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# Metal oxide-based gas sensor research: How to?

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#### Abstract

The paper critically reviews the state of the art in the field of experimental techniques possible to be applied to the study of conductometric gas sensors based on semiconducting metal oxides. The used assessment criteria are subordinated to the proposed R&D approach, which focuses on the study, and subsequent modelling, of sensors' performance in realistic operation conditions by means of a combination of phenomenological and spectroscopic techniques. With this viewpoint, the paper presents both the to-date achievements and shortcomings of different experimental techniques, describes - by using selected examples - how the proposed approach can be used and proposes a set of objectives for the near future. © 2006 Elsevier B.V. All rights reserved.

Keywords: Metal oxide; Gas sensor; Transduction; Spectroscopy; Operando

## 1. Introduction

Conductometric gas sensors based on semiconducting metal oxides are actually one of the most investigated groups of gas sensors. They have attracted the attention of many users and scientists interested in gas sensing under atmospheric conditions due to the: low cost and flexibility associated to their production; simplicity of their use; large number of detectable gases/possible application fields [1–4]. The initial momentum was provided by the findings of metal oxide-gas reaction effects of Heiland [5], Bielanski et al. [6] and Seivama et al. [7] and the decisive step was taken when Taguchi brought semiconductor sensors based on metal oxides to an industrial product (Taguchi-type sensors [8]). Nowadays, there are many companies offering this type of sensors, such as Figaro, FIS, MICS, UST, CityTech, Applied-Sensors, NewCosmos, etc. [9–13]. Their applications span from "simple" explosive or toxic gases alarms (see information provided by the gas sensors manufacturers on their homepages) to air intake control in cars [14] to components in complex chemical sensor systems [15].

On the side of the R&D work the most visible result is a large number of publications, generally reporting excellent individual gas sensing performance. The latter is obtained mainly by measuring the signals of laboratory samples (change of sample/sensor's electrical resistance) in quite unrealistic envi-

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ronments from the viewpoint of real sensors' working conditions, id est. in the absence of changing background conditions (e.g. humidity, presence of interfering gases, temperature, etc.). Sometimes, especially when the understanding of the sensing is targeted, some spectroscopic input is also provided. This type of approach, which is still dominant for the time being, is at the basis of most of R&D shortcomings and explains why, in spite of so many excellent laboratory results, the choice of devices to be used in real applications is still rather limited. It also explains why the modelling of gas sensing with metal oxide-based gas sensors is still in its infancy.

To understand what is wrong with the above-mentioned approach we need to realise that the reasons for high sensitivity to a particular gas and, simultaneously, low selectivity are related to the metal oxides-based sensors working principle. The cause of the change of sensor resistance (sensor signal) can be traced down to a ionosorption process and explained in terms of a free charge carriers (electrons) transfer from the semiconductor to adsorbed surface species or the other way around. The adsorption process that is responsible for the sensor signal is strongly influenced by the presence of the pre-adsorbed species (like ionosorbed oxygen, hydroxyl groups, carbonates, etc.) and by only measuring the change of resistance upon exposure to the target gas we will only record the overall electrical effect of quite complex surface reactions; summarizing, by only measuring the resistance change we do not have the needed discrimination for the correlation between surface species and their electrical effect. In principle, the discrimination we are missing should be provided by the results obtained by applying

spectroscopic techniques; there is a wealth of data provided by surface physics studies performed on metal oxides [16–18]. The problem here is related to the mismatch between the optimal conditions for measuring sensor performance and acquiring spectroscopic data. Spectroscopic acquisition techniques are extremely powerful for the characterization of metal oxides since they can provide details about the active sites and reveal insight into the reaction process. Unfortunately, the standard spectroscopic investigations are mostly performed in conditions far away from the ones normally encountered in real sensors applications, namely: in UHV [19]; at low temperatures [20,21]; required preconditioning of the samples at high temperatures, quenching and exposure to high concentrations of reactive gases; conducted on simplified systems (transmission measurements on powders [22,23], crystals, thin layers). The latter handicap is quite relevant also because it was demonstrated that the performance of a sensor is very much dependent on the sensors fabrication technologies (type of substrate and electrodes, thickness and morphology of the sensing layer, etc.), which indicates that the spectroscopic input should also be gained on actual sensors and not on sensing material samples. It is possible to take a different approach as it was recently proposed [24]. This one is based on the fact that by applying simultaneously several complementary methods (id est. FTIR and Raman spectroscopy, CEM, KP, ac, dc, conversion) in conditions as close as possible to the real sensors' working conditions, a synergetic effect can be obtained, namely the identification of the sensor effect of the different surface reactions.

The actual contribution aims to provide a critical review of the phenomenological and spectroscopic techniques (and of the interpretation of their results) that can be used in the R&D work dedicated to metal oxides-based gas sensors. The techniques that provide structural input will not be addressed here.

### 2. Objectives and approach of the R&D work

The final objective of the R&D activities is the design and fabrication of good gas sensors id est. suited for solving a certain application. It is important to keep in mind that the quality of a sensor is almost impossible to be defined without understanding the application needs, which besides the target gas/gases, possible cross-interferences and environmental conditions also relate to the cost/price restrictions of the instrument using the sensors. The latter factor is generally described as the fourth S – suitability – that is more and more considered in addition to the three classical ones (sensitivity, selectivity, stability).

In order to understand the challenges of the research in the field, we should have a look at the way in which the sensor signal is generated. A sensor element normally comprises the following parts:

- Sensitive layer deposited over a
- *Substrate* provided with
- *Electrodes* for the measurement of the electrical characteristics. The device is generally heated by its own
- *Heater*; this one is separated from the *sensing layer* and the *electrodes* by an electrical insulating layer.

