ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Procedia Chemistry 1 (2009) 184–187
Procedia Chemistry
www.elsevier.com/locate/procedia

Proceedings of the Eurosensors XXIII conference

Research of the interaction mechanism between HCl and semiconductor metal oxides

T. Tsyrkina[a], L. Obvintseva[a]*, V. Kuchaev[a], A. Avetisov[a], S.Penkin[b], I. Sukhareva[a], M. Dmitrieva[a]

[a]Karpov Institute of Physical Chemistry, 10 Vorontsovo pole st., Moscow, 105064, Russia
[b]Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia

Abstract

Gas-sensitivity was investigated of n- and p-types conductivity semiconductor sensors based on zinc, indium and chrome oxides with the respect to hydrogen chloride (0.06 – 3 ppm). Disclosed were two mechanisms of interaction between HC1 and above metal oxides. It is demonstrated that HCl chemisorption results in decrease, and chlorine generation by HCl oxidation results in increase of semiconductor sensor resistance of n-type conductivity. Inverse relationship is observed for sensors with p-type conductivity. Calculation results of HCl conversion degree under the conditions of thermodynamic equilibrium of the reaction of HCl to Cl_2 oxidation are in good agreement with the experimental results for different sensor temperatures, gas humidity range and oxygen content.

Keywords: semiconductor sensor; hydrogn chloride; hydrogen chloride oxidation

1. Introduction

Low cost semiconductor sensors intended for the determination of HCl trace concentrations are of great interest for HC1 environmental monitoring and control during technological processes in microelectronic and nonferrous metallurgy industries. However, the data on semiconductor sensors for hydrogen chloride are lacking.

In our development [1] the fact was revealed of two types of sensor signals for n-type conductivity sensors based on ZnO and In_2O_3 towards HC1: acceptor signal (sensor resistance increases) and donor signal (sensor resistance decreases). The signal type and magnitude depend on sensor temperature and humidity. The origin of the above phenomena was not clarified.

The purpose of the presented development was the research of the interaction mechanisms between HC1 and metal oxide sensors, which results in various types of sensor signals. Investigated were the laws of resistance changes the n-type conductivity sensors (ZnO and In_2O_3) and p-type conductivity sensors (Cr_2O_3) as a function of sensor temperature, gas mixture humidity and oxygen contents in the inert gas.

2. Experimental

Semiconductor sensor is a polycor isolating substrate with the size of 1,5x1,5 mm. On one of substrate sites there is a Pt heater, on the other there are meander measuring electrodes. Metal oxide sensitive layers were put over the electrodes. The temperature conditions and the measurements of sensor sensetive layers resistance were provided by the automated electronic unit of the sensor analyzer [2]. The accuracy of temperature maintenance was ± 0.5°C. The sensor was placed in a hermetically sealed Teflon flow cap, the flow was pumped out by automatic ejector. The gas-dynamic setup consists of a system for the formation of the analyzed gas mixture and a sensor line. A carrier gas was mixture of Ar and O_2 with different ratio. The ratio of the Ar-O_2 mixture was set out by gas-mixing block with Bronkhorst automatic regulators. Gas humidity was set using special humidity dispenser and measured with an Iva-6B thermal hygrometer ("Microfor" production). Hydrogen chloride was dispensed using a Mikrogaz-M with a diffusion generator HCl ("Ecomonitoring" production). All setup tubing was made of

* Corresponding author. Tel.: +7-495-916-1719; fax: +7-495-917-24-90.
E-mail address: ayumi_osu@mail.ru; obvint@yandex.ru

doi:10.1016/j.proche.2009.07.046

Teflon. The setup is automated, all parameters: Ar and O_2 flows, humidity, sensor parameters (sensor and heater resistance, voltage and current) are displayed under real time conditions and saved in data files. Experiments were carried out in Ar-O_2 mixtures media with oxygen concentration range from 0 to 70%; humidity range from 0.3 to 99% at room temperature, and sensors temperature range from 17 to 450^{o}C and hydrogen chloride concentration 0.06–3 ppm.

