

## Subjective Overview on Oxide Semiconductor Gas Sensors

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The purpose of this article is to give a possibly subjective critical overview on chemical gas sensors, focusing on oxide-semiconductor-based devices. The first part of this work covers - starting from the sensing principles - the elementary physical and chemical steps used in the process, as well as the materials used. The depth of understanding of the elementary processes is treated as a function of the experimental methods applied today. The importance of the layer thickness, grain size and macro and microstructure is considered. The two aspects of gas/solid heterogeneous catalysis are discussed: *a./* for a chemist, the selectivity in the gas phase is important, *b./* for the sensor specialist, the changes in the solid phase during the gas-solid interaction, as well as the selectivity in the analyte, are of importance. As a next step, the experimental aspects of the field are examined. The methods of improving the “3S” properties of a sensor are analysed, mainly from the point of view of materials science. Several less-common principles and new ideas and technical tricks suitable for detecting gases or improving the sensor operation are briefly described. In the above two parts, attention has been paid to the unsolved problems of modern sensor science, such as avoiding cross effects, the undesired damage of the sensor material (corrosion), reproducibility of the sample preparation or insufficient stability. In the last part, the discussed problems, where possible, are illustrated by examples of our own: *a./* The phase transitions in the solid are of special interest. In our experience, the temperature and extent of the phase transitions can be influenced by the presence of another solid or gas component. Here the effect of water is treated. *b./* The authors present their latest results obtained in the detection of CO by Pt and Pd modified SnO<sub>2</sub> using work function measurements.

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## 1. Introduction

The aim of this work is to give a possibly subjective overview of the oxide-semiconductor-based chemical gas sensors, based mainly on the results obtained in the existing classical sensor schools specialised in this discipline, such as Göpel<sup>(1,2)</sup> in Tübingen (Germany), Morrison<sup>(3,4)</sup> in Burnaby (Canada), and Williams,<sup>(5)</sup> in London (England). As is known, a chemical sensor + transducer system transforms thermodynamic activity into electrical signals. Being a very dynamically developing field, with state of the art technology, a critical overview on the oxide-semiconductor based chemical gas sensors is of considerable importance.

In the first and second parts of this work the authors start from the sensing principles, and then touch upon the elementary physical and chemical steps in the process, as well as the materials used, together with the experimental characterisation methods applied currently. The importance of the layer thickness, grain size, and macro and microstructures is treated. They analyse - mainly from the point of view of materials science - the suitable methods required to improve the properties of a sensor.

During the sensing process, the phenomenon of gas/solid heterogeneous catalysis often takes place. Sometimes it is advantageous and sometimes disadvantageous from the point of view of the gas detection. This phenomenon has two main aspects: for a chemist, the selectivity in the gas phase is crucial, while for the sensor specialist, the changes in the solid phase during the gas/solid interaction, as well as the selectivity in the analyte, are of importance.

Several less-common principles, new ideas and technical tricks - appropriate for detecting gases or improving the sensor operation - are described in brief.

Finally, the authors present their own results in two selected fields: *a./*The operation of sensors can be accompanied by phase transitions in the solid. The role of this process has not been investigated extensively in sensor science. In our experience, the temperature and extent of the phase changes could be influenced by the presence of another solid or gas component. Here the effect of water is treated. *b./*The authors present their latest results on the detection of CO by Pd and Pt impregnated SnO<sub>2</sub> thick films, using work function measurements.

## 2. Theory

### 2.1. Steps required for gas sensing by oxides semiconductors

The detection of a gas by a solid oxide semiconductor consists of an ensemble of consecutive and parallel elementary processes. Here we give an overview of these complex interactions, going from the gas phase towards the solid phase.

#### 2.1.1 Gas phase

First, the processes in the gas phase have to be considered, before considering interactions in the solid phase.

As these types of sensors in general work at several hundreds of degrees Celsius (typically between 250–800°C), some degrees of freedom of the gas molecules can be

excited, the molecules can be thermally activated, and their chemical reactivity can be increased. If the sensor is self heated, this activation can be considered only in the near surface (hot) gas region, and the extent of activation is a function of the residence time of molecules in the hot region (a function of the flow rate).

The thermally activated molecules can participate in gas-gas chemical reactions, for example, the oxidation of the reducing gases in an oxygen containing environment. This oxidation can change the composition of the gas mixture reaching the sensor surface.

### 2.1.2 Gas-solid interface

The gas/solid interface is the place where the adsorption (better referred to as the chemisorption) of the gases takes place. The adsorption is generally a dissociative process in which the original chemical bonds of the molecules break, and the fragments are bonded to the surface. The adsorption process is coupled by a charge transfer between the adsorbed species and the solid. This results in, on the one hand, partially ionised adsorbed species and, on the other, a change in the band structure of the solid, through the modification of its space charge region.