Such a device is normally operated in air, in the presence of humidity and residual gases (e.g. carbon dioxide). It is generally accepted that in such conditions, at working temperatures between 200 and 400 °C, at the surface of the sensitive material – the metal oxide – various oxygen, water and carbon dioxide-related species are present. Not all of them have a direct influence on the sensor resistance id est. are involved in free charge carrier exchanges with the metal oxide (ionosorption); for a general discussion on the different types of adsorptions, see [25]. Some species will form bonds by exchanging electrical charge with specific surface sites (surface atoms), meaning that they may form dipoles; the latter will not affect the concentration of free charge carriers so that they will not have an impact on the resistance of the sensitive layer. Those situations are described in Fig. 1 for the simplified case of adsorbed oxygen ions, as electron traps, and hydroxyl groups bound to the metal, as dipoles, at the surface of a n-type metal oxide semiconductor; expressed in the energy bands formalism for the metal oxide, the effect of the former is a band bending while the effect of the latter is a change of the electronic affinity when



Fig. 1. Schematic representation of (left) flat band in n-type semiconductor and (right) band banding model illustrating adsorption at the surface of n-type semiconductor. The changes of the work function ( $\Delta \Phi$ ) are determined by band bending (qVs—due to ionosorption) and changes the electron affinity ( $\Delta \chi$ ) due to building of dipoles at the surface ( $M^{\delta+}$ –OH<sup> $\delta-$ </sup>).

compared to the situation existing before the adsorption took place.

Changes in the band bending, induced by, e.g. the reaction of the oxygen ions with carbon monoxide, will be translated into changes of the overall electrical resistance/conductance of the sensitive layer. It looks simple but it is not and the simple proof is the well-known influence of the ambient humidity on the sensor signal upon CO exposure; this indicates that the reaction cannot be that simple and there should be some involvement of species that do not have an obvious, measurable electrical resistance effect. A lot of questions need to be answered on both the side of the surface reactions and the side of their transduction in an electrical signal especially when one examines the influence of different fabrication technologies:

- How does the reaction between the target gas, in the a.m. case CO, and oxygen really take place? Does it involve atomic oxygen ions or molecular ones? Can it be that the reaction does not involve oxygen ions? Can we measure sensor effects in the absence of ambient oxygen?
- What is the role of the other pre-adsorbed species? Are they involved in the reaction? Is the overall equilibrium influenced?
- Does the reaction take place in the same way in the whole sensing layer? Is the concentration of the gas to be measured the same all over in the sensitive layer? Are there more reactive regions? Does the presence of the electrodes and/or the electrode material play a role? The one of the substrate?
- What will be changed if one uses noble metals additives? How much should one use?
- What does one measure? Free charge carriers concentration changes? Charge carriers mobility effects?
- How important is the sensitive layer morphology in translating microscopic reactions into macroscopic signals? Is the non-linearity of the sensor response a consequence of the surface chemistry or of the transduction? Can that be changed?
- Do the electrode-metal oxide contacts play a role in the overall resistance?

Getting the right answers is not only of academic interest; the modelling/understanding of the sensing is crucial for the sensor design because it will allow the tuning of the performance towards the desired one in a rationale manner. This will help a lot keeping in mind how many parameters can be changed and the amount of work that needs to be invested. If one agrees that the understanding of the sensing is important, it is clear that by only measuring the resistance one can not get enough information. There is a clear need to add both phenomenological and spectroscopic techniques and to apply them, as much as possible, simultaneously in order to gain inputs that will complement each other. When this is not possible we will have to make sure that the samples we are studying are quite similar allowing us to gather information that can be used together.

Also, it is clear that one has enough reasons to believe and convincing proofs [24], that the sensor performance does not only depend on the sensitive material; the final performance is due to the entire device so it should be studied as a whole. If one agrees that it is important to study sensors then one should also make sure that we are preparing them in a reproducible manner, which in fact asks for the evolution from the study of 'unique' samples to the use of samples fulfilling industrial standards. There are investigation techniques that one cannot or it would be prohibitively complicate to apply on sensors (TEM is a simple example); nevertheless the input they provide can be very important so, in such cases, the studies will have to be performed on simplified samples. There are also cases in which it will be important to have, for the sake of completeness or as a control mean, also measurements on, e.g. the sensitive material itself [26-28]. Nevertheless, most of the effort should be dedicated to measurements of sensors, prepared in a reproducible manner and combining as much as possible complementary experimental investigations simultaneously applied. It is also crucial to make sure that the conditions in which the experiments are performed and the ranges in which the parameters will be varied are relevant to the targeted applications. In most of the cases that means to work: at ambient pressure; in the presence of humidity and, possibly, of interfering gases; with sensors heated at application required temperatures; in the concentration range of the target gases expected in practical applications. There are situations in which it will be important to get away from the most encountered application conditions in order to understand some underlying basic phenomena; the most obvious examples are the interaction with oxygen and water vapour in the study of which it makes sense to start from oxygen and/or humidity free conditions. Even in such cases it is important to keep the feet on the ground meaning to dose, e.g. oxygen in nitrogen at ambient pressure and avoid UHV.

## 3. Experimental techniques

In this section, the most important types of experimental techniques - for the investigation of conductometric gas sensors based on semiconducting metal oxides - will be critically reviewed. In each case we will present their inherent possibilities and limitations and the most important results gained so far, according to the authors' opinion. In some cases, when it will be necessary for the interpretation of the results, also targeted basic information will be provided. The techniques will be grouped under the Phenomenological and Spectroscopic headlines; to make things clear, by the former we understand all methods that will not provide microscopic knowledge. The kind of knowledge they provide gives access only to the macroscopic effects - e.g. change of sensor resistance or change of the composition of the ambient atmosphere that follow the detection of CO - of the elementary reaction steps that can be the reaction of CO with ionosorbed oxygen or surface hydroxyl groups. Questions such as "Is the resistance change dominated by free charge concentration or mobility changes?" should be possible to be answered on the basis of the inputs provided by the phenomenological techniques. Discriminating between CO reaction with oxygen ions or hydroxyl groups, if at all possible, cannot be made without spectroscopic input. The other way around, ascribing a sensor effect to a certain surface reaction is not possible on the basis of spectroscopic input alone.

#### 4. Phenomenological experimental techniques

The typical measurement technique for the here-discussed sensors is the one of their conductance or resistance; in fact, in almost all cases it is the resistance/conductance of the sensors, which is linked to the composition of the surrounding atmosphere that is used for gaining the desired chemical information. The measurements are performed in different modes of operation spanning from constant operation temperature and permanent polarization to modulated operation temperature and periodic dc tests (with longer or shorter pulses).

