by embedding metal oxides into the silicate matrix. Altering process conditions, such as temperature, pH, component ratio, and concentration, provides effective regulation of phase composition, particle size, and shape.

The most important parameters in synthesis include the concentration of initial substances, temperature, pH, and the method of mixing the components. Consequently, in our experiments, we examined the influence of composition, component ratios, and temperature on the viscosity, density, electrical conductivity, and stability of the film-forming solution, as well as on the sensitivity and selectivity of the semiconductor films.

RESULTS: In the experiments, the primary focus was on the stages involved in preparing the solution: forming a stable sol, transforming the sol into a gel-like state, and producing oxide films with gas-sensitivity properties. Based on experimental data, which

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examined the effects of various factors such as composition, ratios, temperature, time, and homogenization intensity on the sol-gel process, a method for controlling the processes of producing sensitive films for gas-sensing applications was developed.

The optimization of the sol-gel synthesis of gas-sensitive films is typically conducted through empirical methods, utilizing experimental design techniques within a multifactorial space. The key to success lies in selecting the initial values of critical experimental factors and determining the appropriate variation steps. The molar ratios of the initial components were varied within the following ranges: $Si(OC_2H_5)4:H_2O:ROH:HX = (1-4):(1-40):(1-45):(0.01-0.3)$, where ROH refers to simple alcohols, and HX represents an acid. Aliphatic alcohols, such as ethanol, propanol-2, and isobutanol, were used as organic solvents because of their good solubility for TEOS and most metal salts used as dopants.

In experiments investigating the effect of solvent type on the sol maturation kinetics, the ratio of TEOS to alcohol was varied from 1:1 to 1:45. The change in this ratio was achieved by adding the required amount of alcohol to the initial solution. The results demonstrated that as the solvent content in the hydrolysate increased, the viscosity of the solution decreased for all the tested systems. The viscosity of the hydrolysate, within the range of TEOS: alcohol ratios from 1:1 to 1:45, fluctuated as follows: for ethanol, from 3.10 to 1.85 cPa; for propanol-2, from 3.20 to 1.90 cPa; and for isobutane, from 3.30 to 1.95 cPa. For all alcohols studied, the viscosity change in the solution correlated with the molecular weight of the alcohol. Notably, a significant viscosity change occurred when the alcohol/TEOS ratio was up to 30, after which the viscosity changed less noticeably with further increases in the ratio.

As the ratio of TEOS to ethanol in the solution increased from 1:1 to 1:45, the density (ρ) of the solution decreased from 0.9783 to 0.8350, a reduction of 1.172 times. The most substantial decrease in density occurred for the ethanol/TEOS range up to 30 mol. For isopropanol and isobutane solutions, the density decreased by 1.129 and 1.169 times, respectively, when the alcohol/TEOS ratio increased from 1 to 45.

The stability of the solution also varied depending on the composition and amount of solvent (ethanol) present in the hydrolysate. For all tested solvents (isopropanol and isobutane), a similar trend was observed: increasing the solvent content up to a certain point enhanced the stability of the solution and slowed down the gelation process. However, beyond a certain alcohol content, the stability period of the solution decreased. In ethanol solutions, the stability period ranged from 4 to 18.5 days, depending on the TEOS: ethanol ratio. The highest stability (18.5 days) was observed at a TEOS: ethanol ratio of 30-35, while further increasing the ratio to 1:45 resulted in a slight reduction in stability (down to 17.5 days). For isopropanol solutions, the stability varied from 5 to 20.5 days, and for isobutane solutions, it ranged from 6 to 21.5 days. The maximum stability

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for propanol and butanol solutions occurred at TEOS: alcohol ratios of 1:35 and 1:40, respectively.

The highest stability and viscosity for the ethanol solution were observed at a TEOS: ethanol ratio of 1:30. At this ratio, the viscosity remained stable for up to 450 hours, making it suitable for manufacturing a gas-sensitive element for a semiconductor sensor. The composition of the solvent significantly influences the solution's stability. As the molecular weight of the alcohol increases (from ethanol to butanol), the gelation transition time increases from 18.5 to 21.5 days. Under similar conditions, a higher molecular weight alcohol results in greater solution stability. Additionally, adjusting the water content in the solution allows for the regulation of gelation time from 5 to 18.5 days, which controls the dispersion of the sol and the depth of TEOS polymerization. The optimal ratio for water to TEOS is 20, ensuring sufficient solution stability and homogeneity when a dopant is included.

The introduction of metal oxide dopants such as Zn, Fe, Co, Ni, In, Ag, and others into a silicate matrix enables the production of highly sensitive and selective nanocomposites for use in chemical sensors detecting combustible gases. Thin-film layers based on these metal oxides show promising characteristics but have been less explored in previous studies. The research focused on investigating the processes involved in the formation of structure in TEOS-based sols when doped with a ZnO-based additive.

In the experiments, double-distilled TEOS and pure ethyl alcohol were used, with zinc chloride ($ZnCl_2$) serving as the source of the modifying metal oxide. The preparation of the sols for the creation of gas-sensitive thin films was carried out in three stages. In the first stage, the exchange interaction between tetraethoxysilane (TEOS) and ethanol (referred to as Solution 1) was performed at room temperature for 30 minutes. Specifically, a mixture of TEOS and ethyl alcohol was prepared in a test tube in a predefined ratio. For the sol solution, the ratio of ethanol to TEOS was set at 30, where 88.5 ml of 96% ethanol (equivalent to 85.0 ml of absolute ethanol) was combined with 10.0 ml of freshly distilled TEOS. The mixture was vigorously stirred for 30 minutes at 20°C.

