GAS DETECTION BASED ON SURFACE REACTIVITY OF METAL OXIDE SEMICONDUCTORS

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ABSTRACT

Surface, defined like interface between semiconductor bulk and surrounding atmosphere, plays an important role in all phenomena for which interaction between semiconductor and gaseous surroundings is important. Surface atoms are in the situation in which bonding forces exercised by the bulk atoms cannot be compensated by symmetric forces. Compensation tendency of unsatisfied bonds produces superficial structural modifications and their high chemical reactivity. As consequence, at surface can be present coming from surrounding atmosphere, new species, atoms or molecules. They can react reversibly with surface, or irreversibly providing a new phase (compound).

KEYWORDS : Surface, metal oxide semiconductors, SnO_2, interface, surrounding atmosphere

1.INTRODUCTION

Metal Oxide Semiconductors forms a group of compounds which specific interface and surface properties are intensive used in actual electronics. For this reason, the attention of many users and scientists interested in toxic and explosive gas detection has focused generally to metal oxides (ZnO, Fe_2O_3, In_2O_3, TiO_3, WO_3) and particular to SnO_2.

A specific property for oxide semiconductors is oxygen exchange with the surrounding atmosphere. This property is important in their use as gas sensors. When an oxide layer is formed at surface, specific surface states are created, named interface states. This effect leads to apparition of energetic levels localized at surface, which can be placed in the energy gap of the semiconductor. At MOS sensors, surface phenomena play an essential role. For obtain high sensor effects, the semiconductor should have a higher specific surface. Sensor effect, respectively surface conduction (resistance) variation in the presence of reducing gases in air, is preceded by the chemisorptions of atmospheric oxygen in their forms (O^{2-}, O^{-}, O^{--}) – surface oxidation and consist in – surface reduction, by reaction between reducing gas accidentally present in atmosphere and oxygen previously adsorbed. On the other hands MOS translate a chemical interaction into an electrical signal and for this reason materials used in gas detection is also named chemoresistive materials.

2. TEHNOLOGY

Chemoresistive gas sensors are traducing elements which constructively consist in relative simple and chip structure, formed by gas-sensitive material deposited between two metallic electrodes allowing its electrical resistance measurement.

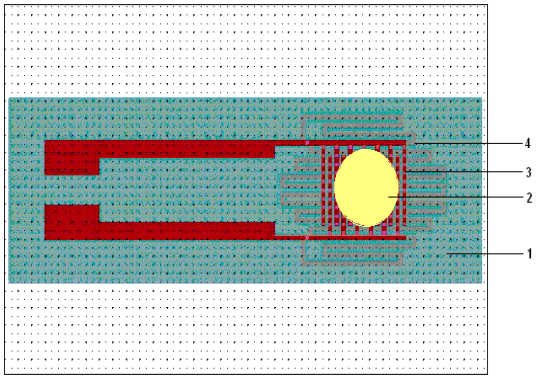

Fig. 1. Sensor Structure: 1- alumina substrate; 2- gas-sensitive material; 3-Electrodes (interdigital resistor);4-Heater

Metallic electrodes are deposited on the top side of an isolated substrate. On the reverse

side of the substrate is deposited the metallic heater which permit temperature variation of the active layer.
Most of research efforts were orientated in the direction of obtaining sensitive, selective and stable sensors, dedicated to applications in which will be used. A way to sensitivity increasing is the incorporation of catalytically active material, e.g. precious metals (0,2% Pd), in the sensitive material. Pd doping involves a spill-over gas interaction mechanism, favours SnO_2 oxidation and respectively dehydrogenation of hydrocarbons at lower temperatures. At higher concentrations, clusters of Pd are created and the specific reaction surface decrease.

3. EXPERIMENTAL

Dynamic study method of sensor effect, respectively electrical resistance variation due to the change of test gas atmosphere, involves measurements in gas flow and presents the advantage of maintaining long time constant reference atmosphere.
Dynamic regime measurements has been realised with the Gas Mixing System. The system is fully computer controlled and its components in contact with the gas are made only of stainless steel, teflon and glass, for avoiding additional interferences.

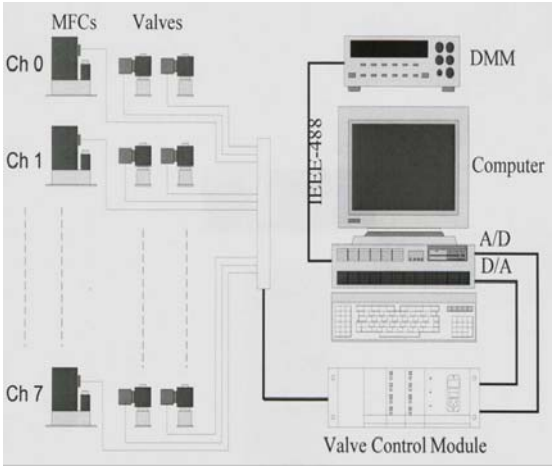

Fig. 2. Gas Mixing Station Component parts and electrical connections

The system has 8 gas flow channels; every channel of the flow system consists of a flow controller, a vaporizer and two electro valves.

