

Characterisation of the catalyst-semiconductor interaction mechanism in metal-oxide gas sensors

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Abstract

Catalysts may affect the intergranular contact regions in polycrystalline metal-oxide films with two mechanisms: spillover and Fermi energy control. In this work, a simple experimental method is proposed consisting of monitoring sensor resistance as a function of oxygen partial pressure, in order to distinguish which of these mechanisms is dominant in certain catalyst-metal oxide interfaces. Interpretation of experimental results, using the theoretical background for these two mechanisms in the case of InO_x sensors with palladium and platinum catalysts, indicates that the electronic interaction of Fermi energy control dominates in the case of palladium, while the chemical interaction of spillover dominates in the case of platinum. These results are also confirmed by Monte Carlo simulation of the spillover process. © 1997 Elsevier Science S.A.

Keywords: Fermi energy control; Metal-oxide gas sensors; Spillover

1. Introduction

Metal-oxide gas sensors exhibit high sensitivity in the case of reducing gases, the presence of which modulates oxygen adatom density. This sensitivity can be further enhanced when additives are included in the sensors, which are believed to act as catalysts to the redox reactions of the detected gases on the sensor surface. Two mechanisms have been proposed for the catalyst control in gas sensors [1]. The first is a chemical interaction in which the metal catalyst dissociates the molecule, the atoms of which can ‘spill over’ onto the surface of the semiconductor support and eventually react with oxygen adatoms, thus controlling intergranular resistance. The second is an electronic interaction in which gas adsorption on the catalyst removes electrons from the catalyst and the catalyst, in turn, removes electrons from the supporting semiconductor, thus controlling again intergranular resistance. In other words, both mechanisms are based on oxygen reactions with the metal-oxide support. The resistance modulation of resistive-type gas sensors by the presence of a reducing

gas is induced by the modulation of oxygen adatom density. Consequently, it is important to investigate the mechanisms by which catalysts affect oxygen adsorption on metal-oxide supports.

Fig. 1 shows schematically the above two situations. When spillover mechanism controls oxide resistance (Fig. 1a), adsorption of oxygen on the catalyst changes the oxidation state of the semiconductor, after it is diffused. When the Fermi energy control mechanism dominates (Fig. 1b), adsorption of oxygen on the catalyst changes the oxidation state of the catalyst, exchanging electrons with the supporting semiconductor.

In this work a simple experimental method for the determination of the dominating catalysis mechanism in InO_x -Pd and InO_x -Pt interfaces is proposed.

2. Experimental techniques

Indium oxide films were deposited by magnetron reactive sputtering in an Ar-O_2 mixture, on alumina oxide (96%) substrates at a thickness of 1000 nm. A plasma emission monitoring technique was used to control film stoichiometry and to provide reproducible films. Catalysts were deposited by electron-beam evapo-

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ration onto indium oxide surface, at an average thickness of a few nanometres, providing a discontinuous film consisting of small islands. Details about the fabrication procedure and information concerning the structure of the samples can be found elsewhere [2].

The sensor characterisation set-up was designed to measure the steady-state and the transient resistance of the samples, testing them at various working temperatures and under different gas compositions. The testing conditions were rigorously controlled via a fully automated computer-controlled system. Purified O₂-N₂ mixture was introduced into a 400 cm³ chamber with a total gas flow of 300 ml min⁻¹. The composition of the mixture was varied from 0% O₂-(O₂+N₂) to 16% O₂-(O₂+N₂) with the use of precise mass flow controllers, with steps of 2% every 10 min. Prior to the characterisation the samples were left in pure N₂ for 60 min at 400°C. The temperature of the samples during characterisation was kept constant at 350°C.

3. Experimental results and discussion

Fig. 2 shows the resistance of an InO_x film with palladium (Pd) catalyst (left axis) and an InO_x film with platinum (Pt) catalyst (right axis), in oxygen concentrations ranging from 0% to 16%. The Pt doped sensor exhibits three orders of magnitude higher resistivity than the Pd doped one. This is due to the different work functions of the two metals, as explained in [3]. A linear dependence of the resistance on oxygen concen-

