

## SIMULTANEOUS EVALUATION OF THE ELECTRICAL RESISTANCE AND WORK FUNCTION CHANGES FOR CHEMORESISTIVE TYPE SENSORS

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*Abstract:* A complex investigation of chemoresistive sensors based on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was carried out by means of simultaneous monitoring of two physical parameters: conductance (resistance) and work function variation. The purpose is to reveal differences induced by various gases and distinguish between a concentration raise and an exposure to different gas species.

*Keywords:* Fe<sub>2</sub>O<sub>3</sub>, chemoresistive sensor, Kelvin Probe technique.

### INTRODUCTION

Semiconductor gas sensors transform chemical interactions into electrical signals via surface reactions by adsorption (chemisorption) process. Since there are many compounds ready to interact at the surface is difficult to obtain selectivity for only one gaseous species.

The basic principle of solid-state chemical sensor operation is the control of the surface potential barrier by adsorbed radicals (surface charge or work function change). This potential change can be produced by different surface interactions and can be read-out by means of Kelvin Probe technique, which is a non-destructive method, and also by resistance measurements.

For compound semiconductors with ionic bonding, the barrier height follows the changes in the work function. As the work function is very sensitive to surface adsorption process, the system which contains compound semiconductors is usually very sensitive. It is known from the theory of adsorption that the surface coverage is usually proportional to work function changes due to adsorption.

Sensor selectivity remains an unsolved problem and it is obvious that resistance alone cannot deliver clear information on environmental conditions. The change in sensor resistance is the same for a certain step change in partial pressure of gaseous species *A* as it would be for another step change in partial pressure of another gas species *B*.

For chemo resistive type sensors, the simultaneous evaluation of the electrical resistance and work function changes seems physically more reasonable than the simple relative change of the resistance.

## METHODS

Both changes in resistance and relative work function can be simultaneously monitored by a special setup combining a Keithley digital multimeter and a McAllister Kelvin probe. The sensor to be investigated is enclosed in a steel chamber of relative small volume where mixture gases are injected with total flow in range of 50-200 ml/min. The gases are delivered by a gas mixing station, which can dilute the target gases in air obtaining mixtures with resolution smaller than 1ppm [1].

The digital multimeter in a two-point setup records resistance changes triggered by changing the gaseous atmosphere. Work function changes induced by surrounding atmosphere at the semiconductor surface are determined by a Kelvin probe system [2], which is basically a vibrating capacitor with an oscillating reference plate while the other being the surface of the sensor.

## RESULTS

The selectivity of a semiconductor gas sensor is a delicate problem and can only be enhanced by using special filters or catalyst additives. Another solution is to find a temperature regime, which allows a certain reaction to take place at the surface of the sensor knowing that temperature is a major player in such a reaction.

Still, at a given temperature, the influence of different gases cannot be clearly read. In our experiments we have used a semiconductor sensor based on  $\text{Fe}_2\text{O}_3$  on alumina substrate with a built-in heater. We have chosen an arbitrary temperature and have tested the response of the sensor to step changes in gas concentration. The gases in different concentrations were diluted in dry synthetic air of high purity, which constitutes the reference atmosphere. As target gases carbon monoxide and methane were chosen for they are most frequent the cause of severe accidents. Water vapors were also considered as they are always present in atmosphere and have a strong influence on sensor response to other gases. All gases were injected separately into the sensor chamber; study on a complex simulated atmosphere will be presented elsewhere.

Figure 1 presents the response of the sensor as different concentrations of target gases are brought to the sensor. One can see the carbon monoxide is clearly "seen" but the output signal is extremely low and it will be overwhelmed by the signal corresponding to water vapors in real conditions. On the other hand, the resistance change triggered by the presence of  $\text{CH}_4$  is almost the same with the one produced by water vapors. In these conditions, the sensor will fail to alarm when explosion conditions are present or will give a false alarm when only mist exists.

It seems the sensor is useless because we have chosen a bad temperature regime or the sensor is not proper designed for gas sensing. In the following, we will present some results showing a distinction can be made regardless special conditions.