In whatever conditions the tests are performed, one has to understand what is measured and how the measurement conditions will influence their result. The former question is related to the transduction of the surface reactions into a change of the electrical resistance of the sensor. The latter has to do with the need of avoiding that, for the same changes of the ambient atmosphere composition, the recorded resistance changes will differ depending on the measurement conditions. In the attempt of making the picture clear we can start by examining the two situations presented in Fig. 2. There, two types of sensitive layers, id est. a compact and a porous one, for an n-type material, are described in a simplified manner (for details, see [29]). Even if in practice the sensitive layers are polycrystalline, for the case of the compact layer the grains and the corresponding grain-grain Schottky barriers were not shown because, not being accessible to the gases, they will not change when the ambient atmosphere composition changes. In the figure are presented the contributions to the overall resistance corresponding to: the changes in the band bending at the material/grain surface and the potential barriers that are appearing due to the metal/metal oxide contact (the former depend on the changes in the ambient atmosphere, the latter ones not [29]; they are still discussed because they represent an add-on to the sensing material properties due the presence of the electrodes). The image of the resistance of the sensitive material being dominated by the gas-dependent grain-grain potential barriers (the height of which modulates the concentration of free charge carriers allowed to travel between the electrodes) is widely accepted but, possibly, over-simplified.

For grains that are small enough it is possible to have an influence on the mobility of the free charge carriers; such effects are reported, modelled but their interpretation is difficult [30,31]. Anyhow, the main idea one can deduce from Fig. 2 is that the contribution of the gas sensing process to the overall resistance of the sensor depends not only on the gas sensing material properties but also on various sensor characteristics (sensitive layer morphology, electrode parameters, etc.).

It is also important to note that in systems that can be described as a series of potential barriers the very value of the measured resistance can depend on the measurement parameters, more precisely on the measurement voltage/current; the potential drop that is used for the measurement will be distributed over the different series resistances in the layer and will be concentrated over the high resistance elements (grain-grain and electrode-grain barriers). In fact, such dependencies are reported in the literature either as such (polarization effects) [32,33] or as "varistor" effects [34–37]; they are also well known to all scientists that are using multimeters operated in autorange mode and have difficulties to connect experimental points acquired in different ranges (due to the different measurement conditions that are range-specific). A good way to forecast the risk of this type of problem occurrence is to guesstimate the potential drop per individual barrier (from the grain size and electrode spacing information) and to compare it to the  $k_{\rm B}T$ , which is the thermal energy at the operation temperature. A value of the grain-grain potential drop above the one of the thermal energy indicates trouble.

The ideas discussed above are related to pure electronic effects. Besides them, one should consider the chemical ones that can be influenced/determined by the nature of the electrodes and different polarizations. The influence of electrodes on the gas sensing performance is well documented [38–44]. There are also reports suggesting that the polarization has something to do with the chemistry at or in the vicinity of the electrodes [45]. An additional problem is related to the fact that in many cases the gas detection is a gas conversion from reactive (CO,  $C_xH_y$ , NO<sub>2</sub>, O<sub>3</sub>, etc.) towards inert or less reactive species (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, etc.) [46–48]. That increases the complexity of the prob-



Fig. 2. Schematic representation of a porous (a) and a compact (b) sensing layer with energy bands. Schematic representation of compact and porous sensing layers with geometry and energetic bands, which shows the possible influence of electrode-sensing layers contacts. RC resistance of the electrode–SnO<sub>2</sub> contact, R11 resistance of the depleted region of the compact layer, R1 equivalent series resistance of R11 and RC, equivalent series resistance of and RC,  $R_{gi}$  average intergrain resistance in the case of porous layer,  $E_b$  minimum of the conduction band in the bulk, qV<sub>S</sub> band bending associated with surface phenomena on the layer, and qV<sub>C</sub> also contains the band bending induced at the electrode–SnO<sub>2</sub> contact.

lem by adding on uncertainties: is the sensitive layer and/or the gas concentration in the layer homogeneous; does the sensitivity depend on the geometry of the electrodes or of the sensitive layer; how many gas sensors can be tested simultaneously; are the test conditions in a dynamic set up comparable to the ones in a real application.

To summarize, one can say that the so-easy-to-measure sensing effect of a gas sensor can be rather complicated to understand and that in the optimization and characterization of the sensor performance one should carefully consider the role of many factors. This asks for investigation methods that are able to provide the appropriate answers and it is clear that the sensor resistance measurement alone is not sufficient.

In the following, examples will be given on the kind of information the different experimental techniques are able to yield. The evaluation of the sensor performance is the first step to be considered. It is important, as already described, to check the influence of the measurement parameters on the results. Fig. 3 [49,50] presents such results obtained in humid air and under exposure to CO and NO<sub>2</sub> in humid air (the tested sensors were thick film SnO<sub>2</sub>-based ones). It is interesting to observe that the R (V) dependence is different for different test conditions. One can still identify a polarization range in which the influence on the test result is minimal (below 500 mV); in the latter case, the recorded sensor resistance will depend only on the target gas concentrations and can be used as input in modelling. There is additional information to gain from the influence of the polarization, as it will be described later on.

One of the first questions to be answered is about the role played by the contacts in the overall sensing and, as already discussed, it is possible to encounter both electrical and electro/chemical aspects. An extremely useful tool for determining



Fig. 3. Influence of measurements voltage V on the sensors resistance in different gas atmospheres. For details see [50].

the electrical contribution of contact resistance is the use of transmission line measurements (TLM); for more details, see [49–51]. In such experiments one uses substrates with different geometric parameters, like the ones presented in Fig. 4b and the results could look like the ones presented in Fig. 5 [24,50]. There, the dependence of the sensor resistance is plotted as a function of the spacing between electrodes (between 10 and 2000  $\mu$ m) for different ambient conditions. The fit of the experimental data can be made by using the formula describing the resistance *R* of an ideal, rectangular shaped layer of homogeneous resistivity  $\rho$ , length *l*, thickness *t* and width *w*:

$$R = \rho \frac{l}{tw} \tag{1}$$

## transmission line





(b)



Fig. 4. Different configurations of the electrodes.