4. RESULTS

The electrical resistance R variation has been observed as:
- Dependence of working temperature (T), for determining the optimum interaction temperature of each specific gas.
- Dependence of relative humidity of surrounding atmosphere (%RH).
-Dependence of test-gas concentration, respectively for CO and CH_4 ;

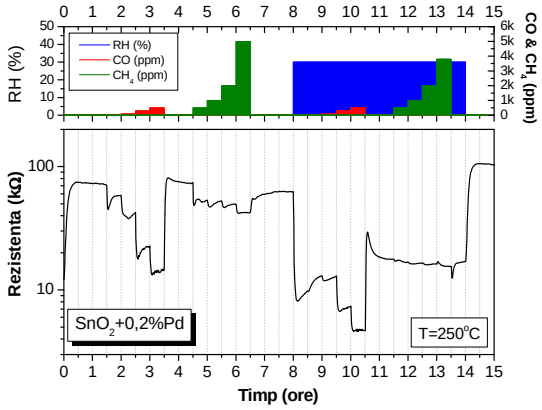

Fig. 3. Dependence R=f(t) on T=250^{0}C, in controlled humid and test-gas atmosphere

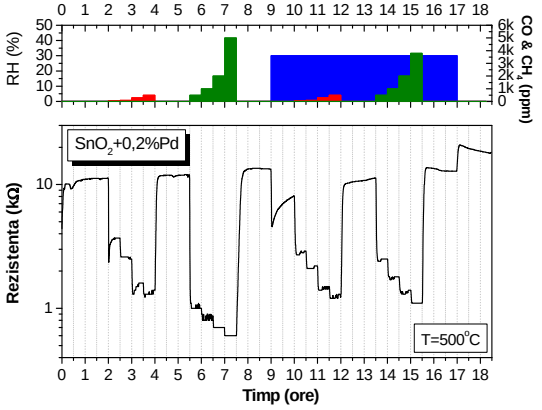

Fig. 4. Dependence R=f(t) on T=500^{0}C, in controlled humid and test-gas atmosphere

Test-gas concentrations were :
CO : 0, 50, 100, 300, 500 ppm
CH_4 : 0, 500, 1000, 2000, 5000 ppm

Based on experimental results the sensitivity defined as (1) has been analysed:

$$S = R_0 / R \qquad (1)$$

were:

R_0 = resistance in air (synthetic air with 0%, respectively 30% humidity),

R = resistance in test-gas atmosphere (CO, respective CH_4).

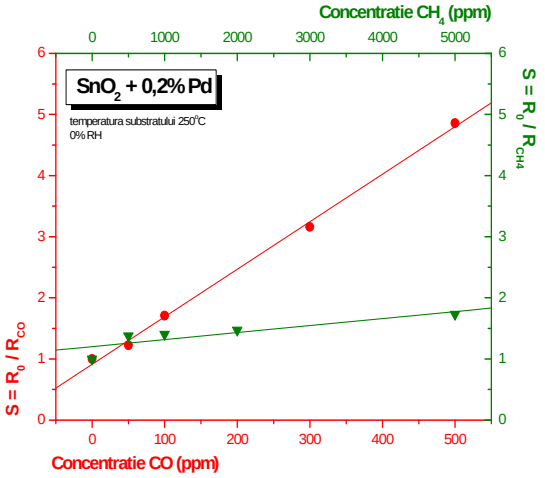

Fig. 5. Sensitivity S=f(Gas conc.)at T=250^{0}C, in dry atmosphere (0%RH)

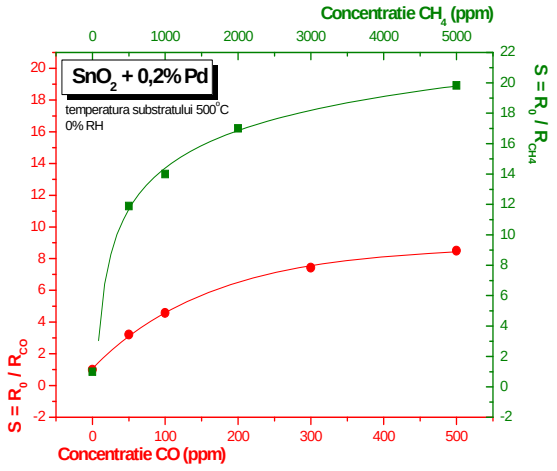

Fig. 6. Sensitivity S=f(Gas conc.)at T=500^{0}C, in dry atmosphere (0%RH)

Figures 5 and 6 illustrate the fact that active layer temperature modulation between 250 and 500^{0}C respectively, facilitates selective detection of the interest gases [1]. The lower temperature is optimal to CO detection relatively to CH_4 and the sensitivity S linear varies related to the gas concentration; the higher temperature is optimal to CH_4 detection relatively to CO and the sensitivity S exponential varies. Surface interactions are strong activated by temperature.