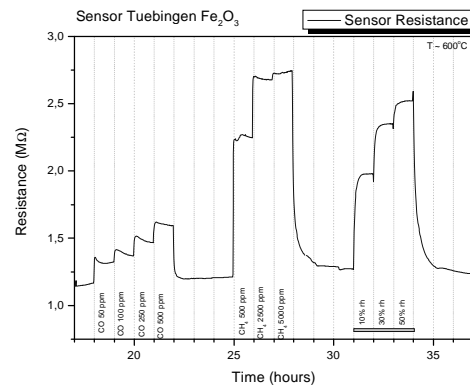


Fig. 1 - Change in the resistance of the sensor at different concentrations of test gases

The work function  $\Phi$  contains three contributions: energy difference between Fermi level and conduction band in the bulk  $(E_C - E_F)_{bulk}$ , band bending  $qV_S$  and electronic affinity  $\chi$ . All three contributions may change to gas exposure [3], [4].

$$\Phi = (E_C - E_F)_{bulk} + qV_S + \chi \quad (1)$$

The conductance of the semiconductor may be described by equation (2).

$$G = G_0 \exp\left\{\frac{(E_F - E_C)_{bulk} - qV_S}{k_B T}\right\} = G_0 \exp\left\{\frac{(\chi - \Phi)}{k_B T}\right\} \quad (2)$$

It follows

$$k_B T \ln(G/G_0) = \chi - \Phi \quad (3)$$

Our setup measurement does not allow an absolute evaluation for the semiconductor work function but only a change  $\Delta\Phi$  with respect to distinct situations  $\Phi_F$  and  $\Phi_I$ , initial situation corresponding to normal atmospheric conditions and final situation corresponding to steady state in contaminated air.

Hence, using (3):

$$\Delta\Phi = \Phi_F - \Phi_I = k_B T \ln(G_I/G_F) + \chi_F - \chi_I = k_B T \ln(R_F/R_I) + \Delta\chi \quad (4)$$

By considering in the final state the parameters of the sensor when exposed to gas while in the initial state the parameters measured in clean air we can combine resistance measurements with relative changes in work function to obtain the variation of the electronic affinity to environment.

The results of such action for our sensor are given below.

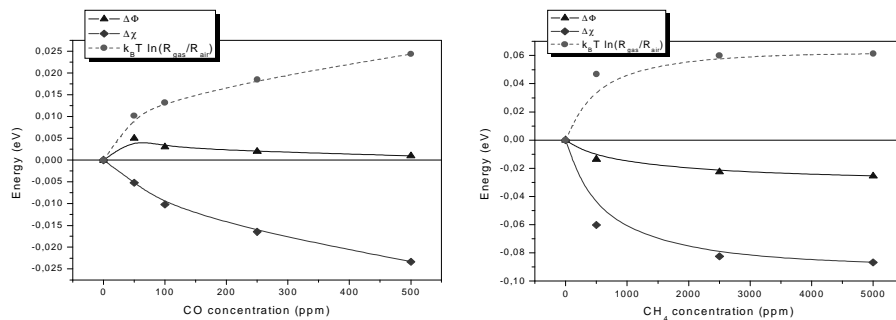


Fig. 2 - Typical changes induced by the presence of a reducing gas  
left: CO effect; right: CH<sub>4</sub> effect

It can be seen the CO has no significant influence on the work function of semiconductor but the affinity is affected. In the case of CH<sub>4</sub>, the influence in work function is relevant and the electronic affinity is strongly affected.

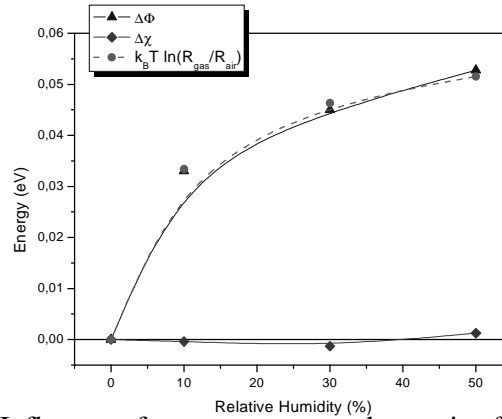


Fig. 3 - Influence of water vapors on electronic affinity and work function

Figure 3 reveal that relative humidity does not affect the electronic affinity of the sensor active material. As a result, although the information read via the resistance of the sensor could not distinguish between methane and water vapors, we can tell methane is present by observing the evolution of the electronic affinity: having a certain variation of this parameter involves methane dissociation at the surface of the sensor.

## CONCLUSIONS

The present paper reveals a method to distinguish different gases in the sensor vicinity by extracting information on stimuli through different parameter that are simultaneously influenced. The relative variation of work function and consequently electronic affinity variation allow not only to differentiate between possible present gases, but also to obtain information on surface coverage, adsorption and path of chemical reactions at the surface of the sensor.

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