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ELECTRON AFFINITY CHANGES INDUCED BY GASEOUS SPECIES PRESENT IN THE SOURROUNDING ATMOSPHERE

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A simultaneous evaluation of variation in electrical resistance and work function was carried out in order to calculate electron affinity changes induced by appearance of surface dipoles at sensor interface triggered by exposure to different gas species, respectively CO, CH_4 and H_2O.

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1. Introduction

Surveillance of gaseous species in the surrounding atmosphere is a large-scale application and is usually made with chemoresistive gas sensors. This is done by simply monitoring the resistance variation of the surface layer of a semiconducting oxide, which physically involves the variation in charge carrier concentration. This quantitative method has the disadvantage of being not fully selective. In order to find new ways for improving the selectivity, investigations of other physical parameters besides electrical resistance has brought new information about the Metal Oxide Semiconductor system – gas interaction [1-3].

In a previous paper [4] we showed one can tell between different gases at the sensor surface and a certain step change in concentration of a single component by simultaneous surveillance of two physical parameters: sensor resistance and semiconductor work function.

In the present paper we considered the *n*- to *p*- transition in α-Fe_2O_3-based thick film sensors already reported [5-8], and focused on electron affinity variation induced by surface dipoles formed due to interaction of α-Fe_2O_3 surface with CO, CH_4 and H_2O gaseous species.

2. Results and discussions

The sample is a α-Fe_2O_3 film which exhibits a p-type behavior [6] based on surface conductivity. Its conduction type depends on the preparation conditions. The Hall effect measurements [7] on α-Fe_2O_3 revealed a n- type semiconductor behaviour. As shown, a switch to a p- type conduction is possible in certain conditions. There are two possibilities: to consider a n-type semiconductor, which develops an inversion layer at the surface due to band bending or to consider the semiconductor as being p-type with an enriched layer at the surface.

Having in mind these presumptions we proceeded to experimental evaluation of the samples in dynamic conditions. We used a computer controlled set-up consisting of a gas mixing station which had the possibility of switching between 6 channels directly to the test gas bottles. The relative variation of the work function was measured with a McAllister Kelvin Probe and the electrical resistance was measured with a digital Keithley 2000 multimeter as illustrated in Fig. 1.

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Simultaneous evaluation of these two physical parameters allow for the calculation of the electron affinity changes.

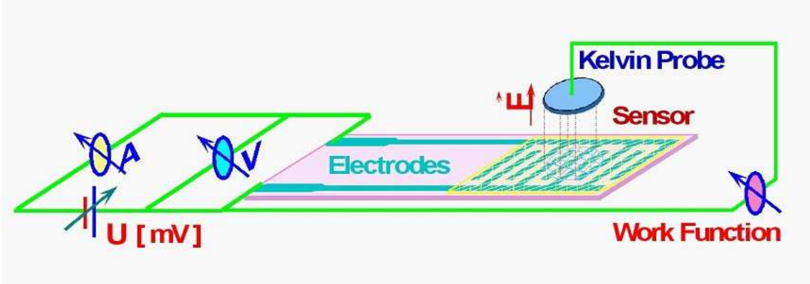

Fig. 1. Setup for simultaneous measurement of resistance and relative work function.

We observed that the resistance increases with increasing the gas concentration, which means we are dealing with a p-type surface behavior of the semiconductor.

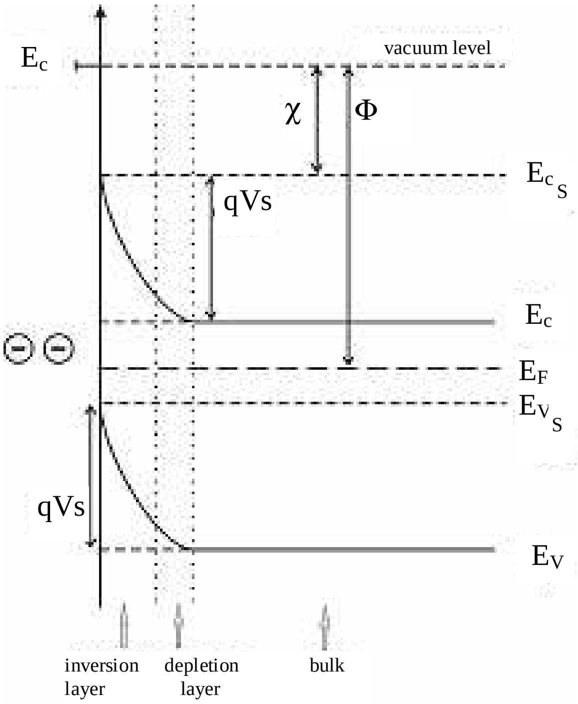

Fig. 2. Band bending on a n-type semiconductor; Changing of the surface conductivity to p-type conductivity under the effect of the surface charge.

Taking into account the surface band bending (Fig. 2), the work function Φ can be written as:

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

where χ is the electron affinity and V_s is the surface potential

The majority carriers (holes) dominate the conductance and their contribution to conductance G_0 is given by:

$$G = G_0 \exp(-\frac{(E_F - E_V)_{bulk} - qV_S}{k_B T}) \tag{2}$$

If one writes $(E_C - E_F)_{bulk} = \Phi - \chi - qV_S$ one gets $(E_F - E_V)_{bulk} = E_g - \Phi + \chi + qV_S$ and, thereafter

$$G = G_0 \exp(-\frac{E_g - \Phi + \chi}{k_B T}) \tag{3}$$

Finally the work function is expressed in terms of conductance:

$$\Phi = \chi + E_g + k_B T \ln(G/G_0) \tag{4}$$

Because both electrical resistance and work function modifications could be measured with respect to the external equilibrium conditions (i.e. no target gas present in the initial situation and a certain concentration of the target gas in the final situation), it is possible to extract information related with changes in electronic affinity due to the presence of the gases in the sensor chamber. This is expreseds by the following relation:

$$\begin{aligned} \Delta\Phi = \Phi_F - \Phi_I = \chi_F - \chi_I + k_B T \ln(G_F/G_0) - k_B T \ln(G_I/G_0) = \\ \Delta\chi + k_B T \ln(G_F/G_I) = \Delta\chi + k_B T \ln(R_I/R_F) \end{aligned} \tag{5}$$

where G_I is the initial conductance and G_F is the final conductance,

R_I is the initial resistance and R_F is the final resistance.

