Silicon dioxide films prepared by the sol-gel method for use in elements of microsystem technique

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Abstract. Silicon dioxide films prepared by the sol-gel method from a solution based on tetraethoxysilane by spin-coating and subsequent thermal annealing in the temperature range from 200 to 600 °C are considered. The transmission spectra of the pure and impregnated with methyl orange silicon dioxide films are studied. It was found that the transmission of the all films depends on the annealing temperature and the impregnated films have the lower transmission than the pure ones. Studying the transmission difference between the pure and impregnated films in the band at 464 nm, corresponding to the highest absorption of methyl orange, it was determined that films annealed at 400 °C have the highest porosity.

Keywords: sol-gel method, tetraethoxysilane, silicon dioxide film, impregnated film, methyl orange, transmission spectrum, porosity

1. Introduction
MEMS devices widely use layers with various properties which perform manifold functions. Among these layers there are porous ones. They implement the following functions in microsystem elements: structural layers; heat-insulating layers; adsorption layers; membrane layers; layers for functional groups incorporation; immobilization layers (matrices). The following porous layers are widely used in microsystems: porous silicon [1, 2], porous silicon dioxide (silica) [3-5], silica gel, porous titanium dioxide [6], porous aluminium oxide [7, 8].

Porous layers with controlled porosity are created by the following main methods: electrochemical oxidation or etching and sol-gel one. The electrochemical oxidation is used to obtain the porous aluminium oxide and titan dioxide. The electrochemical etching of silicon allows one to create porous silicon layers on its surface. Using the sol-gel method makes it possible to obtain porous layers of various materials on any surface. Therefore, this method is now regarded as one of the most suitable means to fabricate porous layers for various applications in microsystem technique [9].

2. Formation of the problem
An important parameter in preparation of porous layers is the control of their porosity. The basic parameters characterizing the porosity are the fraction of the pore volume over the total volume and the nature of porosity depending on pore size (average size of pores). The sol-gel method allows one to control both the parameters of the obtained porous layers. The porosity of sol-gel layers and films depend on all stage of their formation beginning with preparation of the solutions and ending the thermal annealing. An important role in obtaining sol-gel films is assigned to the thermal treatment. It is final stage and is carried out at high temperatures, which have a significant effect on the porosity of
these films. Nevertheless, the role of the previous stages in the formation of porous sol-gel films must not be underestimated. To obtain the sol-gel layers with maximal porosity it is necessary to investigate their porosity as a function of the thermal treatment with taking into account the concrete conditions on the previous stages.

In this connection, the goal of the paper is to present the method makes it possible to determine the temperature of thermal annealing at which maximum porosity of the layer is achieved under specific conditions at other stages of the sol-gel process. As an example, we will consider porous films of silicon dioxide obtained by the sol-gel method.

3. Experimental setup
The sol solution for obtaining the silicon dioxide films was prepared based on tetraethoxysilane (TEOS). Water and ethanol were used as solvent. TEOS, water, ethanol and hydrochloric acid were mixed together and stirred during 90 minutes. For preparing the solution we used the following molar ratio between the components: TEOS:H₂O:C₂H₅OH:HCl=1:16:4:0.08.

The silicon dioxide films were obtained by spin coating method from the solution with the aging time of 72 hours. Fused quartz plates with thickness of 0.5 mm were used as substrates. The resulting films were annealed for 15 minutes at temperatures of 200-600 °C.

For determining the porosity of the obtained sol-gel silicon dioxide films they were impregnated with methyl orange solution [10]. This process was performed by dip-impregnation method.

The UV-Vis-IR transmission spectra of the obtained pure and impregnated sol-gel silicon dioxide films are recorded in the wavelength range of 190 - 1100 nm using the spectrophotometer SF-56 (OKB SPECTR LLC).

4. Results and discussion
The transmission spectra of sol-gel silicon dioxide films annealed at various temperatures are shown in Figs. 1-6. The spectra of these films impregnated with methyl orange are also presented here. The transmission spectrum of the methyl orange solution used to impregnate silicon dioxide films is shown in Fig. 7. The main absorption band of the used methyl orange solution is 464 nm. This can see from its UV–Vis–IR transmission spectrum (Fig. 7).

Figure 1. Transmission spectra of the pure and impregnated non-annealed sol-gel silicon dioxide films.
Figure 2. Transmission spectra of the pure and impregnated sol-gel silicon dioxide films annealed at 200 °C.

Figure 3. Transmission spectra of the pure and impregnated sol-gel silicon dioxide films annealed at 300 °C.

