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Influence of H_2S and H_2 adsorption on characteristics of MIS structures with Si porous layers

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Abstract. The adsorboelectric effect arising in multilayered semiconductor structures based on the porous Si with catalytically active Pd electrodes due to action of low concentrations of hydrogen containing gases (H_2, H_2S) at the room temperature is studied. The kinetic dependences of the change in output signals of the samples upon action of different concentrations of gas molecules are studied using the capacitance-voltage characteristic method. The isotherms of adsorption are derived. A physical model of the adsorption of hydrogen containing gases in these structures is proposed to explain the observed phenomena.

Keywords: adsorboelectric effect, porous silicon, MIS gas sensor.

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1. Introduction

Recently, porous silicon (PS) is suggested as a perspective material for the formation of microelectronic solid state gas sensors [1-5]. Semiconductor gas sensors with a porous Si (PS) layer are advantageous due to (i) the large internal surface area of PS (up to 200-500 m^2/cm^3), which enhances the adsorption properties of structures, (ii) its high chemical activity, (iii) a simple and cheap formation technology that is compatible with silicon CMOS technology, and (iv) the possibility of a formation of multisensor arrays. At present, sensors with a porous silicon layer exist for a number of gases such as O_2, H_2, CO, CO_2, NO, NO_2, NH_3, *etc*., water vapour, organic and biological molecules [6-9]. Porous Si based sensors use different physical principles and are formed by several technologies: Shottky diodes, MIS structures, optical sensors, *etc*. [10-24].

Study of the physical principles of gas adsorption on porous silicon enables to extend the research of the properties of semiconductor materials as well as their practical application for gas sensing. Study of adsorboelectric effect in the PS based structures makes it possible to determine both adsorption and electrical properties of this material at the same time.

Detection and determination of low concentrations of ecologically harmful and explosive gases are an important scientific and technical problem. Hydrogen sulphide is one example of such gases. The importance of detection is related to the necessity to monitor and to control hydrogen and hydrogen sulphide leaks in many technological processes such as oil and gas production and conversion, storage and processing in food industry, and ecological control of surrounding. Therefore, it is important to have a stable sensor of H_2 та H_2S gases with high sensitivity and selectivity.

In this paper, an adsorboelectric effect in the structures with porous Si layers is studied experimentally. The peculiarities of the kinetics of signal change upon the action of different concentrations of hydrogen and hydrogen sulphide gases are investigated. The concentration dependences of the influence of gas on the change of a response signal of structures are derived. A physical model of gas adsorption in the MIS structures under investigation is suggested as based on the obtained experimental results.

2. Experimental

A porous Si layer was obtained by the electrochemical etching of monocrystalline (100) oriented Si wafers doped with boron up to the concentration of $N_A = 4\times10^{15}$ cm^{-3}. The anodisation current density was within the range of j = 5-20 mA/cm^2. The 4:1 solution of HF (48 %) and ethanol C_2H_5OH was used as electrolyte (HF ~ 80 %). The thickness of the porous Si layers obtained was determined by profilometry to be 1 μm. The porosity of layers was 60 to 70 %, according to the results of gravimetry. An average pore size lay within the range of 2 to 8 nm, as determined from the low temperature nitrogen adsorption.

The layers of mesoporous Si were annealed at once after preparation in weakly oxidising atmosphere (~20 % O_2+80 % Ar/N_2) at 450 °C. Catalytically active

palladium films with a thickness of ~ 50 nm were deposited onto the surface of oxidised mesoporous Si by magnetron sputtering and Al contacts by thermal vacuum sputtering, respectively. Metal-dielectric-semiconductor structures of Pd-PS-Si-Al with a top Pd electrode of 4 mm in diameter were formed (Fig. 1). Kinetic $C_{FB}(t)$ and capacitance-voltage $C(V)$ characteristics of Pd-PS-Si-Al structures were measured using the capacitance-voltage curve tracer АМЦ 1594 at the frequency of testing signal 1 MHz. The investigations of the influence of gas on the electrophysical characteristics of structures were carried out at room temperature in the concentration range of 10-1000 ppm for hydrogen and 5-80 ppm for hydrogen sulphide, respectively. During the investigation of gas adsorption the «injection» regime of start-up of gases was used. In more details of experiment it is described in works [4, 24].

3. Results and discussion

Kinetic dependences of the change of the signal of Pd-PS-Si-Al structures under the action of different concentrations of gases were measured at fixed voltage (U_{fix}) at the flat band level (C_{FB}). The kinetic dependences, $\Delta C(t)$ ($\Delta C = C - C_0$, C_0 being the capacitance before the gas inlet and C the capacitance after the gas inlet, respectively) under the action of different concentrations of hydrogen sulphide (a) and hydrogen (b) are shown in Fig. 2. It is seen that hydrogen leads to the decrease of signal measured ($C < C_0$) and hydrogen sulphide results in the signal increase ($C > C_0$), i.e. hydrogen shows donor properties and hydrogen sulphide acceptor properties, respectively. It was found that even at low gas concentrations the MIS structures had a high speed of performance and short times of response ≤ 10 s.

