Detection of Chlorine by field effect sensor

N N Samotaev, A V Litvinov and M O Etrekova

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe highway, Moscow, 115409, Russia

E-mail: nnsamotaev@mephi.ru

Abstract. The gas analytical system for chlorine gas measurement based on metal-insulator-semiconductor field effect (MIS FE) type sensor has been developed. High sensitivity of MIS FE sensor to chlorine allows measuring concentrations in the sub-ppb level and to be stable for overload hydrogen gas concentration typically present in industrial electrolysis application. With the pulse heating mode, the response and relaxation times of the MIS sensor are reduced by an order of magnitude which gives chance to use one for high precision environmental control.

1. Introduction

The Chlorine gas concentration measurement in air is a very specific problem because hazardous concentration for human health is very low (for residential area is around 20 ppb and 670 ppb for working zone by Russian standard of environmental protection). Sub-ppb level detection is not possible by liquid electrochemical sensors [1], even using sensor arrays [2] or special mathematical processing [3] and also there are several important applications where these sensors non-applicable from a short operation 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 Cl2. Therefore, the purpose of the present work was to create inexpensive and useful sensor system for low Cl2 concentration measurement in presence of H2 based on stable and solid state MIS FE sensors. The MIS FE sensors (capacity and transistor types) have a high sensitivity to the concentrations of various gases [4, 5]. The sensitivity of MIS FE sensor of the Pd-SiO2-Si type to H2 was first demonstrated in [6]. Later was found sensitivity of MIS FE sensors to non-content hydrogen gases in [7].

The MIS structures presented in this work were fabricated using the method of pulsed laser deposition of thin films. With this method of evaporation, the vaporized substance consists of neutral atoms and ions, and their energies can be tens and hundreds of electron volts [8]. Such high energy values allow atoms and ions to penetrate deep enough into the substrate. Therefore, in this case, the metal-dielectric interface is a layer with a variable stoichiometric composition — from the pure material of the metal gate to the pure material of the dielectric. Morphological studies of the palladium film showed that the film deposited on the dielectric layer using the method of pulsed laser deposition consists of nanocrystals with sizes from 10 to 100 nm and contains numerous pores of different sizes. Therefore, when diffused into the film, gas molecules easily reach the region of the metal-dielectric interface, by passing diffusion through the bulk of palladium crystallites.

According to the model of the sensitivity mechanism described in [9], when gas appears above the surface of the metal gate of the sensor, a diffusion flow of gas molecules to the metal-dielectric
interface appears through the gate film. To change the electrical capacitance of a MIS structure, a gas molecule that approaches the metal-dielectric interface must change the electric field in the dielectric and near-surface region of the semiconductor, which can change the distribution of free current carriers in the semiconductor and, accordingly, the sensor capacitance at a fixed bias voltage at the MIS structure. The retention of gas molecules in the region of the metal-dielectric interface is performed by trapping centers. The characteristics of capture centers — their charge, size, and surface density depend on the material of the metal gate, the material of the dielectric, and the method of spraying [10]. Since the interface is a layer of variable stoichiometric composition, there is a whole set of different types of capture centers with different values of activation energy. The probability of gas capture by pores during diffusion and capture centers at the interface is determined by the capture cross sections of certain capture centers. Since the pore sizes are different, then molecules need different activation energies to overcome the pores. The diffusion coefficient of gas molecules in the film depends on the technology of film production (sputtering method, sprayed material, film thickness) and temperature. MIS sensors with the Pd-Ta$_2$O$_5$-SiO$_2$-Si structure were used in the work.