The adsorbed species can participate in catalytic chemical reactions. If two adsorbed species react, the kinetics is described by the Langmuir-Hinshelwood mechanism, while the reaction between one adsorbed species and another one arriving from the gas phase corresponds to the Rideal mechanism.

The above chemical reactions modify the coverage of the surface. For example, if the sensor is in air, a certain equilibrium oxygen coverage forms on its surface. The appearance of reducing gas(es) modifies the oxygen coverage. The consequences of this modification provide the bases of sensor operation which are discussed below.

### 2.1.3 In the near-surface region

The result of the gas adsorption in the near surface region corresponds to the above-mentioned modification of the space charge region, the band bending, characterised by the Debye length.

In addition to this process, the possibility of certain chemical reactions between the gas and the solid can also be taken into consideration. According to the existence of the excess surface Gibbs free energy (known also as surface tension, surface energy) the reactivity of the topmost several atomic layers is higher than that of the bulk.<sup>(6,7)</sup> In the case of oxides, the removal of a certain amount of lattice oxygen from the uppermost layer by reducing gases (or just by autoreduction) is possible, giving rise to oxygen vacancies. These will diffuse into the solid. On the other hand, the chemical reaction of the solid with a reactive gas is possible. For example, halogens can react with the lattice, resulting in metal halogenides; being volatile, they leave the surface, consuming (corroding) the sensor. The formation of surface compounds with, *e.g.*, SO<sub>2</sub><sup>(8)</sup> or CO<sub>2</sub> was also found, modifying in this manner the surface (and sensing) properties of the solid.

### 2.1.4 Solid bulk

From the point of view of sensor operation in the solid bulk, the most important process is the diffusion. The in- and/or outdiffusion of the vacancies during the sensing lead to the

modification of the charge carriers concentration. The atomic movement along the grain boundaries is generally very fast. As a special case, we have to mention the segregation phenomenon. The system tends to minimise its Gibbs free energy, so the component(s) of smaller surface excess Gibbs free energy are enriched on the surface. In many cases, the segregation is assisted by the effect of the adsorbed gases (reaction induced segregation).

## 2.2 *The operation principles of oxide semiconductor sensors*

The basis of the sensor operation is the change in the resistance under the effect of gas adsorption on the oxide semiconductor solid surface. It has to be mentioned that the application of the n-type semiconductors is preferred, as the p-type ones proved to be less stable and less reversible.<sup>(4)</sup> The above-mentioned change in the charge carrier (electron) concentration can be realised in several ways:

1. The most accepted mechanism takes into consideration the role of the chemisorbed oxygen. As a function of the oxygen partial pressure - before the appearance of the gases to be detected - an equilibrium oxygen coverage is established on the surface. This oxygen chemisorption means the formation of  $O_2^-$ ,  $O^-$ ,  $O^{2-}$  species on the surface. Amongst them,  $O^-$  proved to be more reactive than  $O_2^-$ , while the  $O^{2-}$  is not stable. So the dominant species is the  $O^-$  species.<sup>(4,9)</sup> The oxygen chemisorption results in a modification of the space charge region towards depletion. The resistance corresponding to this state is considered as base resistance. The appearance of a reducing gas leads to the partial consumption of the adsorbed oxygen, resulting in a resistance decrease, while the appearance of oxygen increases the surface oxygen coverage, and hence the resistance.
2. Another mechanism is the adsorption of the reducing gas, giving rise to positive ions on the surface. The modification of the space charge region towards accumulation represents a resistance decrease.<sup>(10)</sup>
3. Note, that the surface oxygens are much more reactive than the lattice oxygens in the bulk.<sup>(6,7)</sup> The surface oxygen vacancy concentration can change in two ways: a reducing gas removes lattice oxygen, increasing the vacancy concentration, while oxygen fills them in, decreasing their concentration. This effect spreads into the bulk depending on the mobility of vacancies. The vacancies can ionise, providing conducting electrons. In the sensor planning, this third mechanism is unfavourable, unless the vacancy mobility in the lattice is practically zero, or very fast.<sup>(4)</sup>

The above mechanisms suggest the existence of a grain boundary (connected to the modification of the space charge region) and a bulk conduction through a thin film.<sup>(11,12)</sup> The different conduction mechanisms can be identified by impedance spectroscopy, as the processes with different time constants can be distinguished by varying the measuring frequency.<sup>(13)</sup> Our own result will be described later.

## 2.3 *Thin and thick film sensors*

The two main categories of sensors are the thin and thick film sensors. Their preparation involves different techniques. As described below, the different structural properties due to the fabrication and film thickness lead to different sensing properties.

