Multilayer sensor structure based on porous silicon

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The work is devoted to the creation of a sensor structure based on a porous silicon membrane. The structure under study integrates a porous layer used as a gas transport layer and a gas sensitive layer of non-stoichiometric tin oxide. The paper investigates the morphology of the structure and shows the gas permeability of the membrane on porous silicon. The gas sensitivity of the test structure obtained by passing a gas-air mixture containing NO_2 has been studied.

Keywords: porous silicon, membrane, non-stoichiometric tin oxide, thin films, resistive gas sensor.

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1. Introduction

Porous silicon is obtained by anodic etching of single-crystal silicon plates [1,2]. Anodic etching allows for synthesizing of porous layers of different morphology, pore geometry, thus making porous silicon quite an important material for various applications. At present, porous silicon is used as a material for creating thermoelectric energy converters [7], gas sensors [8]. The possibility to form an array of channels having different diameters opens up prospects of porous layer application as porous membranes [9,10]. Thereat, a structure with a vertical hierarchy can be created, where porous layers are perpendicular to the stream of the analyzed gas mixture. Subsequently it is possible to form structures with absorbing and filtering layers which increase gas sensor selectivity.

An important aspect for gas microsensors is the possibility to create integrated structures based on porous silicon, which contain a gas-transport and a gas-sensitive layers separated by a dielectric layer of silicon dioxide [11,12]. This paper shows the possibility to create a test structure of a flow-type resistive gas sensor based on macroporous silicon layers, which comprises integrated gas-permeable and gas-sensitive layers.

2. Gas-permeable membrane based on macroporous silicon

A test element of a flow-type gas sensor was created using structures with gas-permeable channels through which analyzed gases might pass. Macroporous silicon layers were used to implement this idea. Macroporous silicon was obtained by anodic etching on boron-doped plates of *p*-type single-crystal silicon, with the specific resistance of $12\,\mathrm{Ohm}\cdot\mathrm{cm}$, crystallographic orientation (100) and thickness of $380\,\mu$m. Anodic etching was performed in electrolyte being the solution of dip hydrofluoric acid with dimethylformamide $HF:C_3H_7NO$ in the 1 : 9 ration, current density being $5.2\,\mathrm{mA/cm^2}$, for 90 min.

A membrane was formed by mechanical removal of the single-crystal substrate in order to assess the gas-permeable properties of the obtained layers. The substrate was removed using the Gatan Dimple Grinder model 656, hemispherical hollow $\sim 230-240\,\mu$m deep was formed from the substrate side. After a part of the substrate was removed, a self-supported membrane with a gas-permeable layer formed.

Morphology of the macroporous silicon layers and membranes on its basis was studied by scanning electron microscopy (SEM) using the Jeol JSM 6610-LV microscope. The SEM-images of the made specimens were used to measure channel dimensions, and channel density and layer porosity was assessed using the ImageJ software package.

The SEM-image of the obtained macroporous silicon layers is shown in Fig. 1. The macroporous layer obtained by anodic etching consists of vertically oriented pores having a density of approximately $(0.3-0.6)\cdot 10^8\,\mathrm{cm^{-2}}$, layer porosity was $\sim 60\%$, wall thickness ~ 0.2 was up to $0.7\,\mu$m, average pore diameter was $1.6\,\mu$m, layer thickness was $50\,\mu$m. The geometric shape of the pores is conditioned by the crystallographic orientation of the substrate. The SEM-image of the membrane based on the obtained macroporous silicon layer is shown in Fig. 1 (fragments *b, c*).

An experiment to assess gas permeability of membranes based on a macroporous silicon layer was performed as follows. A gas-sensitive film made of non-stoichiometric tin oxide on a sitall substrate, obtained by the chemical vapor deposition method outlined in [13], was placed in a gas chamber with air at the normal atmospheric pressure and room temperature. Resistance of the resistive gas-sensitive element was assessed on the basis of linear current-voltage characteristics measured using the Agilent E4980 LCR-meter.