2. Experiment and results
During the study, the dynamic characteristics of the sensor samples were measured when a step pulse of chlorine concentration was applied to them. Figure 1 shows the electronically transformed response of a 50 ppb chlorine MOS sensor. It should be noted that the capacity of the MIS structure decreases under the action of chlorine. As can be seen from figure 1, MIS sensors have large response times ($\tau_{0.9} \sim 70$ min) and relaxation ($\tau_{0.1} \rightarrow \infty$) at the operating temperature of the sensor $T = 100^\circ$C. For comparison, at the same temperature, the response and relaxation times of the sensors to the hydrogen concentration in several ppm are: $\tau_{0.9} = \tau_{0.1} = 10$ min. According to the sensitivity mechanism model [9], the response time of the MIS sensor is largely determined by the diffusion rate of gas molecules through the pores of the metal gate and in the transition layer. The diffusion coefficient increases with increasing temperature. Therefore, increasing the temperature of the sensor reduces its response time to chlorine concentration. But with increasing temperature, the sensitivity of the sensor will decrease due to the degeneration of its Volt-Farad (C-V) characteristics. Figure 2 shows the C-V characteristics at different temperatures. It can be seen that as the temperature increases, the slope of the linear part of the C-V characteristic decreases significantly, which leads to a decrease in the sensitivity of the sensor to zero at high temperatures. This contradiction can be resolved with the help of pulsed heating of the sensor. The essence of the method is as follows (figure 3).

![Figure 1](image1.png)

**Figure 1.** Sensor reaction to 50 ppb chlorine in a stationary temperature mode at $T = 100^\circ$C. The signal is presented after the electronic converter.

![Figure 2](image2.png)

**Figure 2.** Voltage-farad characteristic of the MIS structure at different heating temperatures. 1 - 100 °C; 2 - 150 °C; 3 - 190 °C; $U_{cm}$ - offset voltage. The dotted curve corresponds to the shift of the C-V characteristic when exposed to chlorine.
Figure 3. The principle of measuring the concentration of gaseous using a MIS sensor in the mode of pulsed heating (tp is the time between two measurements of the concentration of gaseous Cl₂).

We will change the temperature of the sensor, as shown in figure 3(a), with a period tp, i.e. we will periodically heat and cool the sensor. The mode is selected so that by the end of the tp interval the sensor has time to cool down to the initial temperature of 100°C. The corresponding sensor response is shown in figure 3(b); it corresponds to a strong displacement of the C-V sensor characteristic when the temperature rises to 190 °C (points 2, 4, 6, 8, 10) and returns to a temperature of 100 °C (points 1, 3, 5, 7, 9, 11). The electronic circuit records the sensor readings only at points 1, 3, 5, 7, 9, 11, ..., when the sensor is at T = 100°C. The corresponding readings of the converted sensor signal are shown in figure 3(c). With this method of measurement for the 1st cycle due to the increased temperature, the sensor readings reach a maximum value corresponding to the Cl₂ concentration applied to it (figure 3(d)). In the normal measurement mode, this does not occur, because τ₀,0 > tp. By the end of the 1st cycle, the instrument readings are already stabilized, and this continues as long as the Cl₂ concentration is constant. If now after the n-th cycle the concentration becomes equal to zero, then for (n+1)th cycle the instrument readings decrease faster than in the normal mode, since part of the tp sensor period is at elevated temperature. Relaxation becomes complete if kTₘₐₓ ≥ Eₐ, where Eₐ is the maximum energy of detachment of the molecules of the measured gas from the traps in the transition region, and Tₘₐₓ is the maximum temperature of the sensor during the period tp. At a temperature of 220°C, the palladium film of the sensor gate begins to oxidize, therefore Tₘₐₓ is chosen to be 190°C.
Thus, periodic pulse heating allows you to increase the reaction rate of the sensor and thereby ensure the suitability of the sensor for its installation in gas analyzers.

The results of measurements of the sensitivity of MIS sensors to chlorine in the pulse heating mode are shown in figure 4. In this mode, the instrument sensitivity of the sensor is 200 V/ppm, the response time is $\tau_{0.9} = 10$ min, the relaxation time is $\tau_{0.1} = 7$ min. The values of parameters $\tau_{0.9}$ and $\tau_{0.1}$ are already acceptable for using the sensor as a sensitive element of a gas analyzer.

Figure 5 shows the static characteristic of a MIS sensor for different chlorine concentrations, which in the indicated concentration range represents a logarithmic relationship. Sensor temperature was maintained at 150 °C.

![Figure 4](image1.png)  
**Figure 4.** Sensor response to 50 ppb chlorine in the mode of pulsed heating at an operating temperature of 190 °C / 100 °C. The signal is presented after the electronic converter.

