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MIS – Field Effect Sensors for Low Concentration of H_2S for Environmental Monitoring

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Abstract

It was found, that Metal Insulator Semiconductor Field Effect (MIS-FE) sensors with structures Pd-Si_3N_4-SiO_2-Si and Pd-Ta_2O_5-SiO_2-Si have sufficient concentration resolution to H_2S gas and acceptable response time in mixture of H_2S gas with air. Results of MIS-FE gas sensor operation in periodic regime are presented and allow us to be sure, that low detection level of H_2S for MIS-FE sensor with Ta_2O_5-SiO_2 insulator is of about 5 ppb.

Keywords: Field effect; gas sensor; hydrogen sulphide.

1. Introduction

H_2S gas measurement in air is a very specific problem because hazardous concentration for human health is very low (for residence area is around 5 ppb and 14 ppm for working zone according to Russian standard of environmental protection); ppb-level delectability is not achieved for usual liquid electrochemical sensors, and also there are several important applications, where these sensors non-applicable because of short life time and extremely working condition such as humidity extremes (very dry or too much humid atmosphere), temperature drop or operation under permanently high concentration of H_2S. Therefore, the purpose of this work was the creation of inexpensive and simple device for low H_2S concentration measurement based on chip solid state gas sensor.

2. Experiment

To block necessary ppb - ppm ranges H_2S concentrations we have developed in these work two types of MIS-FE sensors with structure Pd-Ta_2O_5-SiO_2-Si for ppb and Pd-Si_3N_4-SiO_2-Si for ppm ranges concentration measurement [1]. Thin film of palladium of these structures was deposited by laser technical [2]. The photo of substrate after

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palladium laser deposition, Atomic Force microscope (AFM) imagination morphology of Pd gate MIS-FE structures are presented in fig.1.

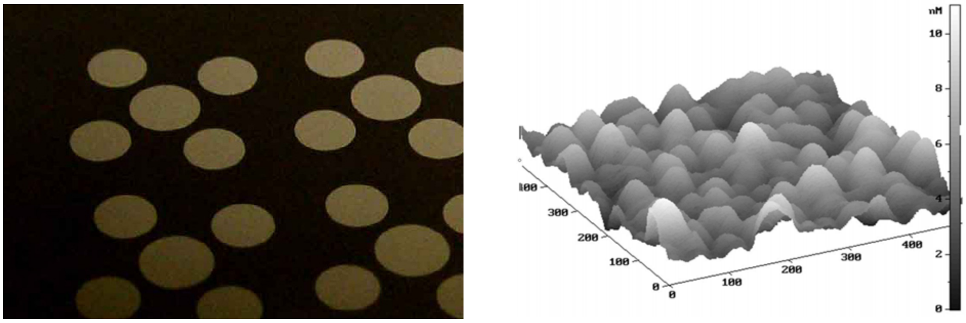

Fig. 1. (a) Photo of Si substrate with laser deposit Pd gates on insulator before cutting on sensor's chips; (b) AFM photo of Pd thin film used as a gate in MIS-FE structures. Area on the AFM photo is 500×500 nm

The sensors were operated in constant heating regime with temperature around 100 ^{o}C suitable for H_2S gas detection. In order to hate chip with MIS-FE structure a resistive heater was integrated under chip. The average consumption power of that assemblage was equal to 500 mW. Photo of assembling are presented in fig.2 (a).

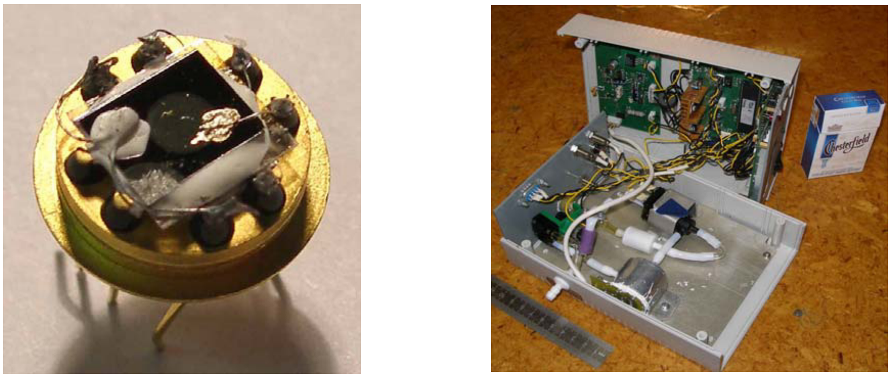

Fig. 2. (a) Photo of MIS-FE sensor chip bonded in TO-8 package. Diameter of the package is equal to ~ 10 mm, chip size is ~ 6.0 × 6.0 × 0.25 mm; (b) Photo of unsealed H_2S gas measurement device using MIS-FE gas sensing element. Front side – air-driven setup with two channels measuring system, back side – electronic controller.