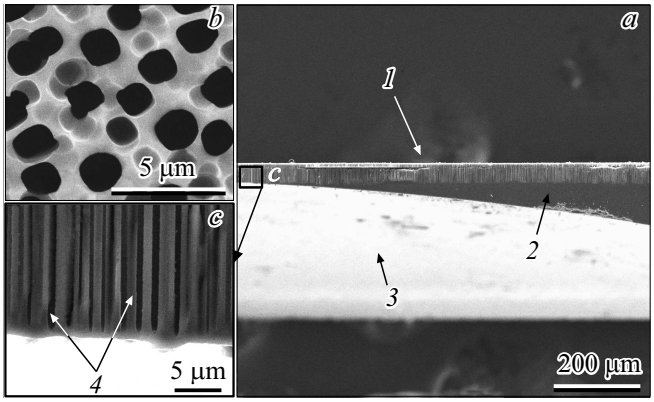

Figure 1. SEM-image: *a* — cross-section of the membrane based on the macroporous silicon layer; *b* — surfaces of the macroporous silicon layer; *c* — area „*c*“ highlighted in fragment *a*. *1* — macroporous silicon layer, *2* — single-crystal substrate, *3* — area where the substrate was mechanically removed, *4* — gas-transport channels.

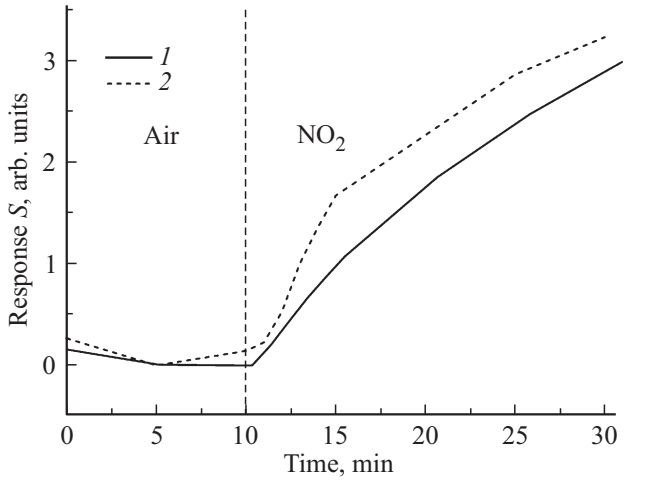

Figure 2. Response of SnO_x film to the exposure in 30 ppm of NO_2. *1* — NO_2 inflow into the gas chamber without a membrane, *2* — NO_2 inflow into the gas chamber through a membrane.

NO_2 was supplied into the chamber through the membrane, resistance of the gas-sensitive film before and during gas exposure was measured. Sensor response of the SnO_x film was determined using the formula

$$S = (R_g - R_a)/R_a, \qquad (1)$$

where R_g is film resistance after gas exposure, R_a is resistance before gas exposure. The obtained sensor response values were compared to the film response data obtained in case of NO_2 supply into the chamber without a membrane.

Figure 2 shows the plots of SnO_x film sensitivity vs. time of exposure in NO_2. There are no significant changes in the response of the SnO_x film, which means complete passage of NO_2 through the membrane.

3. Test structure of the flow-type gas sensor

The structure of the flow-type resistive gas sensor consists of integrated gas-permeable layer based on a macroporous membrane and gas-sensitive layer, being a film of non-stoichiometric tin oxide. Creation of such a structure requires electric isolation of the sensitive layer from the conducting substrate. To do so, thermal oxidation was carried out at 1000°C in wet oxygen atmosphere for 3 h after synthesis of macroporous silicon obtained according to the above-mentioned procedure in Section 2. As a result, a homogeneous layer of silicon oxide [13] 250 nm thick forms on the macropore walls (Fig. 3). Then the gas-permeable layer was opened by removal of single-crystal silicon from the substrate side. The gas-permeable layer was opened according to the above-mentioned procedure for membrane making. Gas-sensitive SnO_x film was applied on the macroporous layer surface after opening of the gas-permeable layer. The SnO_x film was deposited by chemical vapor deposition [13]. The SnO_x film was deposited for 10 min. The obtained layer of non-stoichiometric tin oxide has a polycrystal structure and covers the macropore walls in a 100 nm film, crystallite size is 30–70 nm (Fig. 3).