### 2.3.1 Thin film sensors

The film thickness is typically 5–500 nm, in special cases even 1 micrometer. The most common preparation process is by sputtering, where the grains are closely packed, and the gas cannot diffuse between them. The grain size and vacancy concentration are controlled by the temperature of the treatment during the preparation. Two cases are distinguished:<sup>(4)</sup>

1. *The mobility of the defects is high.* This means that the surface effects spread quickly through the layer, and the grain boundaries practically do not influence the resistance, resulting in a good reproducibility and stable operation.
2. *The mobility of the defects is low.* In this case, the grain boundaries seriously influence the conduction. The resistance is determined by the characteristics of the space charge region and by the grain boundary diffusion of defects. The reproducibility of the results is poor.

### 2.3.2 Thick film sensors

The film thickness is in general several hundreds (typically 2–300) of micrometers, and the most common preparation technique is that of screen printing. The layer itself is a porous body, and the gases diffuse into it, so the inner surface also becomes a working surface. The microstructure is a function of grain sintering conditions, as *e.g.*, the temperature during the preparation (heat treatment). The conductance is dominated by the contact resistance between the grains, leading to good sensitivity. However, the intergranular contacts may vary in area. A high conductance path can be formed which can vary from sensor to sensor, resulting in a poor reproducibility.

## 2.4 Chemical reactions on the solid. Catalysis

Heterogeneous catalysis as a phenomenon is almost inevitable in the sensor operation. The catalytic processes and sensing are two aspects of the same phenomenon, that of the gas-solid interaction, only the points of view are different.

The aim of a *chemical engineer* is to attain a high conversion in the gas phase in the desired chemical reaction, to have a selectivity in the product gas. From this viewpoint the processes in the solid are of minor importance.

On the other hand, the aim of a *sensor specialist* is selectivity in the reactant gas, to induce a gas specific change in the properties of the solid. The gas-phase chemical transformation is in general undesired, as it changes the composition of the neighbouring gas phase. In the case of sensor arrays this may result in a chemical crosstalk.<sup>(14)</sup> In addition to this, the reaction heat can alter the near-surface temperature. A good catalyst which can selectively form a product may not be a good catalyst for sensors.<sup>(4)</sup>

However, in certain cases, the catalysis is required for sensing. In this case, in general, finely dispersed particles or ultrathin islands of noble metals (*e.g.*, Pt, Pd) are prepared on the oxide surface. Two methods of operation of such catalysts have been accepted:<sup>(4,15)</sup> the spillover mechanism and the electronic mechanism. In both cases, it is the oxygen coverage of the oxide that is modified.

### 2.4.1 Spillover mechanism

The molecules are dissociatively adsorbed on the metallic particles and the fragments move along the surface towards the oxide. The chemical reaction between the reducing gas and the adsorbed oxygen changes the surface oxygen coverage, and hence the resistance.

### 2.4.2 Electronic mechanism

The Fermi level in the catalyst particle and the oxide semiconductor are isoenergetic. The changes in the energetics of the catalyst - caused by the adsorption of the analyte gas(es) - spread to the oxide semiconductor. The gas/catalyst electron exchange is followed by a catalyst/semiconductor electron exchange, leading to the modification of the resistance.

## 2.5 Chemical reactions of the solid

Among the desired reactions, the modification of the surface has to be mentioned. This means the blocking of certain types of surface sites or the enhancement of some properties of other sites (*e.g.*, acidity).

The reaction-induced surface segregation means the surface enrichment of those components whose chemical affinity is higher towards the gas phase. If the reactivity of some gas phase component is too high, an undesired process, the partial destruction, namely a corrosion, of the solid can take place. For example, a longer exposure to hydrogen at high temperature proved to be destructive for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The corrosion may mean the formation of a stable surface compound, or the volatilisation of the solid, *e.g.*, under the effect of halogens.

In the experiments conducted by the authors, special chemical reactions were found, which take place on the surface, even if they are thermodynamically strongly unfavoured in the bulk.<sup>(6,7)</sup> The reason for this is the existence of the excess surface Gibbs free energy, which indicates a much higher reactivity of the surface and near-surface layers, than that of the bulk. It was found that the surface is not only more reactive, but its excess energy is distributed in a strongly heterogeneous manner. This means that the energy (reactivity) of the sites is different. At the appearance of a gaseous reactant, at first the most reactive surface sites react. As the reaction advances, the reactive surface sites react in decreasing order of reactivity. So the surface reactivity can be considered as a continuous function of the reaction coordinate, or in other words, the degree of advancement of the reaction. The last surface area has the same reactivity as the bulk and if all the reactive surface sites are consumed, the chemical reaction practically stops. The authors succeeded in describing the correlation between the reacted surface fraction and the excess reactivity. The equilibrium constant of the reaction defined for the most reactive sites is about 10<sup>20</sup> times higher than that for the bulk. The overall equilibrium constant defined for the whole surface is a weighted average of the equilibrium constants of the surface elements of different reactivities. This value is about 10<sup>9</sup> times higher than that of the bulk. This helps to clarify the difference in the chemical reactivity between the surface and the bulk. Note that in the case of sensors, we have to consider surface processes in general.