In experiments aimed at studying the impact of the dopant on the sensitivity and selectivity of the resulting nanocomposite, the molar ratio of SiO_2 to ZnO in the sol was varied between 1:0.1 and 1:2.0. It was observed that the dynamic viscosity of dopant-containing solutions (3.8 cPa) was higher than that of the solution without the dopant (2.1 cPa). Additionally, the stability period of the solutions with the dopant was shorter compared to those without. Specifically, when ZnO was added to the solution with the composition $TEOS:H_2O:C_2H_5OH:HCl = 1:20:30:0.05$ (and a SiO_2/ZnO ratio of 2), there was an increase in viscosity along with a decrease in the stability period. The kinetic

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relationship between viscosity changes and the experiment duration for dopant-containing solutions is illustrated in Figure 4.1.

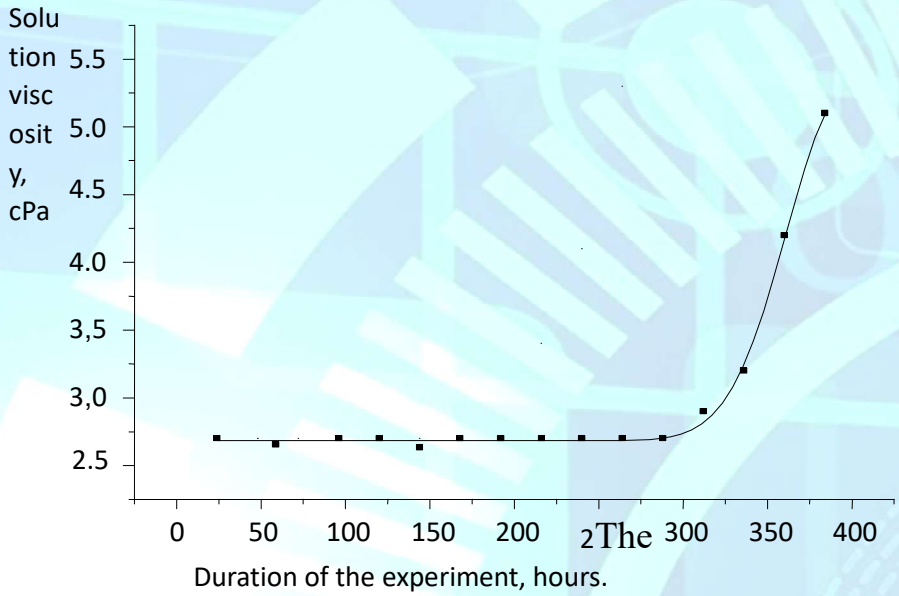


Fig.4. 1. Dependence of the viscosity of $ZnCl_2$-containing solutions on the duration of the experiment

As follows from the data presented in Fig. 4.1, the dopant-containing solution is characterized by a certain period of stable values of the solution viscosity, ensuring the formation of a homogeneous gas-sensitive film. The results of experiments to determine the effect of the amount of dopant on the properties of the solution were carried out in the range of SlO2: ZnO ratios from 1.0:0.1 to 1.0:2.0. The results of the experiments are presented in Table 4.2.

Table 4.2.

Effect of dopant amount on solution properties

№	SiO_2:ZnO	Knitting, spa	Stability, days
1	1.0:0.1	2.4	15.5
2	1.0:0.4	2.6	14.5

The data indicates that in the investigated Tetraethyl orthosilicate (TEOS) solutions with added dopants, the gelation rate of the sol varies widely depending on the composition and quantity of the dopant. Experimental results show that the viscosity of sols with a dopant is higher compared to the corresponding sols without any dopant. In all the systems studied, increasing the metal oxide content in the solution led to a rise in viscosity. Furthermore, the stability of the doped systems is inversely proportional to the amount of metal oxide present, meaning that as the dopant concentration increases, the stability of the solution decreases.

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In solutions with SiO2:MexOy ratios ranging from 1.0:0.1 to 1.0:2.0 (in moles), the solution's stability decreases by a factor of 2.6 when using ZnCl2 as the dopant. This suggests that a higher dopant content results in a shorter lifespan for the solution. Films were produced from the zinc-containing solutions by applying them to glass substrates. The film was applied by pouring the solution onto the substrate and then centrifuging at 2000 rpm. The resulting films adhered firmly to the glass surface. When the zinc oxide content exceeded 10%, the films began to develop a more pronounced crystalline structure. After annealing the films at 450°C, those made from this specific sol composition showed the highest degree of crystallinity. Increasing the annealing time from 30 minutes to 60 minutes also led to an increase in pore size, although the overall porosity of the film decreased.

CONCLUSION: This suggests that the presence of an inorganic modifying additive in the sol helps form pores in the resulting silicate films. In this case, the dopant acts similarly to a loosening agent in the inorganic polymer structure, as seen in glass-making processes. Our research further revealed that when applying gas-sensitive coatings derived from TEOS solutions containing inorganic zinc compounds, it is crucial to maintain the environmental temperature at least between 20-25°C and ensure the relative humidity remains between 55-60%.

Therefore, the study demonstrates that using sol-gel technology enables the creation of gas-sensitive films based on metal oxides. These films exhibit sensitivity to flammable and toxic gases, including methane. The semiconductor sensor elements developed from these films can be utilized in air quality monitoring systems, particularly for hazardous zones in industrial settings.

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