The kinetic dependences reveal the important peculiarities of adsorption process on the porous surface of structures under investigation. Namely, the delay in the signal, which shows the slowing down the motion of molecules being adsorbed to the internal surface of semiconductor layer, can be possibly caused by the spilover effect. This effect appears due to the discontinuity (micro- and nanostructure) of metal layer and the gradual migration of adsorbed molecules under the surface of "metal islands". It is supported by a weak dependence of the measured time of the establishment of a signal of adsorption effect upon changing the gas concentration in the surrounding (the pressure change is several orders of magnitude), an exponential character of the signal as well as a correlation of the time for formation of initial electric surface layer with the delay time (of signal) and a considerable increase of this time for high pressures.

The dependences of the signal of Pd-PS-Si-Al structures upon adsorption of various concentrations of gases within the range of 5-1000 ppm are shown in Fig. 3. Experimental points correspond to various concentrations. They are compared to the theoretical curves (curve 1 is for hydrogen sulphide and curve 2 for hydrogen, respectively). It can be seen that the gas sensing structure shows a high-level activity even to the low gas concentrations, ≤ 5 ppm. The isotherms gradually saturate upon increasing the gas concentration.

Analysis of adsorption isotherms for hydrogen sulphide and hydrogen on the samples under investigation demonstrated at least two mechanisms of gas adsorption. After a theoretical analysis of experimental data, the isotherms of gas adsorption were re-plotted (Fig. 4).

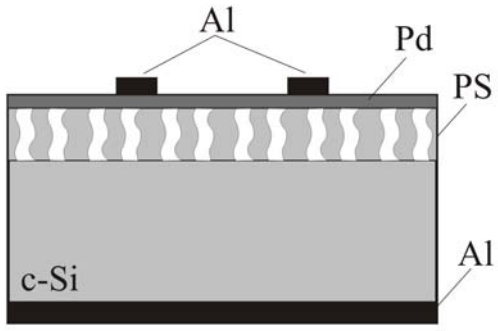
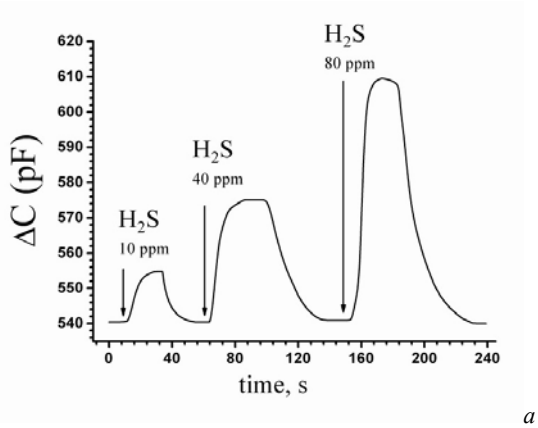
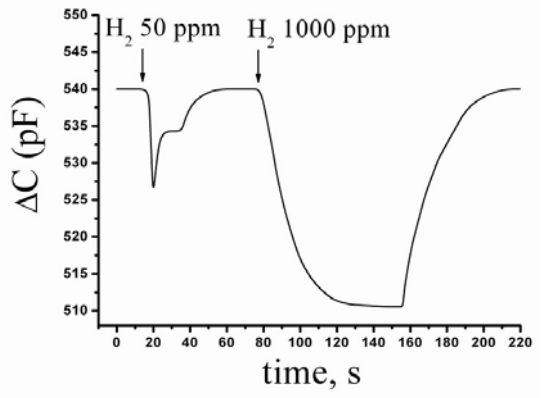


Fig. 1. Schematic image of Pd-PS-Si-Al MIS structure.



a



b

Fig. 2. Kinetics of the signal response under action of various concentrations of gases (hydrogen sulphide (a) and hydrogen (b)).

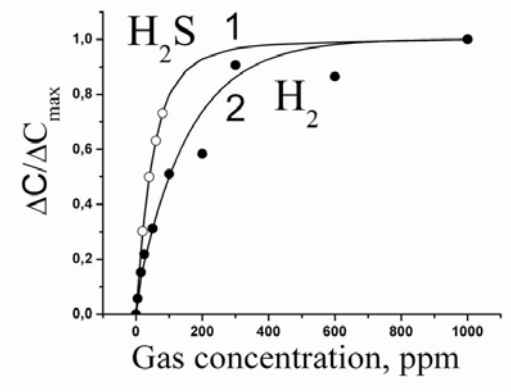


Fig. 3. Isotherms of gas adsorption (1 – hydrogen sulphide, 2 – hydrogen).

