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Low-Power Gas Sensor on Nanostructured Dielectric Membrane

The article presents a technology for manufacture of a gas sensor with a two-layer nanostructured dielectric membrane on a silicon substrate and its characteristics. Selection of the correct mathematical model ensures a good correlation between the experimental and calculated current-voltage characteristics of the sensor and makes it possible to evaluate the effect of porosity of the dielectric membrane on the value of the sensor's power consumption, temperature of its sensitive layer and the related thermomechanical stresses. It demonstrates that the temperature range (150—350 °C) of the sensor's sensitive layer, where the sensor's response to 1 ppm CO is detected, is ensured due to power consumption from 5,0 mW up to 15,5 mW.

Keywords: *semiconductor gas sensor, double-layer nanostructured membrane, porous anodic alumina oxide*

Introduction

In recent decades, much attention is paid to development of the new gas sensors which can measure low concentrations of pollutants in the environment. These sensors are considered as a variant of chemical sensors, where catalytic and semiconductor materials are used as the sensitive layer (SL), which provides formation of the analytical signal. One of the most widely used sensors is chemically resistive gas sensor, which sensitive layer may be formed of thin or thick semiconductor films.

In manufacture of the gas sensors with nanoscale metal oxide SL, it is necessary to form highly ordered nanoporous dielectric layers on the surface of silicon or dielectric substrates. The nanoporous anodic aluminum oxide (AAO) is generally used for this purpose. Firstly, its films on the silicon substrates were used in 2002 for manufacture of a gas sensor for detecting of NH_3 in a humidified atmosphere [1]. A few years later, the approach found its development in creation of a gas sensor with SL of WO_3 for detection of the nitrogen oxides (NO_x) [2, 3]. In this case, gas sensors were formed on monolithic silicon substrates with a thin film of nanoporous AAO with the thickness of about 1 um, used as the base for deposited SL.

As one of the most promising directions in manufacture of the low-power semiconductor gas sensors is use of the silicon micromachining [4, 5], the technological route of manufacture of the sensor with the two-layer nanostructured dielectric membrane on a silicon substrate was developed in the framework of the article. The results of simulation of the thermomechanical properties of a gas sensor comprising a bilayer dielectric membrane of silicon nitride and the nanoporous AAO are also presented in the article, as well as its basic functional characteristics were investigated.

The gas sensor on a silicon substrate comprising a bilayer dielectric membrane of silicon nitride and nanoporous AAO

The technological route of manufacturing of a gas sensor on two-layer dielectric membrane of silicon nitride and nanoporous AAO consists of three blocks, each of which includes a specific sequence of operations.

The first block was related to creation of the two-layer dielectric membrane. The silicon wafers CDB 4.5 (100) were used as the substrates, on which surface the unstressed nitride Si_xN_y layer with the thickness of 0,8 μm was precipitated after chemical cleaning. The photolithography, plasma chemical etching (PCTs) of a dielectric by the silicon and the anisotropic alkaline etching of silicon were performed from the non-planar side of the plate (fig. 1, *a*). The silicon layer with the thickness of about 40 μm was kept underetched to ensure the strength of the membrane, which was removed later. Then, the aluminum layer with the thickness of 1,5 μm was deposited on the planar surface of the wafer and its two-step anodization (fig. 1, *b*) under electrochemical conditions similar to [6] was performed. The first step of aluminum anodizing was performed on the depth of 0,8 μm, after which the formed oxide was selectively removed. After reanodizing of the remaining aluminum, the AAO ordered layer with the thickness of 0,9 μm was formed on the surface of Si_xN_y.

The second block united operations for production of a heater, information electrodes to the SL and contact pads. A platinum film with the thickness of 0,45 μm was sputtered on the formed porous AAO layer, on which the photolithography and ion beam etching to the porous oxide followed by removal of the photoresist (fig. 1, *c*) were performed. Next, the planar side of the wafer was masked with vanadium layer, on which the companion plate was adhered using wax (fig. 1, *d*) and etching of the remaining silicon to the dielectric membrane was carried out, after which the masking layer was removed (fig. 1, *e*).

Fig. 2 showed the images obtained using a scanning electron microscope (SEM) Hitachi S-806, where the back side of the silicon substrate of the sensor after the anisotropic etching (fig. 2, *a*), the cross sections of the substrate with a membrane (fig. 2, *b*) and of the two-layer dielectric membrane Si_xN_y/Al_2O_3 (fig. 2, *c*) formed by the described technological route were presented.

The third unit of technological operations comprised applying of the semiconductor SL $In_2O_3—GaO_2$ and its heat treatment for a good contact to the platinum electrodes and formation of the desired structure. At the final stage, the plate was scribed, divided into the crystals and the leads were tenderized with Pt-wire. The sensor's crystal was placed into the housing and the characteristics were measured.

