

Effect of Composition and Formation Conditions on Characteristics of Ammonia Sensor

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Abstract:

The properties of nanostructured SiO_x films doped with Dawson-type heteropolycompounds at room temperature in clean air and in air containing ammonia were examined. It was studied adsorption activity of the sensors and found that the films formed at the surface of electrodes have a highly developed surface with nano-size pores. It has been shown that heteropolyanion composition and cation type have a significant influence on a sensor behavior of doped films. The study shows that the conditions of the environment affect the sensors characteristics markedly, which can be improved by choosing of the right procedure of forming and processing.

Key words: nanostructured film, Dawson-type polyoxometalate, ammonia

Introduction

Sorption type sensors based on complex composition sorbents, which represent a matrix of basic sorbent activated with various additives, hold a special position among the microelectronic gas sensors. It is wise to select a nanostructure matrix of basic sorbent, into which some adjuvant is incorporated, as a base element of the sensor. The adjuvant helps to promote or provide the formation of analytic signal when the sorbent surface interacts with variable composition gas environment.

Nano-size SiO_x films doped with catalytic additives are the most promising materials for gas sensitive layers of microelectronic chemical sorption sensors [1, 2]. Different mechanism may exist to increase a gas sensitivity of activated oxide films depending on additive type and conditions of their formation.

Heteropolycompounds (HPCs) attract a special attention among various substances that can be used as the sensor's components of active layer because of unique combination of their various physical and chemical properties. HPCs are widely used in heterogeneous catalysis and analytical chemistry as catalysts for reduction-oxidation processes [3, 4]. HPCs are classified as complex polyoxocompounds. HPC redox properties can be varied in wide ranges by changing a heteropolyanion composition. These compounds can act as reversible reagents in the reactions of ligand exchange and redox transformations, accompanied by changes in

current carrier concentration or catalysts of such transformations that can be used in chemical sensors. HPCs can be incorporated directly into the initial matrix of basic sorbent to improve gas sensitivity and selectivity and to reduce intrinsic resistance of sorption nanostructure films.

Modifying the surface of initial sorbent or using the complex composition sorbents is one of the most efficient methods to change the properties of sorption films. Thus, considering that the same base sorbent can be used in various types of sensors, it is possible to specify a general requirement for a method to produce gas-sensitive layers for microelectronic gas sensors. The method must provide a reproducible formation of the thin high-porous nano-size films with complex composition and highly developed specific surface on the substrate at minimum possible temperature. In our opinion, the method of hydrolytic polycondensation of solutions of various organometallic compounds optimally meets the above listed requirements when producing activated SiO_x films. It was selected to form doped sensitive layers of gas sensors as one of the most cost effective and manufacturable methods of thin oxide films production, including ones with complex composition [6, 7].

This paper examines an effect of composition and formation conditions on sensitivity of nanostructured silica films doped with Dawson-type heteropolycompounds for ammonia.

Experimental

The method of hydrolytic polycondensation from tetraethyl orthosilicate solutions was used for forming nanostructured doped films in this work. Analytical pure reagent TEOS was used to prepare the porous silica gel films. TEOS was thoroughly mixed with alcohol and water. Various quantities of HPCs were used to polymerization of the TEOS to form a sol solution.

Composite films were deposited to 15.0 x 5.0 mm test structures with a system of interdigital metal electrodes formed at their surface (see Fig. 1); active zone of the sensor was 4.0 x 4.0 mm.

Different composition heteropolycompounds incorporated into the initial solution. The conditions of film formation varied during the tests: solution composition, temperature, and application modes. Standard gas mixtures (MGPZ, Russia), Dräger test gas ampoules (Dräger, Germany) and Environics – 4000 gas-mixture generator (Environics, USA) were used to measure the properties of sensors. Electrical parameters of the sensors have been measured electronically in real-time mode.

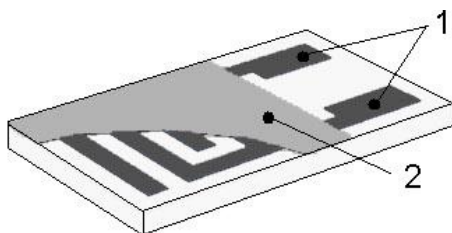


Fig. 1. Test structure for measurements:
1-interdigitated electrodes; 2-nanostructured film.

Results

The introduction of various synthesized polyoxometalates into SiO_x films results in selectivity and high sensitivity to NH_3 . The composition of heteropolyanion and cation type markedly influence on sensor behaviour of complex film (see Fig. 2).

Increase of sensitivity and selectivity of such sensors can be received owing to complexing reaction of tested substance with cationic part of polyoxometalate. This fact results in intramolecular redox reaction which sharply change electrophysical properties of polyoxometalate. Thereby sensitive film's characteristics modify. This process is reversible. It was determined that gas sensitivity increases with rise of molybdenum content in polyoxometalate molecule. Such behaviour is explained by higher reactivity of molybdenum than tungsten.

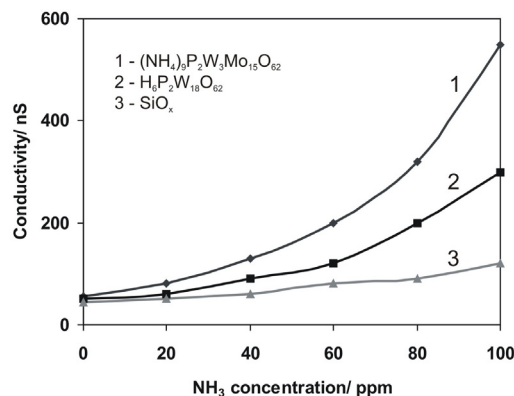


Fig. 2. Typical conductivity dependence of doped SiO_x films on ammonia content in air.