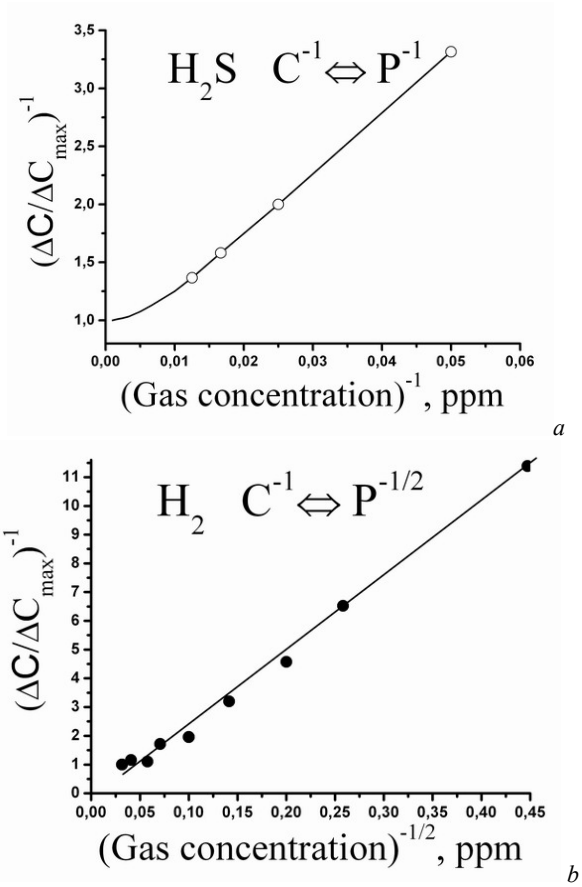


Fig. 4. Re-plotted isotherms of gas adsorption (hydrogen sulphide (a) and hydrogen (b)).

It was found that the surface population upon adsorption of hydrogen sulphide depends on the pressure as $\theta_i \sim P$. The isotherm rectifies in coordinates $P^{-1} \leftrightarrow C^{-1}$, which corresponds to the one-particle adsorption described by the Langmuir law. Therefore, one may suppose the molecular adsorption of hydrogen sulphide and the isotherm maybe expressed as follows:

$$\Delta C^{(0)} = \Delta C_{\max}[a_p P/(1+a_p P)], \qquad (1)$$

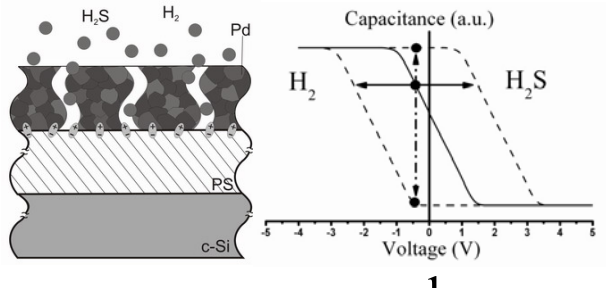


Fig. 5. Schematic image for mechanisms of hydrogen and hydrogen sulphide adsorption.

where $\Delta C^{(0)}$ is the steady (proportional to adsorption concentration) state signal at the given pressure P and temperature T, ΔC_{max} is the signal at the highest concentration of investigated gas, $a_P \sim \exp(E_a/2kT)$, and E_a is the adsorption heat per molecule, respectively.

Analysis of the adsorption isotherm of hydrogen demonstrated that the population of surface upon the pressure corresponds to the dependence $\theta_i \sim P^{1/2}$. The respective isotherm is rectified in coordinates $P^{-1/2} \leftrightarrow \Delta C^{-1}$ and is described by the following law:

$$\Delta C^{(0)} = \Delta C_{\max}[a_p P^{1\backslash 2}/(1+a_p P^{1\backslash 2})] \qquad (2)$$

Such dependence is typical for the dissociative gas adsorption, i.e. the decomposition of hydrogen molecule in two hydrogen atoms, $H_2 = H_a + H_a$, takes place here.

The calculation of gas adsorption isotherms has demonstrated the value of activated energy (E_a) for hydrogen is 0.096 eV and for hydrogen sulphide – 0.084 eV. In both cases, the value of activation energy is rather small close to 0.1 eV, which is typical for the physical adsorption of gases.

The following mechanism of the sensitivity of structures under investigation to the adsorption of hydrogen and hydrogen sulphide can be proposed. Gas molecules adsorb first on the surface of MIS structure and then diffuse to the interface of Pd/porous Si on the pore walls and grain boundaries. A molecule polarisation takes place at the Pd/porous Si interface. With their dipole moments, the polarised molecules make an additional contribution to the contact voltage Fig. 5a. There is change indemnification of electrical charge on the interface of Pd/porous Si (hydrogen increases it while hydrogen sulphide decreases). Such influence of adsorbed molecules leads to respective changes in the structure capacitance and the shift of *C-V* curve in the negative region for hydrogen and in the positive region for hydrogen sulphide (see Fig. 5).

4. Conclusions

The analysis of adsorption isotherms demonstrated the molecular adsorption of hydrogen sulphide and the dissociative adsorption of hydrogen on the surface of MIS structures with porous Si layer. A testing sample of

a sensor was prepared for detecting low concentrations of hydrogen and hydrogen sulphide at room temperature.

Acknowledgements

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