The obtained test microsensors structure was studied for sensitivity upon passing of analytical NO_2 gas mixture with the NO_2 concentration of 25 and 50 ppm through the test structure membrane at the constant flow rate of 2 ml/s. The gas cell layout is shown in Fig. 4, *a*. The test structure was fixed by a flanged connection with the gas analytical mixture source. The test results are given in Fig. 4, *b* and *c*. Electric resistance of the sensitive layer under passage of the gas-air mixture was measured with the sampling rate of 1 measurement per second. When NO_2 molecules were absorbed, the sensitive layer resistance increased due to the acceptor nature of NO_2 molecules and a decreased quantity of charge carriers in the SnO_x film.

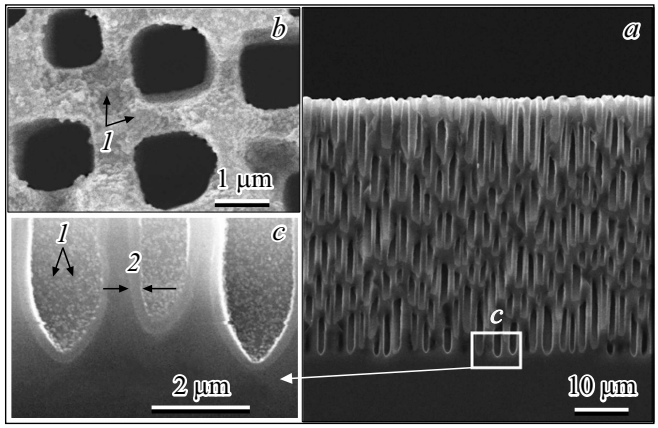

Figure 3. SEM-images of the integrated *por*-SiO_2/SnO_x structure. *a* — cross-section of the structure; *b* — structure surface; *c* — area „*c*“ highlighted in fragment *a*; *1* — crystallites of SnO_x film, *2* — layer of thermally oxidized SiO_2.