The reactions of the surface with water (generally present in ambient conditions) can be considered as a competition between the water and the oxygen for surface vacancies.<sup>(5)</sup>

Water can displace the oxygen, and in this case a smaller rate of catalysed reactions can be observed.

## 2.6 Base materials

At present, for such types of sensors, mainly oxide semiconductors - electron or mixed conductors - are used as base materials. The application of nanocrystals,<sup>(16)</sup> where the Debye length is larger than the crystallite size, means that the charge transfer across the grain boundaries is possible, leading to an enhanced sensitivity. As new materials, the conductive polymers<sup>(17)</sup> and the carbon nanotubes<sup>(18)</sup> have to be mentioned.

## 2.7 Effect of the microstructure on the sensor response

This effect is usually described in three ways:<sup>(16)</sup>

### 1. Relative dimensions of necks, crystallites and $L_D$ .

If the Debye length ( $L_D$ ) is larger, than the crystallite size, the conductivity is surface trap limited. If the necks are short and narrow, the conductivity is Schottky-barrier limited. Finally, if the size of crystallites and necks exceed the Debye length, the conductivity is limited by the width of the conducting channel.

### 2. Percolation theory.

The measuring current spreads through a three-dimensional network of barriers. The effect of an interacting gas modifies the barrier heights.

### 3. Effects of reaction and diffusion within a porous microstructure.

Due to the surface catalysed gas phase oxidation, a spatial variation of the gas composition and that of the conductivity can be observed through the structure. Due to this, the response may vary with the layer thickness.

## 3. Experimental Aspects

### 3.1 Characterisation of the sensors

According to Sze,<sup>(19)</sup> a sensor can be characterised by its properties, as listed below:

1. Ambient conditions allowed
2. Full scale output
3. Hysteresis
4. Linearity
5. Measurand range
6. Offset
7. Operating life
8. Output format
9. Overload characteristics (characterised by the recovery time)
10. Repeatability
11. Resolution
12. Selectivity
13. Sensitivity
14. Speed of response
15. Stability

The possibilities for improving the three most important characteristics are discussed in brief below:

### 3.1.1 Sensitivity

The sensitivity of a sensor can be improved using the tools of materials science: by doping the oxide, by decreasing its grain size through the application of appropriate heat treatments during preparation and by using mixed or common oxides among others.

However, in several cases, the application of the appropriate - *e.g.*, alternating current - measurement technique instead of the DC one can be also utilised.

As can be seen in Fig. 1(a), between 100 mHz and 10 Hz, the sensitivity measured by AC - the ratio between the imaginary parts ( $X$ ) belonging to the two oxygen concentrations - exceeds that measured by DC. The maximum oxygen sensitivity was found around 1 Hz; it is about twofold the DC sensitivity.<sup>(11)</sup> A similar phenomenon was found for hydrogen (Fig. 1(b)), however, in this case the frequency belonging to the maximal sensitivity was around 10 Hz. This means that the frequency belonging to the maximum sensitivity is gas dependent.

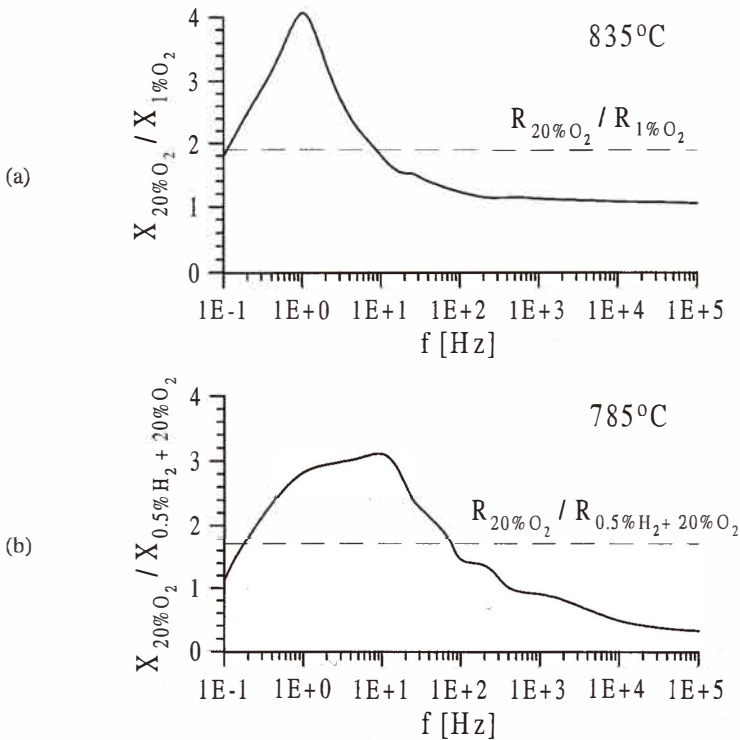


Fig. 1. Frequency dependence of oxygen respective to hydrogen sensitivity of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (related to synthetic air).