The composition with 30 – 50% of the weight content of doping additive in silica matrix enables to obtain a maximum sensitivity to measured gas. It may suppose that the conductivity increase at weight content of modifying admixture less than 50 % connects with increase of charge carriers in the film. Some quantity of extended state protons corresponds to each molecule of polyoxometalate in the film. They can make considerable contribution to proton surface conductivity. It is evident that conductivity decrease of sorption films at weight content of admixture more than 50 % is explained by crystal aggregation of admixture in film volume. The polyoxometalates don't display their catalytic activity at weight content less than 10 % in the film.

It was established that films have highly developed surface with nanoscale pores. The thickness of the doped SiO_x layers was 0,2-0,3 μm . The adsorption activity of sensors has been studied using quartz crystal microbalance (see Fig. 3).

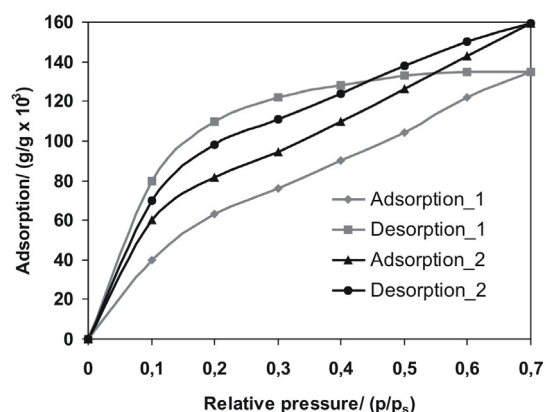


Fig. 3. Adsorption isotherms of ammonia on doped SiO_x films (298 K): 1- $(\text{NH}_4)_9\text{P}_2\text{W}_{18}\text{Mo}_{15}\text{O}_{62}$; 2 – $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$.

It has been found that the films had a highly developed surface with nano-size pores. The

average size of pores was 2-3 nm. The rating value of specific surface measured for sensitive layer is 400–450 m²/g for different samples.

The study shows that the conditions of the environment affect markedly the sensors stability, which can be improved by choosing of the right procedure of forming and processing. Forming process of film is long. However introduction of heteropolycompound into film composition makes for film's mass stabilization. The basic rules of films formation remain at that (see Fig.4).

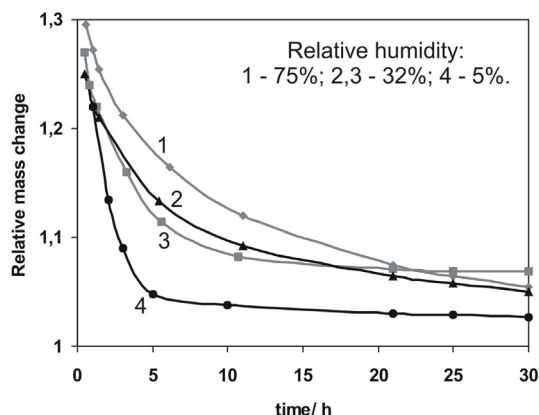


Fig. 4. Dependence of mass change of SiO_x films on time: 1, 2, 4 – undoped silica film; 3 – silica film doped by H₆P₂W₁₈O₆₂.

The temperature increase stabilization of film (see Fig. 5). So, decreasing of environment humidity and temperature treatment lead to acceleration of hydrolytic polycondensation of solutions and stabilization of sensitive films at right conditions.

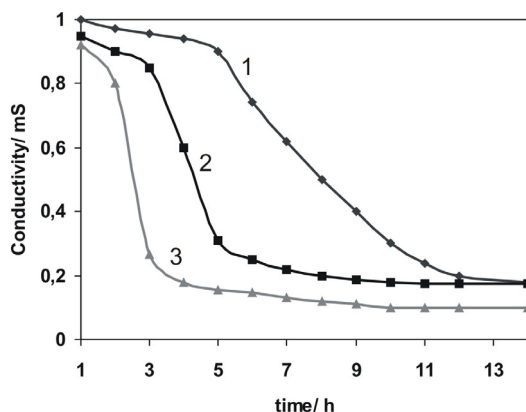


Fig. 5. Conductivity changes for silica film doped by (NH₄)₉P₂W₃Mo₁₅O₆₂: 298 K (1), 353 K (2), 423 K (3).

Threshold sensitivity to NH₃ is 0.5 – 1.0 ppm for SiO_x/(NH₄)₉P₂W₃Mo₁₅O₆₂ sensors; range of measured concentrations – 1–100 ppm; and response time – 20 s. Important property of the sensors consists in their ability to operate at room temperature, and this provides indisputable advantages for the development

and operation of control instruments on their basis.

Conclusion

Inorganic oxide films activated with different admixtures are used as the most perspective sensitive layers for sensors working at room temperature. The sensor properties of films can be varied considerably by introducing different activated or modifying admixtures into them and by film formation technologies. The film activation method which consists in adding of admixture to the base sorbate, with the following adsorption of determined gas on the film surface and selective reaction between admixture and gas, allows approaching for selectivity problem solution. Activated nanostructured SiO_x films at appropriate conditions can get specified sensor properties.

The polyoxometalates based sensor films may be used for measurements of atmosphere content in ecological monitoring system, in industrial applications, in different medical and biological researches.

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