3. Results and discussion

We studied the influence of the conditions when in presence of HCl donor and acceptor sensor signals were observed. The examples of both types of signals in the presence of hydrogen chloride are given in fig.1. The signals are given in relative units R/R_0, where R and R_0 are the current and initial values of the resistance of the sensor, respectively.

3.1. Humidity influence

In fig.1 are given the examples of sensor signal kinetics in presence of HCl in dry (fig.1, curves1-4, 6) and in humid gas (fig.1, curve 5). In the presence of hydrogen chloride gas humidity has great effect on the signal of sensors. The acceptor signal was observed in dry gas (fig.1, curves 1-3) and the donor signal was observed in humid gas (fig.1, curve 5).

It should be noted that under experimental conditions water vapors induce moderate signal of tested sensors (ZnO and In_2O_3). This signal exhibits donor character (decrease of resistance of sensitive layer). Change of humidity from 25 to 85% causes only 3% change of sensor resistance ZnO at 20% of oxygen in Ar-O_2 mixture [1].

3.2. Temperature influence

At the same humidity and oxygen content conditions when sensor temperature decreases acceptor signal increases (fig.1, curves 2, 3), when sensor temperature increases donor signal is observed (fig.1, curve 5). Magnitude of temperature influence on sensor signal depends on gas humidity. The response rate of the sensor decreases at lower temperatures, and its sensitivity decreases at higher temperatures (fig.1, curves 1-3).

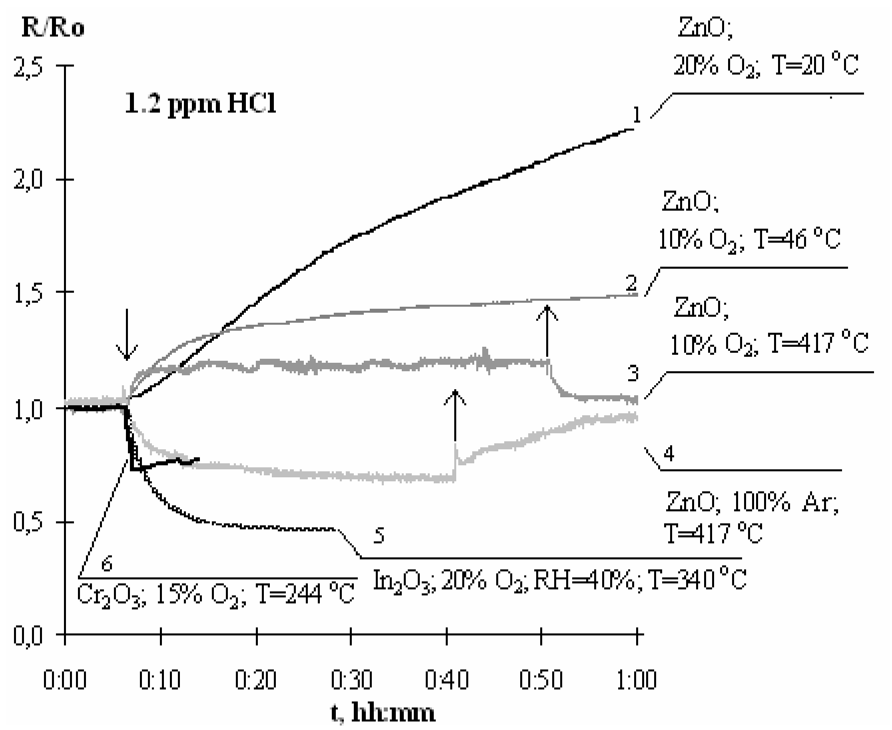

Fig.1. Examples of the acceptor (1-3, 6) and donor (4-5) sensor signals in the presence of 1.2 ppm HCl in different Ar-O_2 mixture media and sensor temperatures. Experiments were carried out in dry gas (curves 1-4 and 6) and under condition of RH=40% (curve 5). Down and up arrows denote the time of the change-over of gas mixtures.