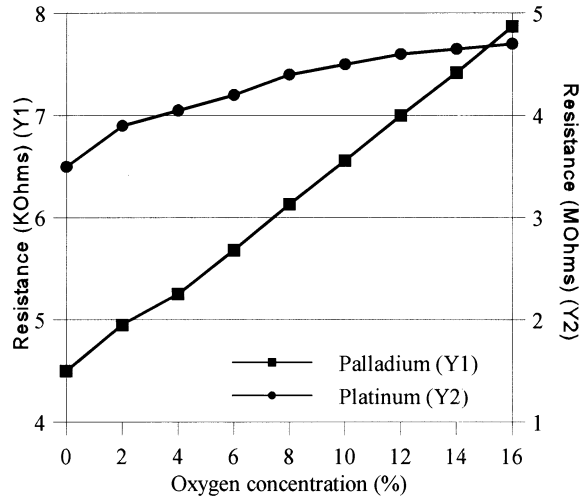


Fig. 2. Resistance of a palladium (left axis) and a platinum (right axis) covered indium oxide sensor.

tration is observed in the case of the Pd doped sensor, while an exponential dependence is observed in the case of the Pt doped sensor.

Considering the electronic interaction mechanism between additive and semiconductor (i.e. Fermi energy control mechanism), a simple ‘adsorption reaction’ route leads to resistance change. The oxygen adsorption mechanism on the additive can be described by the following reaction:



where S denotes an oxygen adsorption site, either on the catalyst or on the semiconductor and A and A' are the reaction rates, as shown in Eq. (1). Then, the adsorbed oxygen concentration at equilibrium θ_{O^-} will be given by:

$$\theta_{O^-} = \frac{A/A'}{A/A' + 1} \tag{2}$$

For $A/A' \ll 1$ (i.e. low oxygen partial pressure), there is an almost linear dependence of oxygen adatoms on oxygen partial pressure, since coefficient A is proportional to oxygen partial pressure. This situation is shown in Fig. 2, in the case of the Pd catalyst.

Considering the chemical interaction mechanism (i.e. spillover mechanism), the reaction route leading to resistance change is ‘adsorption–diffusion reaction’. Thus, it is expected that at low oxygen partial pressure the total reaction rate is controlled by adsorption rate, leading to a linear dependence of oxygen adatom density on oxygen partial pressure. At high oxygen partial pressure, when the area of indium oxide surrounding catalyst particles is filled with oxygen adatoms, diffusion speed of oxygen adatoms decreases, thus leading to a saturation of the resistance [4]. This situation is shown in Fig. 2, in the case of the Pt catalyst.

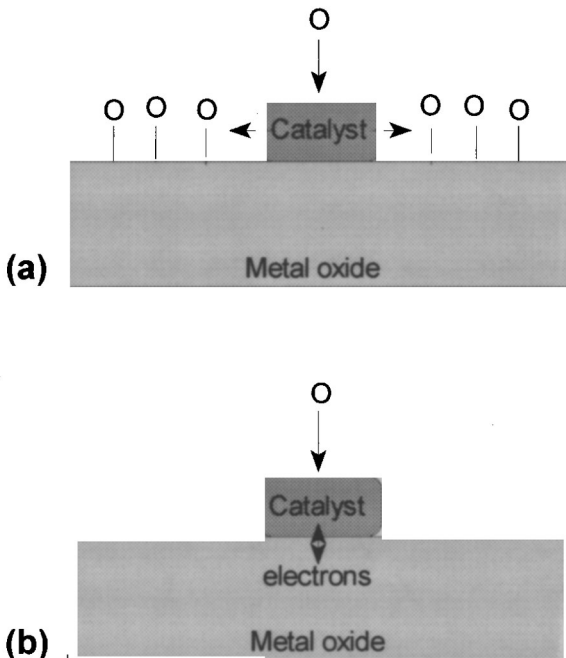


Fig. 1. (a) Spillover mechanism, (b) Fermi energy control mechanism.

4. Simulation results

The Monte Carlo simulation is applied in the case of the spillover mechanism and employs an algorithm which takes into consideration an active surface, which is represented by a two-dimensional matrix. Each site of the matrix represents an active site for oxygen adsorption, either on the additive or on the semiconductor. To obtain size independent results within a short computation time, periodic boundary conditions were adopted. A detailed description of the simulation algorithm is given in [5] and [6].

Fig. 3a shows an instance of the surface for small oxygen adsorption probability (small oxygen partial pressure). Since a uniform distribution of oxygen adatoms on the surface is observed, it is obvious that oxygen adatoms spill over as soon as they adsorb. Fig. 3b shows an instance of the surface, but for relatively high oxygen adsorption probability (high oxygen partial pressure). It is apparent that oxygen adatoms are located mainly around the catalyst particles, due to the reduction of the diffusion speed, restricting oxygen adsorption rate and thus saturating sensor resistance.