### 3.1.2 Selectivity

The selectivity can be improved by selecting or preparing appropriate materials. An applied filter selectively removes the undesired component(s). However, the filter saturates and requires regeneration. The use of a catalyst results in the selective transformation of the cross-effect-giving component(s), into neutral component(s) or only the desired component. Theoretically, the catalyst cannot saturate. A promoter improves the properties of the catalyst: it stabilises the surface, or a favourable valence state, or induces favourable phase changes in the catalyst.

As the optimum detection temperature is different for almost every component, the appropriate modification of the temperature may result in an important increase in the selectivity. The appropriate measurement technique - *e.g.*, utilisation of the optimal frequency in AC measurements - also improves the selectivity.

### 3.1.3 Stability

During the operation, a slow change in the sensor properties is almost inevitable, as the system tends towards the energetically most stable state. This involves, *e.g.*, the change in vacancy concentration or a slow phase transition. In addition, the presence of, *e.g.*, sulphur, acids or other corrosive agents leads to the chemical degradation of the sensing properties.

## 3.2 Complex experimental characterisation of the sensors

To characterise the sensors, the experimental techniques given below are recommended, starting from an as-prepared sample:

1. Surface compositional analysis of the fresh sample: Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), photoelectron spectroscopy (XPS) and so forth.
2. Surface structure: porosity, Brunnauer-Emmett-Teller (BET) specific surface, surface acidity-basicity.
3. DC characteristics: resistance ( $R$ ) vs  $p_{\text{gas}}$ ,  $R$  vs temperature,  $R$  vs time.
4. AC characteristics: impedance ( $Z$ ) vs  $p_{\text{gas}}$ ,  $Z$  vs temperature,  $Z$  vs time.
5. Work function measurements.
6. Thermal measurements: thermogravimetry (TG), differential thermogravimetry (DTG), differential scanning calorimetry (DSC), differential thermal analysis (DTA).
7. Structural studies: X-ray diffraction (XRD).
8. Analysis of the near-surface gas environment: mass spectrometry (MS).
9. Long-term aging and corrosion tests.
10. Field tests in realistic operation conditions.
11. AES, SIMS and XPS study of the surface changes produced during the tests.

### 3.3 Technical tricks

Below several tricks are elucidated, which can improve the effectiveness of the sensing.

*Multielectrode arrays.*<sup>(5)</sup> The actual in-depth gas composition in the sensing layer is a function of the porous structure, the diffusion of the gases and the rate of the chemical reactions<sup>(20)</sup> on the inner and outer surfaces. If the electrode distance is small on the

substrate, the measuring current flows near the base of the oxide layer. However, if this distance is large, the current probes the whole layer thickness. By varying the electrode distance we can obtain in-depth information on the gas diffusion and the chemical processes. By applying different electrode distances on the same chip, a microarray can be obtained.

*Temperature modulation.*<sup>(21)</sup> The rate of elementary sensing steps is temperature dependent. Analysis of the transient response upon temperature change is a tool for selectivity increase. In practice, generally, temperature cycling is applied.

*Zeolite filters.*<sup>(22,23)</sup> The molecular sieves have channels and cavities of the order of molecular size. If they are applied as separate filters or are deposited only on the sensing layer, they can retain the undesired component(s) from the gas mixture. As the zeolites have a very high catalytic activity - due to their crystal field effect - they can also selectively transform the undesired components or preactivate the analyte.

*Serial sensing elements.*<sup>(24)</sup> Let us connect two resistive sensor elements in series and apply a common voltage on the two resistors. The higher the sensitivity of a sensing element to a given component, the smaller will be the voltage drop on it (the larger will be its resistance decrease). Thus the response (the ratio of voltage drops) will depend on the ratio of the sensitivities of the two sensors to a given component.

*Semiconductive pellistor - semistor.*<sup>(25)</sup> This is a more sophisticated pellistor, consisting of a catalytically active oxide semiconductor paste on a platinum coil. The overall resistance is composed of the distributed resistance of the oxide and the parallel resistance of the coil. All the resistance values are affected by the reaction heat, while the oxide resistance also depends on the direct effect of the gas.

*Closed reactor.*<sup>(26)</sup> Take an operating flow type reactor, containing the sensor. Close the two ends, keeping a certain amount of the analyte gas inside. The catalytic activity of the sensor induces measurable compositional changes in the gas phase. The time evolution of the effect of reactant and product gases carries information on the nature of the inlet gases and on the processes going on in the reactor.