Fig. 5. Dependence of the sensor resistance (at 330  $^\circ\text{C}$ ) on the electrode spacing of inline electrodes for different gas atmospheres. The thickness of the layer was 22  $\mu\text{m}.$ 

The conclusion for the case presented in Fig. 5 is that the electrical role played by the contacts between the sensitive material and the electrodes is negligible, which is not a surprise due to the fact that the sensors were thick porous films ones; as suggested in Fig. 2a (for details see [29]), for such layers the contribution of the metal-sensing layer resistance is made negligible by the large number of grain–grain contributions. On the opposite, for thin compact films – Fig. 2b – it was demonstrated that the contact resistance plays an important role [52]. It is also expected that the contribution of the contact resistance is extremely important in the case in which individual nano-rods, wires, ribbons are to

be used as "sensing layers" (for a review of this field, see [53]). Besides the dc techniques, the ac impedance spectroscopy can be very useful in identifying contact-related elements (grain-grain or electrode-grain in Fig. 2), in fact the presence of surface depletion regions. The reason is that in ac, the surface band bending (see Fig. 6) - determined by the negative charging of the surface counterbalanced by the overall positive charge of the bulk of the depletion layer - behaves like a charged capacitor [24]. Without going into the details, Fig. 6 presents the equivalent circuits corresponding to different types of contributions possible to be found in a sensing layer [54]. Attention should be paid to the fact that finding parallel RC elements in the equivalent circuit of a sensor does not, automatically indicate the presence of a "contact"; this type of measurements are very sensitive to errors and it is possible to consider some artifacts as real effects. The correct interpretation of error-free experimental results requires the critical analysis of the experimental data in conjunction with information on the morphological and microscopic characteristics of both sensing layer and sensor; it is not difficult to estimate the type of relationship existing between the associated R and C for a standard situation (see Fig. 7) [55]. A very simple calculation, applied in the case of the Schottky approximation allows for the observation of the main trends. It is based on the fact that the total charge trapped,  $Q_S$ , on the surface levels ( $E_S$  in Fig. 1) associated with gas adsorption (oxygen ionosorption in Fig. 1) can be written as

$$Q_{\rm S} = q n_{\rm b} s z_0 \tag{2}$$

where q is the elementary charge;  $n_b$  the bulk electron concentration; s the total surface on each the adsorption takes place;



Fig. 6. Different conduction mechanisms and changes upon  $O_2$  and CO exposure to a sensing layer in overview. This survey shows geometries, electronic band pictures and equivalent circuits.  $E_C$  minimum of the conduction band;  $E_V$  maximum of the valence band;  $E_F$  Fermi level;  $L_D$  Debye length. For details see [2].



Fig. 7. Equivalent circuitry for the different contributions; inter-granular contact  $(R_{\rm gb}C_{\rm gb})$ , bulk  $(R_{\rm b})$  and electrode contact  $(R_c C_c)$ .  $\Delta \Phi$  is the difference between the Fermi levels of the electrode and of the sensing layer material.

 $z_0$  the depth of the depletion region. Just as a reminder, in the Schottky approximation, for the case presented in Fig. 1, it is considered that all the electrons from the conduction band from the depletion layer are captured on the surface trap levels. It is not difficult to show [29,56,57] that one can derive a relationship between the band bending ( $V_S$ ) and  $Q_S$ , which has the form:

$$Q_{\rm S} = s(2q\varepsilon\varepsilon_0 n_{\rm b})^{0.5} (V_{\rm S})^{0.5} \tag{3}$$

The use of the general definition for the capacitance of a depletion layer  $(C_S)$  [58], will result, in our case, in the following expression:

$$C_{\rm S} = \frac{1}{s} \left( \frac{\partial Q_{\rm S}}{\partial V_{\rm S}} \right) = \left( \frac{q \varepsilon \varepsilon_0 n_{\rm b}}{2} \right)^{0.5} V_{\rm S}^{-0.5} \tag{4}$$

In combination with the well-known dependence between the resistance of the depletion layer and the band bending (see Fig. 7) the use of those equations should allow for the elimination of the experimental artifacts and the correct interpretation of the results. ac impedance spectroscopy was already successfully used in gas sensor research and allowed for the optimization of sensors parameters via modifying powder/layer fabrication technology [22,43,59,60] or separation of the gas (O<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>, O<sub>3</sub>, NO) influence on different components of the sensor device [24,61–64]. The method was shown to be especially useful when the sensing device consist of multi-layers or mixtures of different oxides [59,65,66].

The case for the "chemical" effect of the noble metal electrodes is already experimentally proven [38,44,45,67]. It is generally accepted that the reason has something to do with the catalytic activity of the metal but an established model is still missing also due to the lack of useful experimental inputs. It is possible to gain more information on specific issues by applying the available phenomenological techniques. One of the important issues is the extent of the electrode presence influence into the sensitive layer, which can also determine its lack of homogeneity from the gas sensing point of view. The origin of the latter issue is contentious; besides the presence of electrodes [24,50,68] another possible reason can be the fact that the very detection of gases consumes them; this is experimentally well documented in various papers that focus on the catalytic conversion determined by sensing [46,47]. Following on that line of thinking, one can speculate that the effective concentration seen by the sensitive layer depends on the position in the layer (depth) [57,69–73], etc. Coming back to the study of the (possible) lack of homogeneity of the sensitive layer, due to whatever rea-



Fig. 8. Dependence of the sensor resistance (at  $330 \,^{\circ}$ C) on the layer thickness for different gas atmospheres.

sons, one obvious choice is the use of different layer thicknesses on different transducer platforms [68,74–78]; another one is to have electrodes at different position in/on/under the layer and to compare the influence of the electrode position on the sensing performance [74,79,80]. An extremely interesting example is provided by studies performed on sensors realized on substrates provided with inter-digitated electrodes and having sensing layers with different thicknesses in the range  $10-50 \,\mu\text{m}$  (the second part of the work presented in Fig. 5). Fig. 8 shows the dependence of the sensor resistance as a function of the inverse sensing layer thickness for different ambient conditions. It is clear that, on the opposite of what was found for the case in which the length of the sensing layer was varied, the results differ qualitatively when the ambient atmosphere is different. For humid air the expected proportionality with 1/t (see Eq. (1)) is still valid; however, there is a marked difference, namely the existence of a non-zero intercept at high enough layer thicknesses  $(R_0^K)$ . For the case of exposure to CO, one records a thickness-independent sensor resistance the value of which depends on the actual CO concentration; as a consequence, the sensor signal decreases when the sensing layer increases. For the case of exposure to NO<sub>2</sub>, the resistance (nonlinearly) increases when the layer thickness decreases; for the sensor signal, the same trend like the one valid for CO exposure is found. On the basis of the results presented in Figs. 5 and 8 and by using additional inputs provided by four-points resistance and response time measurements it was found that [49]:

- The resistivity of the layers is thickness-dependent in all cases (air, CO and NO<sub>2</sub> exposure).
- The sensitivity to CO is not uniform in the sensing layer, the CO reaction is diffusion controlled and the highest sensitivity is found at the bottom of the layer. One possible explanation could be the assistance of the substrate and electrodes to the CO reaction.
- The sensitivity to NO<sub>2</sub> is also not uniform in the sensing layer but, on the opposite of the CO case, the sensing seems to be reaction limited and it is not possible to identify where the sensing mostly takes place.