Fig. 4 shows the total oxygen adatom concentration as a function of oxygen adsorption probability. Above an adsorption probability of 0.5 the total reaction rate is controlled by the diffusion speed of oxygen adatoms and the surface coverage starts to saturate.

5. Conclusions

A simple experimental method has been suggested that can be used to determine the mechanism of interaction between catalyst and semiconducting oxide gas sensor in the presence of oxygen. In the case of InO_x doped with Pt and Pd, it has been found that Pd controls the Fermi level of the semiconductor, while in the case of Pt a diffusion mechanism like ‘spillover’

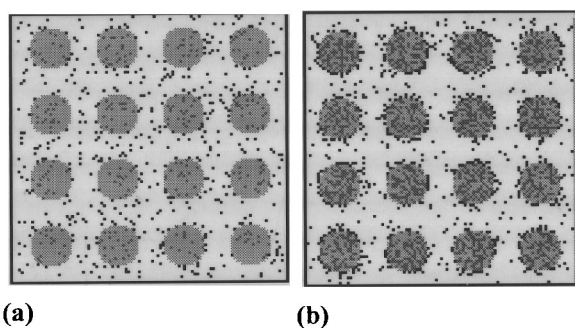


Fig. 3. Oxygen adatom distribution in the case of low oxygen partial pressure (a) and high oxygen partial pressure (b). White area represents the supporting semiconductor, gray circles represent the catalyst particles and black dots represent oxygen adatoms.

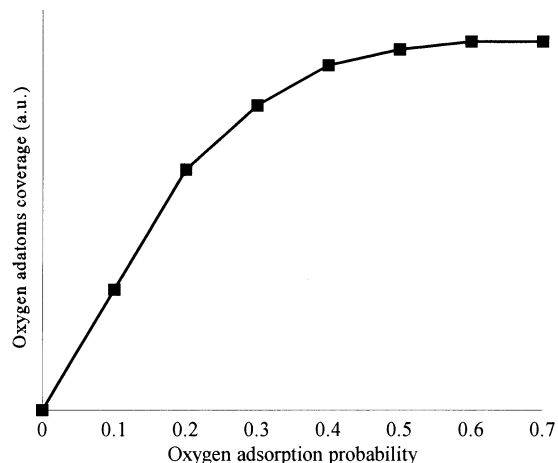


Fig. 4. The saturation of oxygen adatom concentration with increasing oxygen adsorption probability, which corresponds to oxygen partial pressure.

seems to dominate. Both experimental and Monte Carlo simulation results agree with the proposed models for interaction of Pd and Pt found in the literature.

References

- [1] S.R. Morrison, Selectivity in semiconductor gas sensors, *Sensors and Actuators* 12 (1987) 425–440.
- [2] C.A. Papadopoulos, J.N. Avaritsiotis, A model for the gas sensing properties of tin oxide thin films with surface catalysts, *Sensors and Actuators B* 28 (3) (1996) 201–210.
- [3] D.S. Vlachos, C.A. Papadopoulos, J.N. Avaritsiotis, On the electronic interaction between additives and semiconducting oxide gas sensors, *Appl. Phys. Lett.* 69 (1996) 650–652.
- [4] E. De Fresart, J. Darville, J.M. Gilles, Surface properties of tin oxide single crystals, *Surface Sci.* 126 (1983) 518–522.
- [5] P.D. Skafidas, D.S. Vlachos, J.N. Avaritsiotis, Modelling and simulation of tin oxide based thick-film gas sensors using Monte Carlo techniques, *Sensors and Actuators B* 18–19 (1994) 724–728.
- [6] P.D. Skafidas, D.S. Vlachos, J.N. Avaritsiotis, Modelling and simulation of abnormal behaviour of thick-film tin oxide sensors in CO, *Sensors and Actuators B* 21 (1994) 109–121.

Biographies

John Avaritsiotis was born in Greece in 1948. He received his B.Sc. (Hon.) in physics from the Department of Physics of the University of Athens in 1972. His M.Sc. and Ph.D. degrees were obtained from Loughborough University of Technology, in 1974 and 1976, respectively, in the field of thin-film technology and fabrication of thin-film devices.

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