Simulation of the characteristics of a gas sensor comprising a bilayer dielectric membrane on the silicon

Fig. 3 (look at the figure on the 3-rd page of the cover) showed the three-dimensional model of a gas sensor on the two-layer dielectric membrane with a front slit (fig. 3, *a*) and a mesh of the finite elements that was used for simulation (fig. 3, *b*).

The construction of a gas sensor included a silicon substrate with the sizes of 1,35 × 1,35 × 0,38 mm, comprising a bilayer dielectric membrane, placed in the center of a substrate with the dimensions of 400 × 400 × 1,7 μm. The membrane consisted of unstressed silicon nitride and porous aluminum oxide with the thickness of 0,8 and 0,9 μm. The thickness of the platinum information electrodes and a heater is 0,45 μm. The sensitive layer with the thickness of ~20 μm represented the mixture of gallium and indium oxides.

The structured prismatic grid was used for simulation. The type of finite element — a triangular prism with six checkout systems. The number of used items — 86 000, the sensitive layer was divided by the thickness into five elements, the platinum — into two and the silicon substrate — into 40. This number is optimal, because a significant increase of computing resources consumed without substantial changing of the simulation results was observed at an increase in their number.

The associated thermoelectric problem was solved during the simulation to determine:

- current-voltage characteristics (CVC) of a gas sensor;
- influence of the porosity of the Al_2O_3 substrate on warming of the sensing element;
- power consumption of a sensor and its dependence on porosity;
- affection of the porosity on the functioning of a sensor.

The following table showed the parameters used for the simulation.

For the mechanical part of the problem, it was assumed that the lower base of a sensor was fully secured from below:

$$u = v = w = 0, \qquad (1)$$

where u, v, w — the displacements along the axes x, y, z, respectively. The thermomechanical deformation was described by the expression:

$$\varepsilon = \alpha(T - 293), \qquad (2)$$

where ε — the thermomechanical deformation; α — the temperature coefficient of linear expansion (TCLE); T — the temperature in Kelvin.

The heat exchange with the environment was set by taking into account convection and thermal radiation:

$$-n(-k\nabla T) = h(T_{\text{вн}} - T) + \varepsilon(T_{\text{вн}}^4 - T^4), \qquad (3)$$

where $h = 5$ W/m$^2 \cdot$K — the heat transfer coefficient to the environment; $T_{\text{ВН}} = 293$ K and T — the temperature of the environment; n — the normal vector; k — the coefficient of thermal conductivity (shown in the table).

At the boundary between the heater and the substrate, the condition of electrical insulation was specified:

$$nj = 0, \qquad (4)$$

where j — the current density, A/m^2.

The input voltage was set from 0,1 to 1,6 with the step of 0,15 V.

To determine the thermomechanical parameters of Al_2O_3 as a function of porosity, the technique was used, described in [7]. The software package COMSOL Multiphysics 4.4, the workstation with 32 GB RAM running on Windows 7 × 64 were used for simulations and calculations.

Fig. 4 showed the CVC of the working sample of a sensor having a membrane with the volume porosity of about 10 % (curve *1*), and the calculated CVC for 10 and 70 % of the porosity of the membrane (curves *2* and *3*). As can be seen from the figure, the CVC received during the calculation and experiment for the membrane with the same porosity, are practically same. The discrepancy is less than 1 %. It can be seen that the porosity of the dielectric membrane greatly affects ON the CVC. At the sensor's heater current of 17 mA, the calculated values of the supply voltage on it differ by 19 % for membranes with the bulk porosity of 10 and 70 % (fig. 4). This is caused by the fact that the conductivity of the platinum metallization and sensitive layer depends on temperature, and at the temperature higher than 100 °C, this relationship is strong enough for Pt (see table).

Choosing of the right model, providing a good agreement between the calculated and experimental current-voltage characteristics of the sensor, suggests that its use will provide the correct values in the calculation of thermal and thermo-mechanical characteristics of a sensor. Fig. 5 (look at the figure on the 3-rd page of the cover) snowsme calculated temperature field arising during operation ot a sensor when the voltage across the heater is 1 V, which provides the required heating of the sensitive element (SE) of the sensor.

From fig. 5 it was seen that the temperature's maximum is localized near the sensitive element and it does not extend beyond the membrane. The calculations show that the temperature of the edge of the silicon substrate and the contact pads significantly lower (at porosity of the membrane of 10 % in 2 times, while at the porosity of the membrane of 70 % — almost in 3 times).