It is very much possible that the results described above cannot be extrapolated to other sensitive, electrode and substrate materials and/or sensing layer morphology. The investigation approach, however, is a good example for the complexity of the investigation and also for the possible practical benefits because it demonstrated that it is possible to improve the response to CO and NO<sub>2</sub> by simply decreasing the thickness of the sensing layer. The literature data suggest that the limiting factor can be the grains' size. It was shown that when the layer thickness is of the same order of magnitude as the size of the grains, the sensor signal decreases abruptly [74,81]. However, the interpretation of the results is complicated because the changes of the thickness can determine changes of the layer porosity [75–77].

There are also other examples of studies focussed on sensing layer homogeneity that are based on polarisation experiments. By using of intermediates electrodes, see Fig. 4c, the influence of external parallel fields can be investigated [49]. As an example, Liess [82] investigated the electrically generated non-equilibrium areas in the In<sub>2</sub>O<sub>3</sub> film during gas adsorption (O<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>); he found, as a function of the surrounding atmosphere, different time-dependent behaviours during the electrical pulses. This effect has been attributed to migration phenomena of adsorbed species. Also Saurewald et al. [32] used simplified electrodes configuration (only four electrodes in contrast to six depicted in Fig. 4c) to investigate the field induced polarisation and relaxation in tungsten oxide thick films at higher temperatures >400 °C. The anisotropy in conductivity changes has been observed when the voltage of hundreds of mV has been applied, probably due to transport and/or drift processes. However, what kind of ionic species are responsible for these effects has not been determined.

The techniques presented up to now were all based on the measurement of the dc or ac impedance in different conditions on different substrates. One of the basic questions is still what determines the changes of the resistance when the ambient atmosphere changes. For the understanding of the conduction process in the sensing layer it is important to know whether the effect can be ascribed to free charge carriers' concentration variations only or there is also a charge mobility contribution. The most appropriate investigation technique is the Hall effect measurements; the interpretation of the results is straightforward for single crystals where the concentration of the free charge carrier can be unambiguously deduced from the Hall constant of a parallelepiped shaped sample simultaneously submitted to a longitudinal electrical and a transversal magnetic constant field [83–86]. Some additional consideration concerning the carrier-scattering mechanisms are however needed in order to get accurate numerical values. The remaining parameter, the drift mobility, can be afterwards subtracted from conductivity data (normally obtained in four-points measurements). The procedure can be quite easily extrapolated to compact polycrystalline samples using the geometrical models or the effective medium theories [87]. In these models, the material is built up from cells (the grains) containing two media, the bulk and the depleted region. The carrier concentration and the carrier mobility are predicted using the formalism of the classical electrokinetics (superposition and continuity) or, respectively, self-consistent algorithms. Many authors utilized this frame [87] and Hall effect measurements to evaluate the properties of their MOX layers in different conditions; the

investigated materials were SnO<sub>2</sub> [88–93], In<sub>2</sub>O<sub>3</sub> [94–97], WO<sub>3</sub> [98,99] and ZnO [100]. In all mentioned cases, the sensing layers were rather compact and the gas effects rather low; accordingly, the findings indicate an increase of carrier concentration and a decrease of the mobility with the temperature; some of the authors also reported a decrease of the mobility with the doping level (also expected due to the increase of the scattering with the ionised centres). In one case, the increase of the mobility with the temperature (activated mobility) was reported [94]. The kind of approach defined in [86] encounters major difficulties when applied to porous and granular gas sensing films under variable temperature conditions, in order to determine different activation energies and, further on, the electrical properties. As pointed out in [101] the heating of the gas-sensing layers influences not only the physical characteristics of the material, as often accounted, but also the surface/interface chemistry, as described in [29]. In such chases a careful analysis of the experimental data in relation with the morphological properties of the sensing layers is needed. Often it is only possible to consider the investigated sample at different temperatures as different physico-chemical systems and to treat them accordingly.

An example for  $\text{SnO}_2$  evaporated films [101] is depicted in Fig. 9. The decrease of the effective electron mobility under increasing oxygen concentration in a nitrogen background can be mainly explained by the increase of surface scattering rates experienced by the free carriers on the surface centres created by an increased number of adsorbed oxygen species.

All the information resulting from electrical resistance measurements will give access to the averages of the effects of surface processes that will contribute to the build-up of surface net charge (band bending effects in Fig. 1). However, there are surface reactions that will result in surface adsorbates bound through localized charge transfer processes (between specific surface sites and the adsorbates id est. localized chemisorption) or even less strong interactions such as physisorption (weak van



Fig. 9. The dependence of the charge carrier concentration on the oxygen concentration for a 70 nm-thick SnO<sub>2</sub> sensing layer prepared by e-beam evaporation. The sample temperature was kept constant at: 20, 153, 260, 365 and 418 °C during the increase of the O<sub>2</sub> concentration in dry N<sub>2</sub>. Other measuring conditions: 100 secm total flow, 50  $\mu$ A drift current; 1 T magnetic field. After [101].

der Waals forces between non-polar adsorbed molecule on nonpolar solids) and H-bonds. The analysis of surface adsorption processes exceeds the scope of this paper; for details, please consult the classical textbooks, e.g. of Morrison [56]. What is relevant for the discussion here is that species adsorbed by such processes will have no impact on the free charge carrier concentration (no band bending effect) and, accordingly, no direct influence on the sensor resistance. This does not at all mean that their presence at the surface as pre-adsorbed species or the changes of their surface concentration due to changes in the ambient conditions will not have an impact on the target gases sensing. There are phenomenological experimental techniques that will provide additional inputs by giving access to sensor parameters such as electron affinity or permittivity. In both cases the microscopic effect is the build-up of dipoles like the ones shown in Fig. 1 corresponding to hydroxyl groups. The permittivity is accessible through ac impedance measurements and an example of how its variation can be included in the overall picture of CO sensing in the presence of humidity is given in [24]. The changes of the electron affinity are accessible, in realistic conditions, through measurements of work function ( $\Phi$ ) changes by the Kelvin probe (KP) method combined with resistance measurements (for details on the method and its use in the field of gas sensors see [102,103]). By using a KP measurement set-up and for a type of sensing layer as the ones described in Fig. 10 and in the case that the work function of the reference electrode is not modified by the changes in the ambient atmosphere, it is possible to extract the band bending information from the resistance measurements and to use it in order to extract the electron affinity  $(\chi)$  contribution by using the following relationship:

$$\Delta \chi = \Delta \Phi - k_{\rm B} T \ln \left(\frac{R_{\rm F}}{R_{\rm I}}\right) \tag{5}$$

where  $R_{\rm F}$  and  $R_{\rm I}$  are the resistances measured after and before changing the ambient conditions. In case of different sensing layer morphology the relationship between the electron affinity, resistance and work function can be different. A closer look to the situation described by Fig. 10 (parts a and b) highlights a possible source of errors, namely the fact that the resistance measurement will provide an average value of all band bending values between the two electrodes on the substrates while the work function measurement will reflect the changes in the work function of the top most layer only (Fig. 10b). If the sensing layer is not homogeneous, as it was shown to be possible in the example presented in Figs. 5 and 8, the resulting value for the electron affinity will be affected by errors. It is clear that one should very carefully check all assumptions made for the electron affinity extraction procedure (e.g. the influence of different layer thicknesses on the work function changes values, etc.) in order to ensure the validity of the results.

There are already interesting data obtained by using the KP work function measurements in the field of metal oxide-based gas sensors [24,25,103–108]. An example is provided in Fig. 11, which shows results of simultaneously performed resistance and work function measurements on tin dioxide-based sen-



Fig. 10. (a) Circuitry for simultaneous resistance and work function measurements and (b) schematic representation of the surface parameters measured during gas adsorption:  $\phi_{KP}$ , work function of the reference tip of the Kelvin probe (KP);  $\phi_{SC}$ , work function of the semiconductor (SC);  $\phi_E$ , work function of the electrode (E);  $V_C$ , contact potential;  $\chi$ , electron affinity of the semiconductor. Air and gas denotes, respectively, the parameters recorded in air or in the presence of the target gas.

sors (SnO<sub>2</sub> powders were prepared in sol-gel technology and screen printed on alumina substrates provided with Pt heater and inter-digitated electrodes); the target gas was propane, the sensor was operated at 200 °C in dry air [109]. One can see in the figure that upon propane exposure the only parameter that changes significantly is the band bending. That means, due to the almost complete lack of change in electron affinity, that the concentration of the dipole-carrying surface species either remains unchanged or the creation/annihilation of one type is compensated by the annihilation/creation of a different type of such surface species. This type of dilemma is a good example for the lack of discrimination power that is the main drawback of phenomenological investigations; it is impossible to distinguish between the two possible explanations given above on the basis of phenomenological results only. For the case presented in Fig. 11 one can only say that, in this case, the net changes of surface charge dominate the phenomenological picture of the sensing process. This suggests the concentration changes of surface ions as origin of the recorded results. This example will be discussed again, in the following section, in relation to the



Fig. 11. (a) Results of simultaneous contact potential difference and resistance measurement on tin dioxide thick film sensor at 200 °C for successive propane exposure: 100, 200, 500, 750 and 1000 ppm. (b) The corresponding energy changes: ( $\Delta eVs$ ) band banding; ( $\Delta \phi$ ) work function; ( $\Delta \chi$ ) electron affinity.

manner in which the phenomenological and spectroscopic information can complement each other.

An important input that can still be provided by phenomenological measurements is the one dealing with the changes in the ambient atmosphere composition determined by the interaction with the sensors. The reactivity of the target gases makes them change as a result of the surface reactions that determine the sensor effect. Accordingly, it is useful to record such changes and compare them with the other phenomenological and spectroscopic results. There are practical implications related to the testing of the sensing performances such as: the limit of the number of sensors that can be simultaneously tested without causing a major disturbance of the test atmospheres; how valid are the results obtained in a specific test configuration for real applications; how much trust one can put when comparing results obtained in different laboratories that use different test set-ups, etc. If the effect is used for modelling it is important to take into account how much the substrate contributes to the overall change. There are also possible benefits if one uses the effects for gaining additional information on the composition of the ambient atmosphere, as proposed in [110,111].

Examples of interesting results are presented in a series of publications where such effects were studied in combination

with other phenomenological techniques [47] or even spectroscopic ones [109]. In [46] it was demonstrated that the nonlinearity of the sensor response originates from the transduction and not from the adsorption on the basis of the founding that the catalytic conversion of CO, and implicitly the adsorption/reaction, is linearly depending on the CO concentration. Also there, it was shown that the conversion effect of the sensor is more than the simple add-on of the conversions corresponding to its parts (substrate, electrodes, and sensing layer). The difference between the reaction taking place between NO<sub>2</sub> and  $SnO_2$ , on the one side, and  $In_2O_3$ , on the other side, as input for modelling was determined in [48]; there, it was observed that in one case the NO<sub>2</sub> concentration was left unchanged, which suggested a direct charge transfer between the metal oxide and the  $NO_2$  molecule, while in the other the changes in the  $NO_2$ concentration suggested a mechanism in which pre-adsorbed oxygen ions play a role.

It is clear that even if the phenomenological techniques are not able to provide a direct access to the elementary reaction steps that are at the origin of the sensor effect, their input is crucial for the understanding of sensors' functioning. There is a wealth of information to be gained on the role of different sensor parts in the overall sensing performance and, also, it is possible to help direct the spectroscopic investigations towards the most relevant targets.

There is an important remark to make, especially in relation with the stated objective of the R&D work, which is the understanding of the functioning of real sensors. In most cases this approach asks for the study of the actual sensors but there are cases in which it is important to concentrate on model samples that will be able to provide the required insights. This is the case when in the outputs of the experimental techniques – the measured parameters such as conductance, electron affinity, etc. – the influence of certain factors – e.g. the presence of electrodes – is masked by the way in which the measurements are performed or altered by the way in which information provided by different experimental techniques is combined. There is nothing wrong with the use of model samples as long as they are in line with the R&D approach and are designed to serve the main objective.