3.3. Oxygen influence

Under inert gas conditions only donor signal is observed within the whole investigated sensor temperature range (fig.1, curve 4). Oxygen presence causes the appearance of acceptor signal at the same sensor temperature (fig.1, curve 3). Increase of oxygen concentration intensify acceptor signal.

For the n- (ZnO and In_2O_3) and p-type conductivity (Cr_2O_3) sensors the influence of the above factors (gas humidity, sensor temperature, O_2 concentration) is identical at the qualitative level. Naturally, the signals of n- and p- type sensors differ by sign only (fig.1, curves 6 and 3).

At intermediate experimental conditions, both sensor signals and transformation one into another can be observed. As the above factors influence the process of HCl and sensor sensitive layer simultaneously, extraction of the influence of separate factors is an intricate problem.

4. Interaction mechanisms

To assess the above signal behavior we assume the donor signal to be caused by adsorption of HC1 and acceptor signal to be caused by formation of Cl_2 through the oxidation of HC1 by oxygen according to reaction:

$$4HCl + O_2 = 2Cl_2 + 2H_2O \quad (1)$$

It is known that chlorine increases resistance of n-type conductivity sensors [3, 4]. Water that is present in gas mixture inhibits formation of chlorine and thus suppresses acceptor signal. Hydrogen chloride degree of conversion, as well as concentrations of chlorine C_{C12} and hydrogen chloride C_{HC1} are calculated for the condition of thermodynamic equilibrium of the reaction (1). Calculations were carried out for concentration of oxygen in Ar-O_2 mixture 20%. Oxygen content was postulated to be constant. The initial water concentration C^0_{H2O} is also constant, which is true under the conditions: $C^o_{H2O} >> C^o_{HCl}$ (initial concentrations). In the dry gas $C_{Cl2} = C_{H2O}$. Calculations were carried out for concentration of hydrogen chloride C^0_{HC1} = 1,2ppm at zero gas humidity (dry gas) and humidity: RH=25; 40; 99%, temperature range from 0 to 700 ^{0}C. Results of calculation of C_{HC1} and C_{C12} are given in fig. 2.