*Fuel cell.* Construct a micro fuel cell and keep it in air. A cell voltage is produced if the anode comes into contact with reducing analyte gas(es). The voltage value is characteristic of the gases.

## 4. Selected Results of the Authors

### 4.1 AC measurements

The authors demonstrate below that the application of AC instead of DC measurement technique increases not only the sensitivity of the sensor (Figs. 1(a), 1(b)) but also offers a new tool to distinguish the gaseous components. As the comparison of the above two figures suggests, the maximum sensitivity varies in function of the frequency, and this optimal frequency is characteristic of the respective gas. The AC method also proved appropriate for giving an insight into the mechanism of the sensing process.

Figure 2 shows the impedance spectra of a  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin film sample, when different oxygen concentrations are applied at 835°C. These curves were evaluated considering the equivalent circuit shown in Fig. 3.<sup>(11-13)</sup> Here  $R_b$  corresponds to the bulk resistance,  $C_b$

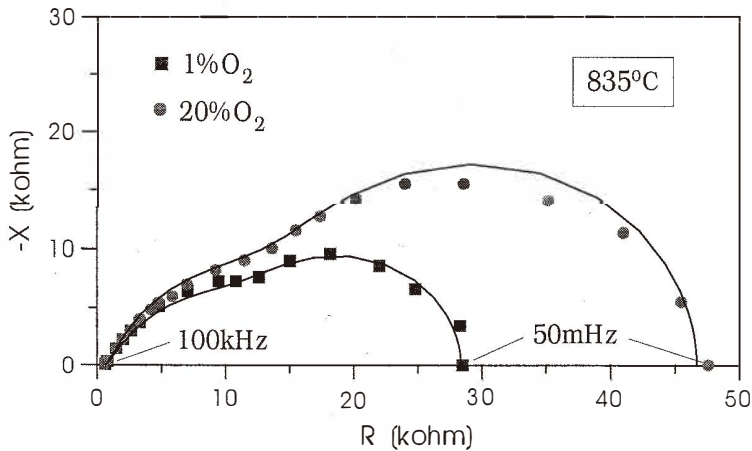


Fig. 2. Impedance spectra of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, at 835°C, in 1% and 20% O<sub>2</sub> containing nitrogen.

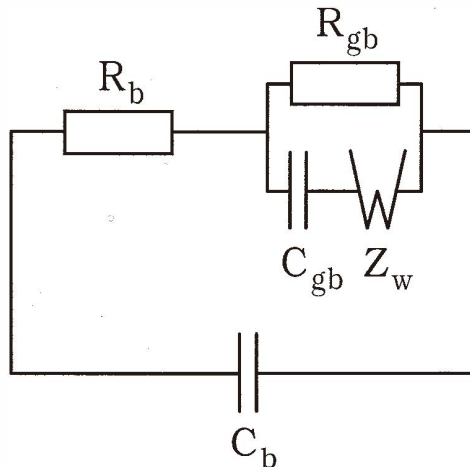


Fig. 3. The equivalent circuit of the polycrystalline  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> sample.

represents the geometric capacitance of the sample, and  $R_{gb}$  and  $C_{gb}$  stand for the space charge regions formed on the grain boundaries. The Warburg impedance ( $Z_w$ ) has been introduced to fit the impedance spectrum of polycrystalline samples.<sup>(13)</sup>

According to this, as shown in Fig. 2, the semicircle at high frequencies corresponds to the bulk resistance ( $R_b$ ). However, the semicircle in the low-frequency range stands for the resistance of the space charge region formed at the grain boundaries ( $R_{gb}$ ). The results obtained by fitting<sup>(27)</sup> the experimental data are shown in Table 1.

Table 1  
Bulk and grain boundary resistance values in 1% and 20% O<sub>2</sub>, at 835°C.

Gas mixture	$R_b$ (k $\Omega$ )	$R_{gb}$ (k $\Omega$ )
1%O <sub>2</sub> +N <sub>2</sub>	11.6	16.2
20%O <sub>2</sub> +N <sub>2</sub>	15.1	32.0

As can be seen (Fig. 2. and Table 1), the change in the oxygen concentration from 1% to 20% mainly affects the low-frequency range of the impedance spectrum:  $R_{gb}$  increases. This phenomenon can be explained as follows. Oxygen is adsorbed as negative ions on the grain boundaries<sup>(10,28)</sup> giving rise to a depletion layer in the n-type sample. This results in an increase in the grain boundary resistance ( $R_{gb}$ ). On the other hand, the oxygen can decrease the concentration of oxygen vacancies in the bulk.<sup>(29)</sup> This leads to a decrease in the bulk electron concentration and to an increase in the bulk resistance ( $R_b$ ).