The data plots corresponding to the experimental results are presented in Fig. 3.

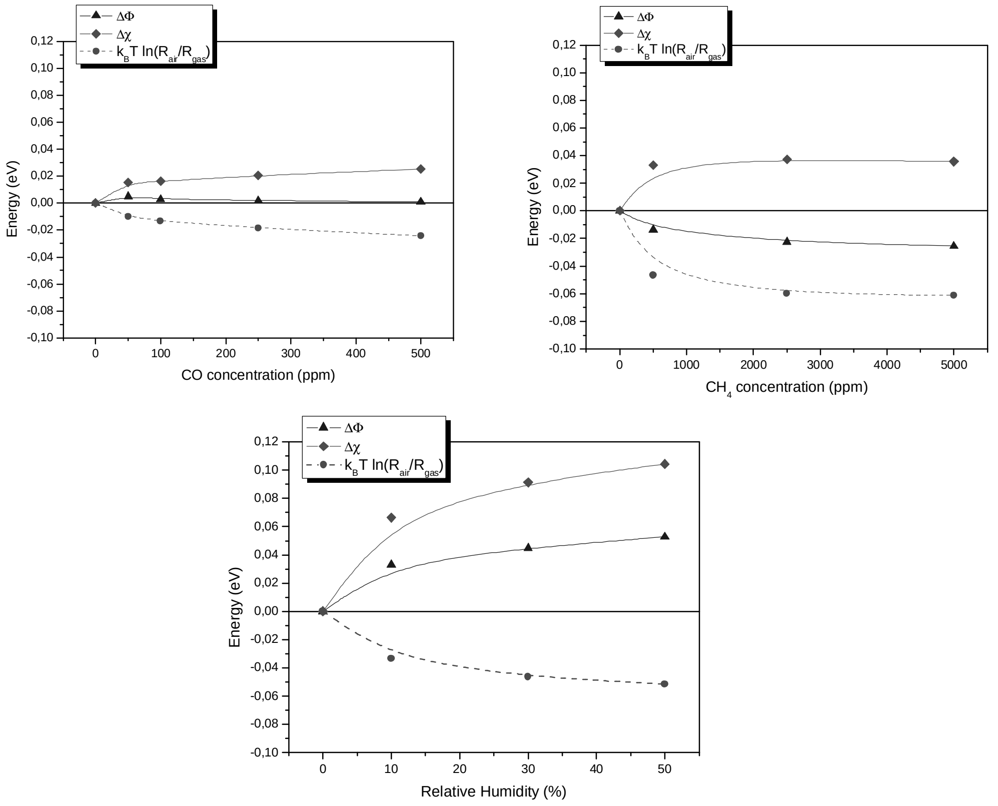

Fig. 3. Electron affinity, work function and band bending changes induced by test gas concentrations.

3. Conclusions

High reactivity of the α-Fe_2O_3 surface leads to an increased coverage of surface species coming from the atmosphere. The interaction with CO, CH_4 and H_2O (which leads to the increase of resistance, respectively decrease of band-bending) takes place through the oxygen, previously adsorbed on surface or also through the lattice oxygen. For all surface interactions with reducing gases we qualitatively observed a decrease of band-bending respectively a variation in carrier concentration.

Adsorption of CO^{ads}, $CH_4^{ads}(CH_3\text{-}H)$ and $H_2O^{ads}(OH\text{-}H)$ leads to the increase of surface dipoles density which produces the affinity changes in the α-Fe_2O_3. The coverage of the surface with perpendicular-oriented dipoles affects the carrier exchange with the bulk [9].

Being a difference between relative variation of the work function and band bending, the evolution of the electron affinity is different for different gases which affect both experimental parameters.

For mentioned reducing gases completely different evolution of electron affinity and work function was observed, even if the evolution of the resistance is the same for each gas.

$$\Delta\chi = \Delta\Phi - k_B T \ln\left({}^{R_I}\!/_{R_F}\right) \qquad (6)$$

It is revealed that electron affinity calculated on the basis of the experimental results depends both on gas type and its concentration, and one demonstrates that the simple monitoring of the variation in resistance of the surface layer does not completely illustrate the surface interactions.

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References

[1] R. Ionescu, Sensors and Actuators B, **48**, 392 (1998).
[2] A. Vancu, C. Moise, R. Ionescu, Proceedings of CIMTEC ‘98 SIX-1: p. 29 (1998).
[3] A. Heiling, N. Barsan, U. Weimar, W. Goepel, Sensors and Actuators B, **58**, 302 (1999).
[4] R. Roescu, I. Dumitriu, A. Tomescu, Romanian Rep. Phys. **56**(4), 607 (2004).
[5] R. Ionescu, Sensors and Actuators B, **58**, 375 (1999).
[6] A. Gurlo, M. Sahm et al., Sensors and Actuators B **102**, 291 (2004).
[7] F. J. Morin, Phys. Review **83**(5), 1005 (1951).
[8] G. I. Yepifanov, Yu. A. Moma, Mir Publisher, Moscow p. 302 (1984).
[9] N. Barsan, U. Weimar, J. Phys: Condensed Matter **15**, 813 (2003).