#### 5. Spectroscopic experimental techniques

As already mentioned, the main obstacle for an effective use of the spectroscopic inputs is related to the conditions in which those ones are, usually, gained. This fact is not relevant just to sensor research but also to catalysis, where the goal is to study catalysts inside a reactor by spectroscopic means, and it is not difficult to understand that in both fields the interest for adapting spectroscopic techniques to the operation conditions is high. This explains the parallel developments in both areas and the actual convergence towards common approaches and standards (see session on sensors at Operando conference [112]). It is useful to take now a look to the terminology; in order to distinguish between in situ experiments and experiments in working conditions, the new term "operando" spectroscopy has been proposed by people studying catalysis [113]. It originates from the Latin gerund, meaning operating or working, so operando spectroscopy is the abbreviation for spectroscopic studies of an operando or working catalyst or spectroscopy in modus operandi [114].

In the context of gas sensing we will use the term of operando spectroscopy when the spectroscopic investigations are performed on real sensors, in conditions close to the ones encountered in real sensors applications; an additional requirement, not valid for catalysts but extremely important for sensors, is the simultaneous recording of the sensor signal. The research approach we are pleading for here, is to combine operando spectroscopy with the relevant phenomenological investigations.

It is useful to take a look to the attempts for the establishment of an operando approach in sensor research. One should note, before presenting the work on sensors, that considerable efforts have been made to enable direct experiments under real sensors' working conditions on sensitive materials (powders) [28,62,115,116] and to combine them with the phenomenological techniques (mainly dc resistance measurements on real sensors [117–121]).

On sensors we start with the work of Sharma et al. [121], who have shown that the data observed from CEM spectrometry (in situ Conversion Electron Mössbauer spectrometry) can support the electrical resistance data (simultaneously recorded) as well as models of absorption and desorption of inflammable gases like CO and CH<sub>4</sub> on Sn–Bi oxide-based sensors.

In situ X-ray absorption spectroscopy (XAS) and simultaneously performed conductivity measurements have been applied to investigate the influence of Pd and Pt clusters on the CO,  $H_2$ , NO, NO<sub>2</sub> sensing mechanism of SnO<sub>2</sub>-based sensors. Variations in the Pd and Pt XAS spectra and of the conductivity have been observed [120].

Until now, most of the successful operando spectroscopy techniques were the ones based on IR spectroscopy. Benitez et al. [117,118] have shown that diffuse reflectance infrared Fourier transformed spectroscopy (DRIFT spectroscopy) and conductivity measurements can be simultaneously performed under in situ conditions on CdGeON-based sensors. Since than, several authors have applied this technique to the study of the gas detection mechanism in real sensors' working conditions either on sensing materials [28,122,123], on metal oxide sensors [109,119,124-126], or on Pt/SiO<sub>2</sub> as a model system for the top layer of MISiCFET sensors [127]. The first real operando study of target gas detection, in which DRIFT was used, was the one dealing with CO detection mechanism of SnO<sub>2</sub> and Pd:SnO<sub>2</sub> sensors in presence of water vapour [119]. It is important to underline that in the interpretation of the DRIFT spectroscopy results there are obstacles; one of the most serious is the effect on the quality of diffuse reflectance spectra of the background absorbance changes, which is an inherent effect of the exposure to target gases. A gas adsorbing at the sensor's surface changes the free charge carriers density (resistance change effect) and this, in turn, determines the variation of the IR light scattering and changes the spectrum baseline. The authors' experience [109,126] shows that in the relatively high resistance range (above 1 M $\Omega$  at an aspect ratio of around 20 and for layer thicknesses of approximately 20 µm) this effect can be neglected. However, for sensors with relatively low baseline resistance (low

 $k\Omega$  range and below in the same conditions as above) the strong changes of the baseline can mask the absorption bands and the recorded spectra become non-interpretable. It is ironic, however, that an effect that is bad for one IR technique can be used by another one. The direct correlation of the absorbance of a material (at a given wavelength) to its electrical conductivity was used to determine the type of conduction (n or p) in the case of gas sensors (SnO<sub>2</sub>, n-CuO/BaTiO<sub>3</sub>) under exposure to oxidizing or reducing gases [23]. Additionally, the modulation of the free charge carriers density due to the adsorption of a target gas leads to a variation of the infrared energy transmitted through the sensitive material, which can be directly related to its electrical response. In this way the performance of the investigated materials can be estimated with all caveats, described in the first two sections of this article, for the extrapolation of the results to real sensors [27,128].

Coming back to IR techniques applied to sensors, Pohle et al. have adapted the IR emission spectroscopy (IRES) for studying the adsorption of water and hydrogen-containing gases on Ga<sub>2</sub>O<sub>3</sub>-based sensors [125] and adsorption of oxygen on WO<sub>3</sub>, AIVO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> [124]-based sensors at high temperatures (>400 °C). Additionally, they made an attempt to compare DRIFT and IRES performance that ended with the conclusion that below 300 °C DRIFT gives good results and above 300 °C IRES is better [129]. The latter finding is, however, disputable because the loss of diffuse reflectance signal at elevated temperature can be attributed to the loss of sensitivity of the MCT detector or preamplifier itself (saturation of the conduction band in the MCT detector element due to un-modulated IR radiation) and not directly to the loss of the diffuse reflected light [130].

Raman spectroscopy is also a candidate as it has been already shown that one can couple it with impedance spectroscopy or simply with dc resistance measurements in order to investigate the  $H_2S$  sensing mechanism on SnO<sub>2</sub>-based pellets with painted silver electrodes (at elevated temperature and in the gas stream) [131]. However, to our best knowledge, up to now there are no truly operando gas sensors studies by means of Raman spectroscopy.

Unfortunately, the conclusion is that there are not too many spectroscopic techniques that were/can be successfully operando applied to sensor research; this fact is a serious problem because of the lack of balance between the wealth of available phenomenological techniques and the scarcity of the spectroscopic ones. In what follows, we will analyze what kind of input is already available, what different operando approaches really mean and what needs are still unanswered on the basis of two examples. The first one deals with the analysis of H<sub>2</sub> sensing mechanism of Pd-doped SnO<sub>2</sub> samples (on alumina substrates) by X-ray absorption spectroscopy (XAS) [132] the second with the analysis of propane sensing with thick film SnO<sub>2</sub>-based sensors [109] (the information presented here completes the one already provided in Section 4).