![Figure 5](image2.png)  
**Figure 5.** Static characteristic of a MIS sensor for chlorine at a temperature of 150 °C.

Figure 6 shows the temperature dependence of the sensitivity of the MIS sensor to chlorine. It can be seen that at a sensor temperature of 190°C, its sensitivity tends to zero.

![Figure 6](image3.png)  
**Figure 6.** The dependence of the sensitivity of the MIS sensor to chlorine on the temperature of the sensor.

High sensitivity to Cl₂ was obtained in the laboratory. The absolute error of such measurements is small and allows you to measure the concentration of Cl₂ at the level of 0.1 ppb. However, when using
a MIS sensor as a sensitive element in a gas analyzer in real (atmospheric) conditions, the measurement error may increase by an order of magnitude due to the influence of uncontrolled external conditions.

Tests have shown that in real (atmospheric) conditions, using a gas analyzer with a MIS sensor, one can measure Cl₂ concentrations ranging from several ppb.

The selectivity of the gas analytical system can be improved by using a two-channel measuring system with filtration of Cl₂, presented in [11] for concentrations of about 0.1 ppb of gaseous H₂S.

3. Conclusion
The significant magnitude of response the MIS sensor to Cl₂ (1.8-2 nF/ppm) makes one possible to use it as a sensitive element of chlorine gas analyzers with sensitivity at ppb level. Significantly speed-up of gas analyzer system response can be done by pulse heating mode of the MIS FE sensor. Simultaneous sensitivity to ppb-level concentrations of chlorine and hydrogen makes the MIS FE sensors, for example, an excellent tool for environmental control in industrial electrochlorination process.

Acknowledgments
This work was supported by the Russian Science Foundation (Grant Agreement 18-79-10230 of August 08, 2018).

References
[1] Yunusa Z, Hamidon M N, Kaiser A and Awang Z 2014 Gas Sensors: A Review Sensors & Transducers 168 61-75
[2] Chiu S-W and Tang K-T 2013 Towards a Chemiresistive Sensor-Integrated Electronic Nose: A Review Sensors 13 14214-14247
[3] Belozertsev A, Cheremisina O, El-Salim S, Manoilov V and Zarutsky I 2018 Algorithms for data processing in gas-analytical complexes with semiconductor sensors for the detection of vapors of toxic substances in the environment Scientific Instrument Engineering 28 18-29 (in Russian)
[4] Bolodurin B et al 2018 Comprehensive Research on the Response of MIS Sensors of Pd‒SiO₂‒Si and Pd‒Ta₂O₅‒SiO₂‒Si Structures to Various Gases in Air Russian Journal of General Chemistry 88 (getting ready for printing)
[5] Irkha V and Vikulin I 2013 Effect of metals and dielectrics on the sensitivity of MIS structures to hydrogen Scientific works ONAS them. O.S. Popov 1 22-27 (in Russian).
[6] Lundstrom I et al 1975 A hydrogen-sensitive Pd-gate MOS transistor Journal of Applied Physics 46 3876-3881
[7] Nikolaev I and Emelin E 2004 Portable NO₂ gas analyzer in the concentration range 0.02-2 ppm based on a MDS-sensor Measurement Techniques 47 1113-1115
[8] Bykovskiy Y, Degtyarev V, Degtyarenko N, Yelesin V, Laptev I and Nevolin V 1972 Kineticheskiye energii ionov lazernoy plazmy Zhurnal tekhnicheskoy fiziki XLII (3) 658 (in Russian)
[9] Nikolaev I, Litvinov A and Yemelin E 2006 A model of MIS sensors sensitivity mechanism to gas concentration Sensors and Systems (Russian scientific journal) 7 66-73
[10] Nikolaev I, Kalinina L and Litvinov A 2009 The new type of strapping sites for molecules with dipole moments in dielectric Solid state physics (Russian scientific journal) 51 (6) 1065-1069.
[11] Samotaev N et al 2010 MIS-FE sensors for low concentration of H₂S for environmental monitoring Procedia Engineering 5 1216-1219