DOI 10.5162/IMCS2018/P1AP.20

Improving Detection Chlorine by Field Effect Gas Sensor with Using Temperature Pulse Mode.

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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.

Key words: Field effect sensor, gas sensor, Chlorine.

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 is not achieving by liquid electrochemical sensors 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 Cl_2. Therefore, the purpose of the present work was creation inexpensive and useful sensor system for low Cl_2 concentration measurement in presence of H_2 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. The sensitivity of MIS FE sensor of the Pd-SiO2-Si type to H_2 was first demonstrated in [1]. Later was found sensitivity of MIS FE sensors to non-content hydrogen gases in [2].

Experiment

To detect necessary sub-ppb ranges Cl_2 concentrations we have used MIS-FE sensor with structure Pd-Ta_2O_5-SiO_2-Si. Thin film palladium gate of MIS-FE sensor was obtained by pulse laser deposition [3].

Under primary tests the using sensor gives opposite amplitude responses to H_2 and Cl_2 mean that molecules of these gases interact with different types of traps at the metal-insulator interface: H_2 molecules with negatively charged traps and Cl_2 molecules with traps charged positively.

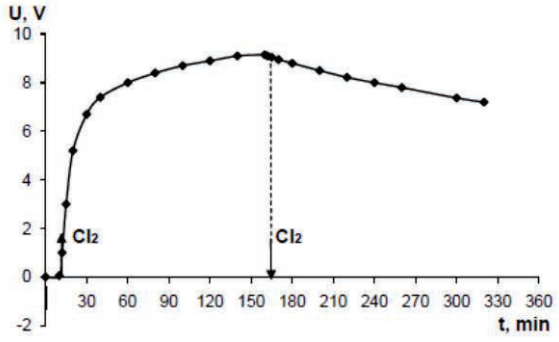

Fig. 1. The response of the MIS-FE sensor to 50 ppb of chlorine at 100 ^{0}C constant working temperature. Signal are given after electronic converter.

As can be seen from Fig. 1, MIS-FE sensors have long response ($\tau_{0,9}$ = 70 min) and relaxation times ($\tau_{0,1} \rightarrow \infty$) at 100 ^{0}C the operating temperature. For comparison, at the same temperature, response and relaxation times of the MIS-FE sensor to hydrogen at a concentration of several 50 ppb ($\tau_{0,9} = \tau_{0,1}$ = 10 min).

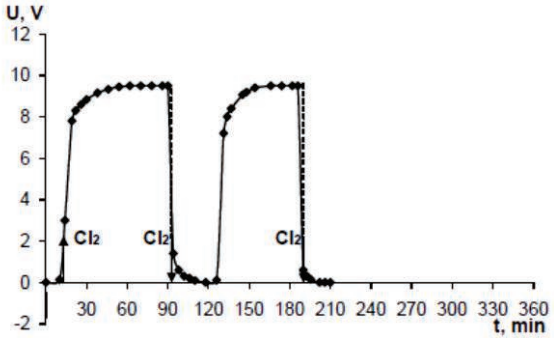

Fig. 2. The response of the MIS-FE sensor to 50 ppb of chlorine at pulse heating mode 190^{0}C / 100 ^{0}C working temperature. Signal is given after electronic converter.

The results of measurements of the sensitivity of MIS FE sensors to Cl_2 in the pulsed heating mode are shown in Fig. 2. In this working mode, the 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. It is not yet clear why in the pulse heating mode the response time of the sensor is longer than the relaxation time, however, the values that parameters are already acceptable for the use as a sensitive element of the gas analyzer. We applied a pulse heating mode for creating a chlorine gas analyzer. The response of the MIS sensor in the gas analyzer has the schematic form shown in Fig. 3.

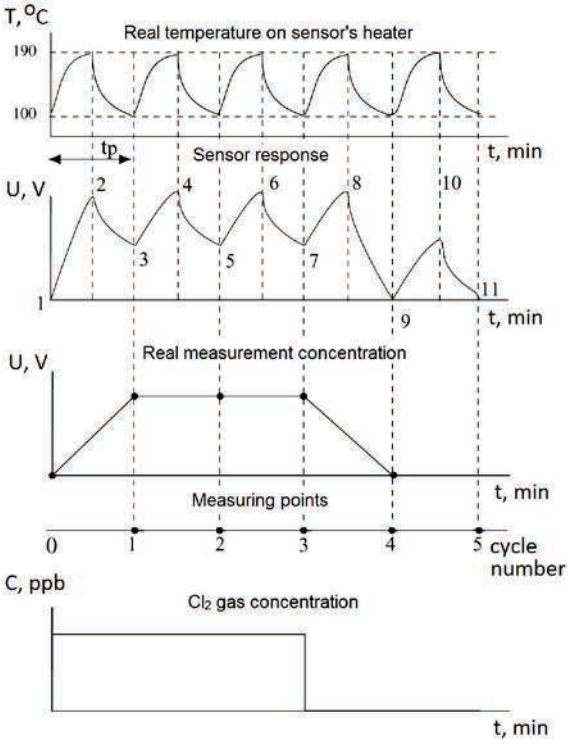

Fig. 3. The measuring principle of the Cl_2 gas concentration by MIS-FE sensor operating in the pulse heating mode (t_p - time between two measurements of the Cl_2 gas concentration).

The high sensitivity to Cl_2 was obtained during measurements in laboratory conditions. The absolute error of such measurements is 10 mV, such error allows one to measure Cl_2 concentrations at the level of 0.1 ppb. However, when we using a MIS FE sensor as a sensitive element in a gas analyzer under real (atmospheric) conditions measurement error may increases by an order of magnitude due to the influence of uncontrolled external factors.

Tests have shown that in real (atmospheric) conditions with a gas analyzer using MIS FE sensor starting to measure Cl_2 concentrations from several ppb. The selectivity of the gas analytical system can be improved by using a two-channel measuring system with Cl_2 filtration as a present in the work [3] for sub-ppb H_2S gas concentration.

Conclusion

The significant magnitude of response the MIS sensor to Cl_2 (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 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 an excellent tool for environmental control in industrial electrochlorination process.

The developed gas analytical system based on MOF FE sensor has been successfully applied to control the environmental in the plant for extraction of platinum group metals from spent automotive catalysts by hydrometallurgy methods in presence of HCl electrolysis products.

Acknowledgement

This work was supported by the Ministry Education and Science Russian Federation (Grant No. 14.575.21.0153 from 26.09.2017, unique identifier RFMEFI57517X0153).

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