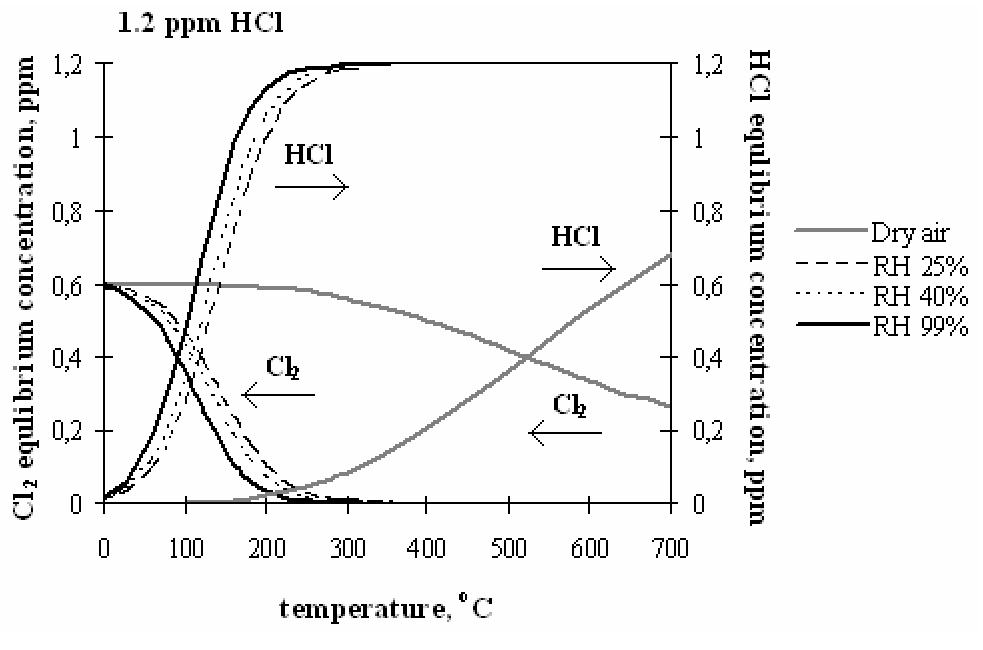

Fig. 2. Calculation results for HCl (right axis) to Cl_2 (left axis) conversion degree under the conditions of thermodynamic equilibrium of the HCl oxidation reaction: for RH = 0; 25; 40; 99% and initial HCl concentration 1.2 ppm.

In dry gas chlorine prevails at temperatures up to 450 ^{0}C, when sensor temperature is 450 -600 ^{0}C concentrations of HCl and Cl_2 are comparable, at higher temperatures HCl prevails. In humid gas chlorine prevails only at temperatures lower than 70 ^{0}C, at temperatures 80-110 ^{0}C concentrations of HCl and Cl_2 are comparable, at higher temperatures HC1 is a prevailing substance. Conversion of HC1 to $C1_2$ slows down with the increase of temperature.

According to the above said, the oxidation of hydrogen chloride to the chlorine does not take place under the conditions of oxygen absence, which means that the acceptor signal is not observed. Only donor signal was observed in the inert gas medium (fig.1, curve 4), and acceptor signal was observed under the identical conditions with the presence of oxygen (fig.1, curve 3).

Decrease of sensor temperature enable formation of chlorine and thus increase acceptor signal of the sensor (fig.1, curves 1, 2). Increase of H_2O concentration in the initial mixture lead to the increase of HCl in gas phase and to emergence of donor sensor signal (fig.1, curve 5).

The obtained result confirms hypothesis about oxidation of HCl to chlorine by oxygen. The surface of sensor sensitive layer can be a catalyst for this reaction. Thereby the results of calculations of HCl conversion degree at thermodynamic equilibrium are in agreement with experimental results.

5. Conclusions

The factors are revealed upon which the sensor signal character (donor or acceptor) is based. They are sensor temperature, gas humidity and oxygen content.

The model is proposed which allows us to explain the fact of various types of signals appearance under various conditions. The above interaction mechanisms go on the supposition that the donor signal to be caused by adsorption of HC1 and acceptor signal to be caused by formation of Cl_2 through the oxidation of HC1 by oxygen according to reaction (1). Results of the calculations for HCl conversion degree at thermodynamic equilibrium are in agreement with experimental results that confirms the proposed model.

Acknowledgements

We express our gratitude to Russian Foundation for Basic Research (RFBR) for financial support of our development. Projects 08-05-01034-a; 09-03-00934-a.

References

1. Obvintseva L.A., Oksengoit E.A., Kuchaev V.L., et.al.; Specific features of the detection of hydrogen chloride in air with semiconductor sensors, Journal of Analytical Chemistry, 2008, Vol. 63, No. 3, pp. 280–284.
2. Belikov I.B., Zhernikov K.V., Obvintseva L.A., Shumsky R.A., Atmosphere gas analyzer based on semiconductor sensors, Pribory i tehnika eksperimenta (Russ. Journ.), 6 (2008) 139-140.
3. Tamaki Jun, Chizuko Naruo, Yoshifumi Yamamoto, Masao Matsuoka, Sensing properties to dilute chlorine gas of indium oxide based thin film sensors prepared by electron beam evaporation Sensors and Actuators B, 2002, v. 83, 1 3, p. 190 - 194.

4.Obvintseva, L.A. and Gubanova, D.P., Rapid Detection of Chlorine and Chlorine Dioxide in Air Using Semiconductor Sensors, Journal of Analytical Chemistry, 2004, vol. 59, no. 8, pp. 871 - 876.