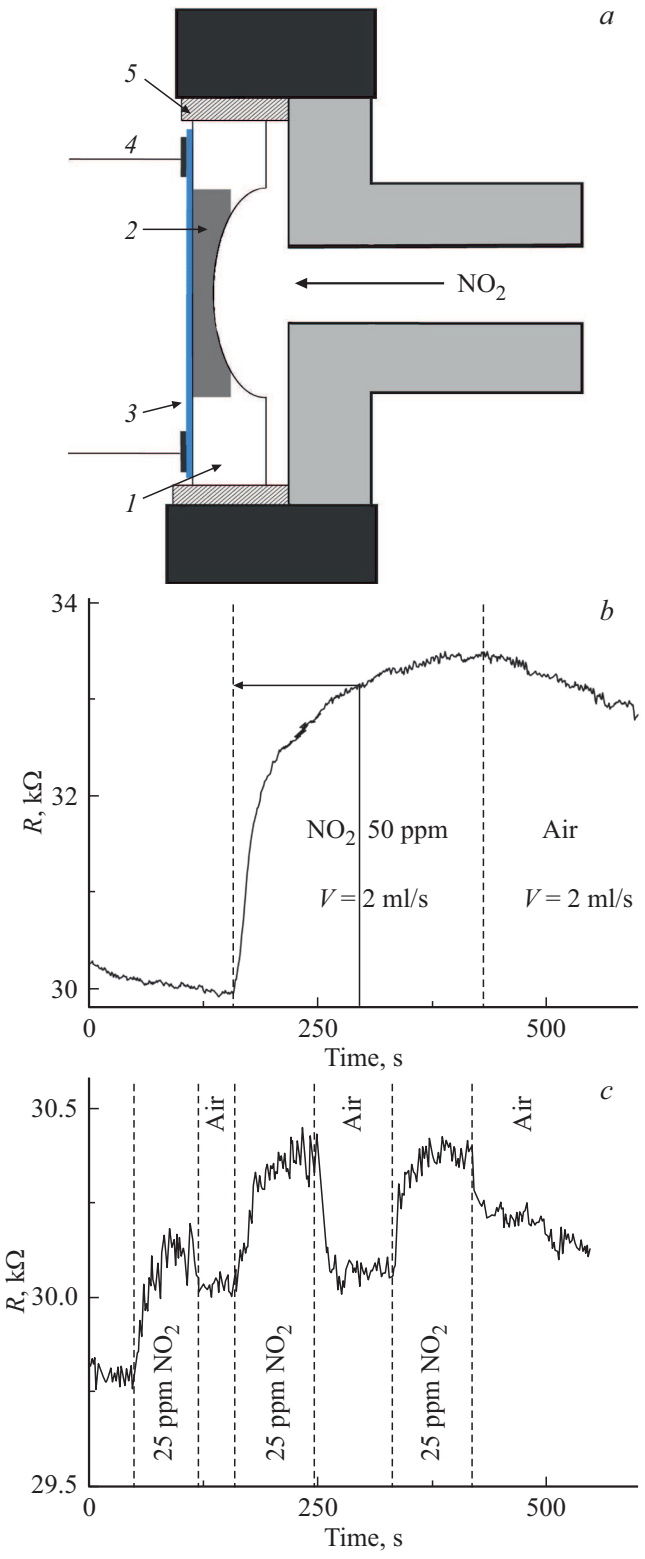

Figure 4. *a* — layout of the gas sensitivity experiment: *1* — single-crystal Si, *2* — oxidized macroporous layer, *3* — SnO_x film, *4* — contact electrodes, *5* — sealing washer; *b* — plot of resistance of the SnO_x film to passage of gas analytical mixture with NO_2 concentration of 50 ppm; *c* — plot of resistance of the SnO_x film to passage of gas analytical mixture with NO_2 concentration of 25 ppm.

The experiments with the structure gas sensitivity were performed in the following conditions. In the first case, gas mixture with the NO_2 concentration of 50 ppm was passed through the test structure at the constant flow rate of 2 ml/s. Then the structure was degassed by passing of gas-air mixture without NO_2 at the same flow rate. A stationary flow of the gas mixture makes it possible to estimate the value of test structure response time, which is defined as time within which the structure response reaches 90% from the maximum response value. The time to reach a stationary value of test structure response was 139 s (Fig. 4, *b*). The test structure response in this experiment mode to the analytical mixture with the NO_2 concentration of 50 pm was 13.2%.

In the second case, gas mixture with the NO_2 concentration of 25 ppm was passed through the test structure in a pulse mode simulating short-time supplies of analyzed gas into the main line. Figure 4, *c* shows the change of test structure resistance to gas mixture passage. There is a correlation of the test structure response to supply of a gas mixture containing NO_2 and to supply of a mixture without analyzed gas. The gas mixture flow rate was 2 ml/s. The structure response was calculated using formula (1) and was equal to 1.1%.

4. Conclusion

A method is suggested for creating a gas-permeable membrane on the basis of macroporous silicon layers. The performed experiments with gas passage through the membranes have shown complete gas permeability for nitrogen dioxide. The obtained results were used to suggest a method for creating a test structure with integrated gas-transport and gas-sensitive layers. The performed gas sensitivity experiments have shown a correlation between the response value and the concentration of the analyzed gas, as well as stable structure response under gas mixture passage in the pulse mode. The results of the performed gas sensitivity studies for the obtained test structure show a possibility to create a microsensor structure based on a gas-permeable membrane on porous silicon and non-stoichiometric tin oxide.

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Conflict of interest

The authors declare that they have no conflict of interest.

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