Fig. 6 showed the temperature dependence of SL and power consumption of a sensor on the porosity of the membrane when the voltage across the heater is 1 V. As can be seen from the dependence (curve *1*), increase in the porosity of the membrane up to 70 % can increase the temperature of the SL by 40 %. The non-linearity in the change of its temperature begins to emerge when the porosity of the membrane is higher than 40 %. This effect is caused by the fact that at the most higher porosity, the most of the heat flux passes along the outer boundaries of the substrate rather than inside it [7].

Reduction of the power consumption of the sensor at a fixed voltage on the heater was observed when the membrane porosity greater than 40 % (curve *2*) and was associated with the achievement of the required temperatures for SL at the lower values of voltage on the sensor. Therefore, it is advisable to use the substrates with the membranes having a high porosity. As can be seen from fig. 6, the power consumption of the sensor can be reduced by 31 % when using a membrane with a porosity of about 70 %.

To predict the reliability of the sensor is of interest to investigate the ability of its construction, especially the membrane to withstand the thermomechanical deformations during operation. Fig. 7 shows the calculated temperature of SE (fig. 7, *a*) and the relative thermomechanical deformation (fig. 7, *b*) from the power consumption of a sensor. (It was found that the porosity has no significant effect on them). In a membrane with the volume porosity of about 70 % (fig. 7, *b*, curve *2*), the thermomechanical deformation is only by 10 % higher than in the membrane with the bulk porosity of ~10 % at power consumption of the sensor of 23 mW. The calculations show that the membrane even with zero porosity is unable to withstand mechanical deformation under a voltage of the heater of 2 V. At such supply voltages of the sensor, the thermomechanical deformation exceeds 0,01, which is critical for this type of membranes.

Fig. 8 shows the distribution of thermomechanical stresses in the membrane obtained from the model experiment, and the photo of the gas sensor at applying of the voltage of 1 V to its heater. The dark contoured line on the photo of the sensor (fig. 8, *b*) shows a line along which there a disruption of the membrane occurs in the experimental sample. It was found that for all values of the porosity of the alumina layer, the membrane bends and entails the metallization and the sensitive layer. Comparison of the model experiment and the real picture of the behavior of the sensor's membrane once again confirms the correctness of the chosen model for calculation of its physical and mechanical characteristics.

Measurement of the sensor response of the manufactured sensor

The study of the response of the sensor to CO was performed at the stand of the measuring cell, the system of creating and maintaining of a gaseous medium in the cell and measuring instruments of sensor's signals with the information transfer on PC. The experiment used a calibration gas mixture of the zero air with carbon monoxide with the concentration of 1 ppm.

The response was defined as the difference between the resistance of the sensor under the influence of the active gas (R_{gas}) and its resistance in the air (R_{air}). The sensitivity was calculated as a percentage dependency R_{gas} and R_{air}: $S = [(R_{air} - R_{gas})/R_{gas}]100\ \%$. Fig. 9 shows the time dependence of sensor response for two values of the consumed power of a sensor — 14,0 and 15,4 mW, which corresponds to SE's heating temperature of about 300 and 340 °C (see fig. 8).

The calculation of the sensitivity of a sensor to 1 ppm CO gave values of this quantity ~23,08 and 9,73 %, respectively, for the consumed power is of a sensor — 14,0 and 15,4 mW. From the obtained data it follows that the optimal temperatures of sensor's SL, necessary for qualitative registration of CO are the temperatures below 300 °C. The rise of SL's temperature above this value leads not only to deterioration of the shape of the curve of the sensing response and decrease of the sensor's sensitivity, but also increases its power consumption.

Conclusion

The technology of manufacturing of a gas sensor with the two-layer nanostructured dielectric membrane was developed. It comprised sequential formation of the silicon nitride layers and the nanoporous AAO layer on the planar side of the silicon substrate and fluid volume etching of the back side of silicon for membrane creation. The results of the simulation of the thermomechanical properties of the gas sensor on a silicon substrate containing the two-layer dielectric membrane of silicon nitride and nanoporous AAO were presented. Selection of the correct mathematical model provided a good agreement between the calculated the experimental CVC characteristics of the sensor and allowd to evaluate the effect of the porous dielectric membrane on changes in the power consumption of the sensor, the temperature of its SL and emerging thermomechanical stresses. It was shown that the heating temperature range of the sensitive layer of the sensor is 150...350 °C, in which to the sensor response to 1 ppm CO is registered, was provided with the sensor's power consumption from 5,0 to 15,5 mW. The calculation of the sensitivity of the sensor to 1 ppm CO gave the values of ~9,73 and 23,08 % for the sensor's power consumption of 14 and 15,4 mW.

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