For the determination of MIS-FE sensors cross sensitivity to different gases presented in tab. 1, were computer controlled system equipped with mass-flow controller produced gas mixture with dry air. In order to improve the precision and to protect the sensor from the influence of interfering gases we used two channels measuring system with gas filter selective to H_2S, working in periodic regime with 20 minute duration (operating 5 minutes with pure channel and 15 minutes with filter).Photo of unsealed measuring system are presented in fig.1 (b).

The response curves of the sensors to H_2S are presented in fig.3 and quantitative sensitivity to different gases as a shift of C-V characteristics are presented in tab.1 (appendix A). Since the sensitivity of the sensors to H_2S gas is high and flow creation of this sub-ppb range concentration gas mixture was difficult, we determined the low detection limit by a calculus of approximations. The extrapolation of our measurement result allows making sure, that low detection level of H2S in air (three amplitude of noise) of MIS-FE sensor with Ta_2O_5-SiO_2 insulator is 5ppb.

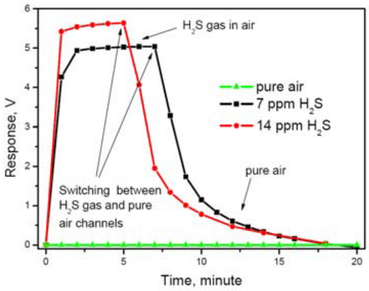

Fig. 3. The responses (after amplifiers circuit) of the MIS-FE sensor with structure Pd-Si3N4-SiO2-Si to H2S. Gas concentrations are given in the plot.

3. Results and discussions

Experiments show that the sensors has stable reversible response and one order higher sensitivity to H_2S then others gases, but physical properties of thin films Pd gate and insulator change in time under the influence of high chemical activity of H_2S [3]. To find the service resource of MIS-FE sensor with Ta_2O_5-SiO_2 insulator we used integrated dose of H_2S multiplied by time of the gas exposition. Experiment shows that integrated dose of 2×10^4ppm×hour degrade H_2S concentration conversion tolerance to 20%. It means that service time of MIS sensor worked in air with 20 ppm per hour in a day average H_2S concentration is around 3 years, after that time afresh recalibration of gas sensing device is required.

Resource of MIS-FE sensor with Si_3N_4-SiO_2 insulator is several times better when Ta_2O_5-SiO_2. It seems connecting with presence oxygen in structure of insulator because experiments show that if stay only SiO_2 as insulator velocity degradation of sensitivity will be compared with Ta_2O_5-SiO_2 insulator.

4. Conclusion

In this work, we continue our investigations [1, 2, 4 - 8] in field of physics MIS-FE gas sensors and as result design device suitable for selective detection of low concentration of H_2S gas in air.

Results of MIS-FE gas sensor operation in periodic regime allow us to be sure, that low detection level of H_2S for MIS-FE sensor with Ta_2O_5-SiO_2 insulator is of about 5 ppb. Confirming by experiment storage life without losses of quality of sensors is more when one year. Experimental data is evidence that achieve characteristic of sensor's properties typical for completely commercial product.

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Appendix A. Sensitivity of MIS-FE sensors to different gases.

Table 1. Sensitivity of MIS-FE sensors to different gases, sensor with structure Pd-Ta_2O_5-SiO_2-Si designating as the "Type 1"to and with structure Pd-Si_3N_4-SiO_2-Si as the "Type 2".

Gas	Sensitivity, pF/ppm	
	Type 1	Type 2
H_2S	10^3	25
NO_2	10^2	2,5
C_2H_5SH	10^2	2,5
NO	10	0,3
H_2	5	0,1
NH_3	2	0,05
HF	0,5	0,01
SO_2	0,1	2×10^{-3}
CO	0,01	2×10^{-4}
CO_2	3×10^{-4}	0
O_2	2×10^{-4}	0
N_2	0	0
He	0	0
Ar	0	0
CH_4	0	0
C_3H_8	0	0