The above findings suggest that for the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the adsorption of oxygen mainly affects the characteristics of the space charge region formed at the grain boundaries.

#### 4.2 Effect of water

It has been known for a long time that the presence of water affects the detection of the reducing gases. The effect of water significantly differs from oxide to oxide, and is also influenced by the presence of oxygen. The early experiments of the authors clearly demonstrate the complexity of the water/oxide interaction,<sup>(30,31)</sup> as is shown in Fig. 4. At that time, on one hand, we accepted the idea of Seiyama *et al.*<sup>(32)</sup> regarding the adsorption of water in molecular form. On the other hand, we gave an explanation of the time evolution of the water effect on the basis of DC resistance measurements, emphasising the role of the terminal OH groups formed. Today the mechanism of the process, the role, and position of the OH groups is much better understood, due mainly to the sophisticated IR measurements carried out in the Tübingen school.<sup>(33,34)</sup> However, it is generally accepted that it is of great technological importance to overcome the water cross effect in the sensing process.

#### 4.3 Detection of CO by measuring the work function change in the PtO/SnO<sub>2</sub> and PdO/SnO<sub>2</sub> systems

There is a real need to develop gas sensors of low operation temperatures. For this purpose the application of a new sensing principle, that of the work function change, has to be applied. In our case the CO sensitivity of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> and Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> impregnated SnO<sub>2</sub> thick layers was measured by following the work function change, using the Kelvin method,<sup>(35)</sup> at a low temperature (90°C). The complexes were decomposed by heat treatments in air, between 150–350°C.

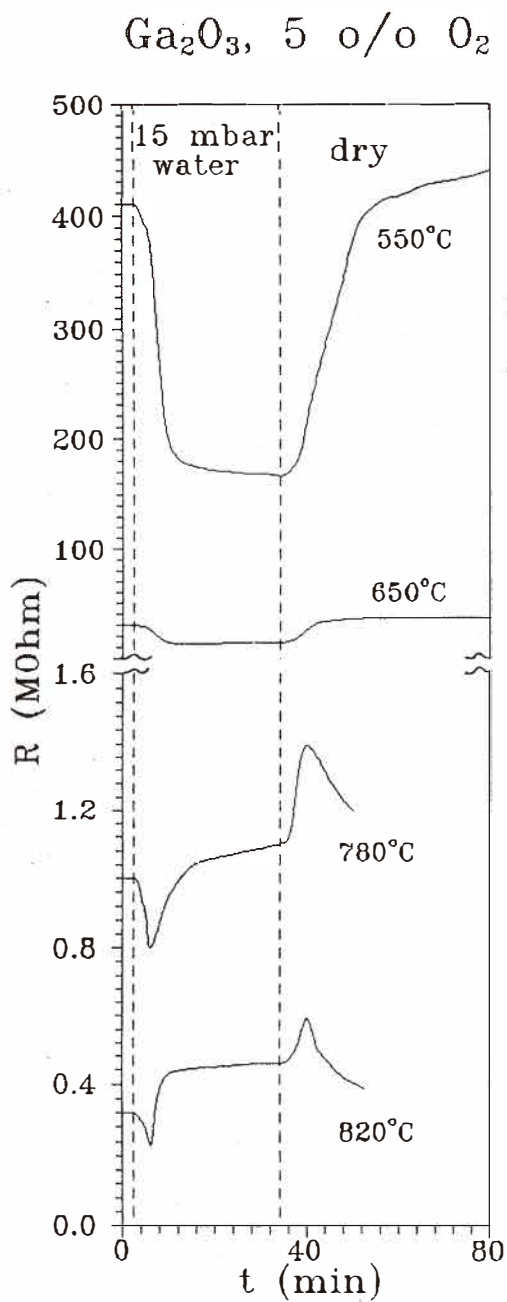


Fig. 4. Time and temperature dependence of the resistance of  $\beta\text{-Ga}_2\text{O}_3$  under the influence of water.

For the Pt-complex/SnO<sub>2</sub> structure, the CO sensitivity was found to be maximum, if the complex was decomposed at 300°C (Fig. 5). However, for the Pd-complex/SnO<sub>2</sub> structure, the  $\Delta\phi$  caused by the CO was maximum for a 200°C decomposition temperature (Fig. 6). XPS measurements suggest that the CO sensitivity of the Pt or Pd sensitised SnO<sub>2</sub> sample is maximum if the platinum or palladium is present as PtO or PdO, respectively, on its surface.