The non-annealed silicon dioxide films have higher transmittance (Fig. 1) than annealed ones. With increasing the annealing temperature from 200 to 600 °C the transmission of the silicon dioxide films increases. This is clearly confirmed by the data presented in Fig. 8. The transmission of pure silicon dioxide films in the band of 464 nanometers increases monotonously with increasing the annealing temperature.

The sol-gel silicon dioxide films impregnated with methyl orange have lower transmittance than the pure films (Figs. 1-6). The transmission of the impregnated films in the band of 464 nanometers as a function of the annealing temperature is presented in Fig. 8. The nature of this dependence differs from that for pure films. It has a minimum at the annealing temperature equal to 400 °C. Such a behavior of silicon dioxide films impregnated with methyl orange can be explained the feature of their...
structure. The silicon dioxide films obtained by sol-gel method have the porous structure the porosity of which varies depending on the composition of the initial solution and the annealing conditions. The structure of the non-annealed silicon dioxide films is close to a xerogel one. Xerogels have the high porosity with very small pore size (1–10 nm). At low-temperature annealing of nanoporous films, water and ethanol are removed from the outer surface of the xerogel particles and process of forming the pores of various dimensions by coalescence of nanopores begins. With increasing the temperature annealing of the sol-gel films the process of forming the pores continues and their sintering process begins. In the sintering process the porosity of the films and their volume decrease. Obviously, at a certain annealing temperature, the films will have the greatest porosity. For the sol-gel silicon dioxide films under investigation, the indicated temperature corresponds to the maximum difference between the transmission of the pure and impregnated films in the maximum absorption band of methyl orange (464 nm). The dependence of the difference between the transmission of the pure and impregnated silicon dioxide films on their annealing temperature is shown on Fig. 9. This dependence exhibits that the maximum difference between the transmission of the pure and impregnated silicon dioxide films is observed for films annealed at the temperature of 400 °C. From this it follows that the sol-gel silicon dioxide films annealed at the given temperature have maximum porosity.

![Figure 4](image_url)

**Figure 4.** Transmission spectra of the pure and impregnated sol-gel silicon dioxide films annealed at 400 °C.

5. Conclusion
In the paper, the silicon dioxide films were prepared by the sol-gel method and their transmission spectra were investigated. An analysis of the transmission spectra exhibited that with increasing the annealing temperature of the films, their transmission increases. From comparison of the transmission spectra of the pure silicon dioxide films and the films impregnated with methyl orange, it was found that the highest porosity is observed in films annealed at 400 °C.

The presented data show that it is possible to use the method of comparing the transmission spectra of sol-gel films to determine the optimal annealing temperature at which the ones have the maximum porosity. However, it is necessary to take into account the composition of the initial solution used for film coating and the conditions of its preparation.
Figure 5. Transmission spectra of the pure and impregnated sol-gel silicon dioxide films annealed at 500 °C.

Figure 6. Transmission spectra of the pure and impregnated sol-gel silicon dioxide films annealed at 600 °C.
Figure 7. Transmission spectrum of methyl orange solution.

Figure 8. Annealing temperature dependences of the transmission of the pure and impregnated sol-gel silicon dioxide films in the band of 464 nm: 1 – pure films; 2 – impregnated films.
Figure 9. Annealing temperature dependence of the transmission difference between the pure and impregnated sol-gel silicon dioxide films in the band of 464 nm.

References
[1] Sailor M J 2012 Porous Silicon in Practice (Weinheim: Wiley-VCH Verlag)
[2] DeLouise L A and Miller B L 2005 Analytical Chemistry 77 1950
[3] Kandimalla V B, Tripathi V S and Ju H 2006 Critical Reviews in Analytical Chemistry 36 73
[4] Hartmann M and Kostrov X 2013 Chemical Society Reviews 42 6277
[5] Chaudhari P S, Gokarna A, Kulkarni M, Karve M S and Bhoraskar S V 2005 Sensors and Actuators B 107 258
[6] Yu J and Ju H 2002 Analytical Chemistry 74 3579
[7] Milka P, Krest I and Keusgen M 2000 Biotechnology and Bioengineering 69 344
[8] Nofz M 2018 Alumina Thin Films Handbook of Sol-Gel Science and Technology. Processing, Characterization and Applications vol 1, ed L Klein, M Aparicio and A Jitianu (Cham: Springer) pp 765-808
[9] Sakka S 2018 The Outline of Applications of the Sol-Gel Method Handbook of Sol-Gel Science and Technology. Processing, Characterization and Applications vol 3, ed L Klein, M Aparicio and A Jitianu (Cham: Springer) pp 1905-1937
[10] Ponchel A, Abramson S, Quartararo J, Bormann D, Barbaux Y and Monflier E 2004 Microporous and Mesoporous Materials 75 261