The influence induced by the presence of water vapours in the test atmosphere, has completed the sensitivity study (Fig.7, 8). The evaluation of the applicative potential of the material should take into consideration the water effect.

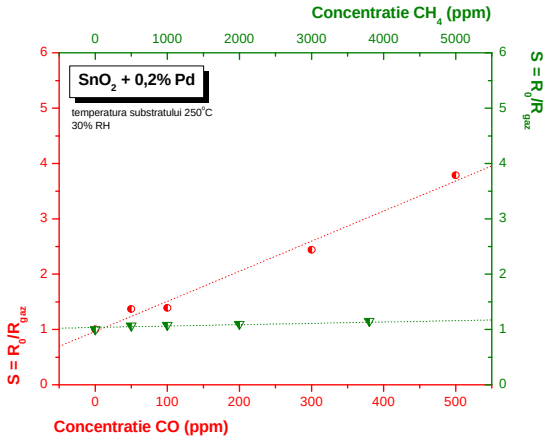

Fig. 7. Sensitivity S=f(Gas conc.)at T=250^{0}C, in humid atmosphere (30%RH)

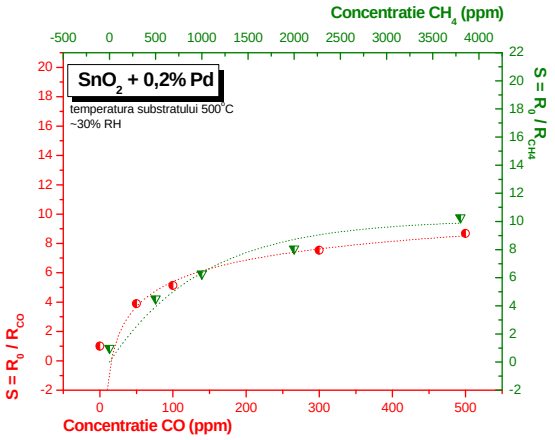

Fig. 8. Sensitivity S=f(Gas conc.)at T=500^{0}C, in humid atmosphere (30%RH)

Figures 7 and 8 illustrate the influence of atmosphere humidity on the material sensitivity, in the sense of its decreasing.

As time as from the point of view of carbon monoxide, the sensitivity is low affected, in terms of methane (at T = 500^{0}C) air humidity strongly modifies the sensitivity of the material.

5. CONCLUSIONS

Oxygen : At temperatures between 100 and 500°C semiconductor interaction with

atmospheric oxygen leads to its ionosorption as molecular (O^{2-}) and atomic (O^{-}, O^{--}) species. It is proved by TPD, FTIR, and ESR that below 150°C the molecular and above this temperature the atomic species dominate [2÷4]. The presence of these species leads to a depletion layer at the surface of tin oxide.

Water vapours: At temperatures between 100 and 500°C the interaction with water vapour leads to molecular water and hydroxyl groups. Water molecules may be adsorbed by physisorption or hydrogen bonding. TPD and IR studies show that at temperatures above 200^0C molecular water is no longer present at the surface. Hydroxyl groups appear due to an acid/base reaction with the OH^- sharing its electronic pair with the Lewis acid site (Sn) and leaving the weakly bonded proton, H^+, ready for reactions with lattice oxygen (Lewis base) or with adsorbed oxygen. IR studies [5, 6] indicate the presence of hydroxyl groups bound to Sn atoms.

Carbon monoxide: from theoretical point of view is considered to react with pre-adsorbed or lattice oxygen. Experimental results obtained in air, at temperatures between 150 and 500^0C, demonstrate that the CO presence leads to increasing the surface conduction. It is generally accepted in literature [7, 8] that the CO reacts with previously ionosorbed oxygen species.

Methane: the methane (CH_4) reacts with lattice oxygen [9] and leads to apparition of oxygen vacancies, which induces free electrons in conduction band by ionisation, fact that determines the increase of electrical conductivity (decrease of electrical resistance) of the material.

Due these interactions, results the differences in resistance evolution of the material in CO atmosphere, respectively in CH_4 and variable humidity. Even if qualitatively the resistance evolution takes place in the same way, the gas interaction with different oxygen species explains quantitative evolution of the signal. In all these interactions the working temperature plays a very important role, its evolution could be translated by different reaction energies, specific for each reaction.

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