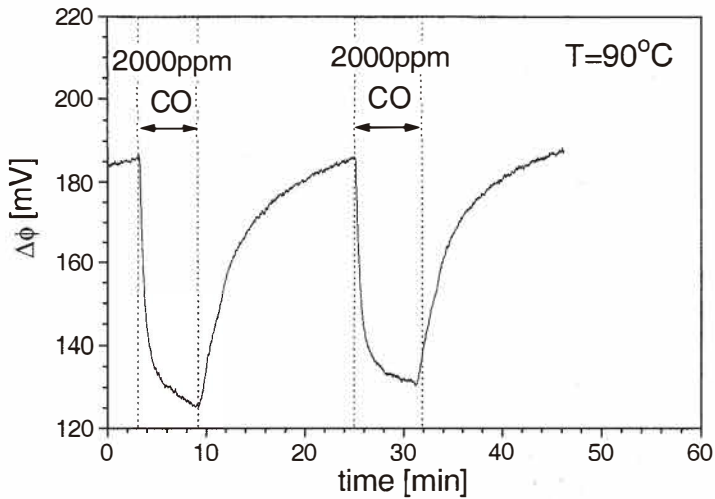


Fig. 5. Work function change of the Pt-complex/SnO<sub>2</sub> sample in CO + wet air. Pt-complex decomposition: 300°C, 30 min, in air.

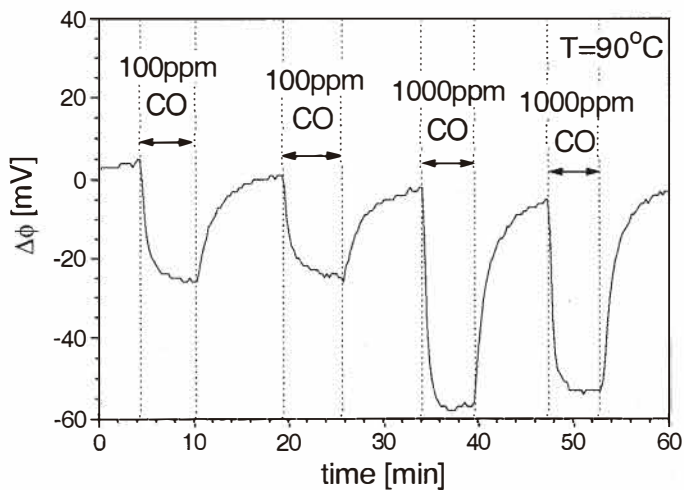


Fig. 6. Work function change of the Pd-complex/SnO<sub>2</sub> sample in CO + wet air. Pd-complex decomposition: 200°C, 30 min, in air.

#### 4.4 Phase transitions in “dry” and “wet” $WO_3$

In earlier publications<sup>(36,37)</sup> the authors reported the effect of  $TiO_2$  on the phase transition of  $WO_3$ , as a candidate for a sensor base material. It was found, that in the presence of  $TiO_2$ , the reversible phase transition  $\gamma$ (monoclinic)  $\rightarrow$   $\beta$ (orthorombic) of  $WO_3$  around  $330^\circ C$  shifts to higher temperatures and “smears” as a function of the temperature. This effect was not found if the sample was prepared by a simple physical mixing of the two oxides, and was only present in a system prepared by the intervention of the sol-gel chemical method. The result was explained by the surface interaction of the oxide particles.

In preliminary experiments,<sup>(38)</sup> it was found that if water can be detected by IR in the  $WO_3$  sample, it may stabilise the structure, and the phase transition becomes undetectable by the DSC (differential scanning calorimetry) method. An explanation could be the interaction of water molecules with the surface of the oxide grains.

### 5. Future Trends

In the opinion of the authors, the development of sensors will proceed in the directions given below. To improve the selectivity, a greater application of materials science is foreseen, *e.g.*, the doping of the oxides or the use of complex oxides. However, to achieve this goal, a deeper knowledge of this field is required. The catalytic filters can help in removing or transforming the undesired compounds. The sensor arrays will lead to increasingly perfect pattern recognition, for the artificial nose. The temperature cycling is a relatively simple tool for improving the selectivity, but it requires sensors chips, whose temperature changes should quickly follow the fast heating power changes. The development of signal evaluation leads to attractive results, however, in some cases, it may serve simply to hide the deficiencies of our knowledge in the field of materials science. Care has to be taken, not to prepare an overcomplicated electronic system with a component (the sensor itself), whose behaviour is not very well known, but to fabricate a simple system whose properties can be handled well.

To improve the sensitivity, the most promising attempts are those related to materials science, namely, the doping and the application of surface sensitising layers. The use of nanomaterials can open new perspectives. The application of the AC measurement technique also contributes to the increase of the sensitivity.

To improve the stability, the materials science approach seems to be the most efficient, with the use of chemically stable materials. Another possibility is to study how the sensor signal changes in time during the ageing process. These characteristics can be stored in a memory and be used for corrections. This approach requires perfect reproducibility.

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