In the first case, conductance and mass spectroscopy measurements were completing the XAS investigation; the former for providing the correlation between the changes in the electronic states of Pd and Sn and the sensor effect, the latter for quantifying the amounts of  $O_2$  and  $H_2$  that take part to the reac-



Fig. 12. (Left) Variation of the electrical conductance (a) normalized absorption at Pd K-edge (b, left scale) and Pd<sup>2+</sup> fraction in the Pd<sup>2+</sup>/Pd<sup>0</sup> mixture (b, right scale) for Pd–SnO<sub>2</sub> film at 100 °C (dotted lines) during the alternative exposure to 20% O<sub>2</sub> in He and 1000 ppm H<sub>2</sub> in He. The dashed lines correspond to pure SnO<sub>2</sub> at 300 °C. (Right) Corresponding correlation between the conductance and the oxidation state of Sn (a) or Pd (b). After [132].

tion with the material. The approach cannot be considered fully operando because the conditions in which the exposure to  $H_2$  and  $O_2$  takes place are neither corresponding to realistic sensor operation conditions nor to any specific/special application (in the experiment the samples were alternately exposed to 20%  $O_2$  in He, 1000 ppm  $H_2$  in He and pure He). The main results of the experiments are presented in Fig. 12. The most significant findings are:

- At the lower temperature, the conductance change without any variation of the Pd and Sn oxidations states (Fig. 12 left and right).
- At the higher temperature, the mechanism becomes more complicated. The oxidation state of Pd depends strongly on the surrounding atmosphere and, additionally, the presence of Pd induced SnO<sub>2</sub> reduction. However, there is no direct correlation between the conductance and the oxidation states of Pd and Sn. At 300 °C (Fig. 12 right) the conductance of the Pd–SnO<sub>2</sub> film can change several order of magnitudes without any variation of the oxidation states for both metals.

These experimental findings indicate that the oxidation and reduction of Pd nanoparticles and  $SnO_2$  lattice are secondary processes, which are not responsible for the sensitivity to H<sub>2</sub>. The result, which directly excludes the interaction of H<sub>2</sub> with surface lattice oxygen or its direct chemisorption at the metal center, can be very much influenced by the absence of the background oxygen (pre-adsorbed oxygen-related species) during the reaction with H<sub>2</sub>. One can identify here typical problems that can appear when the conditions in which the studies are performed do not match the conditions in which the sensors are operated. This fact does not at all affect the importance of the pioneering approach of Safonova et al. [132] and the prospects of their method in future studies.

In the second case, we already knew (see Fig. 11 and the related discussion) that the reaction with propane determines only changes in the band bending. To learn more, we applied, simultaneously to the electrical measurements, direct IR surface spectroscopic measurements (DRIFT) completed with catalytic conversion measurements of the exhaust gases; the latter indicated that the propane conversion is complete to water vapour and  $CO_2$ . By combining the phenomenological and spectroscopic inputs we found out that (see Figs. 11 and 12) [109]:

- The dissociation of propane is activated on acid–base pair sites (SnL<sup>4+</sup>–OL<sup>2–</sup>) and leads to the formation of propyl radicals, and not to propene or acetone ones.
- The main intermediate surface species during the consecutive conversion of propane are ionic carbonates and carboxylates. It is important to note that both, DRIFT and work function changes measurements suggest that the intermediates (carboxylates and carbonates) are ionic, which means that they really result from a reaction involving adsorbed oxygen species. In case of a reaction with surface lattice oxygen, the intermediates will be coordinated to the surface lattice oxygen and, consequently, they should have a dipolar nature and an effect on the electron affinity that was not observed (Fig. 11). The interpretation given to the results is based on circumstantial evidence because it is not possible to unambiguously observe an effect on oxygen ions with IR methods. In this con-

text one should remember that, anyhow, the input on the effect of oxygen and water vapour, which are background gases relevant to most applications, is based on experiments performed under conditions far away from the ones normally encountered in real sensors applications. Here, one faces severe problems related to either the scarcity of methods giving spectroscopic access to the related surface species (especially, for oxygen) or to the needed adaptation of the experimental conditions (starting from a background free of water vapour and oxygen). In the following, we will specifically address the questions related to the lack of spectroscopic knowledge, acquired in modus operandi, on the effect of the most relevant background gases: oxygen and water vapour.

The first encountered question while modelling the sensing mechanism of metal oxide-based gas sensors is the role of oxygen (adsorbed or in the lattice). However, up to date, there are no unambiguous experimental evidences on the forms of oxygen adsorption, at ambient pressure and elevated temperatures, on real sensors/sensor materials. Based on TPD and EPR studies the following surface oxygen species have been reported to be present at the surface of metal oxides [18,133–136]: at lower temperatures oxygen is considered to adsorb in molecular form (either neutral  $O_{2(ads)}$  or charged:  $O_{2(ads)}^{2-}$ -peroxo,  $O_{2(ads)}^{2-}$ -superoxo); at higher temperatures it dissociates into atomic oxygen (either neutral  $O_{(ads)}$  or charged  $O_{(ads)}^{-}$  and  $O_{(ads)}^{2-}$ ). Finally, at high temperatures the loss of lattice (first surface and then bulk) oxygen takes place. What lower, higher and high really means depends of the specific metal oxide.

Coming back to experimental techniques, it was shown that FTIR could be successfully applied on sensors in operando conditions. However, there is no common agreement upon  $O_{2(ads)}^{-}$  signature in the IR spectra in operando conditions, probably because these species manifest themselves in the same spectral range as the lattice combination metal oxide modes and the deformation vibration of hydroxyl groups (<1200 cm<sup>-1</sup>). While the observation of  $O_2^{-}$  is disputable,  $O^{-}$  is not expected to lead to any infrared absorption.

In order to gain the missing knowledge about the role of oxygen in sensing an indirect approach, in combination with phenomenological techniques [109,137], or another direct spectroscopic method should by applied. For the latter, there are several candidates like EPR, Raman spectroscopy [131,138], XANES or in situ solid state NMR (cross-polarisation <sup>13</sup>C NMR and REDOR) but in most of the cases, in order to work in modus operandi, one still has to face complicate experimental problems. Most results, in conditions coming closer to operando ones, were gathered on the basis of the EPR studies. It is useful to review them because they offer a good example of the difficulties encountered when one tries to adapt spectroscopy to operando conditions. By using EPR, it was shown that there is a certain correlation between the measured electrical conductivity changes and the EPR spectrum. However, the interpretation of the obtained results is controversial: Chang [135] correlates the changes of the conductivity with ionosorption of oxygen (O2<sup>-</sup> and O<sup>-</sup>), Canevali et al. [139] correlate the changes with localized chemisorption of oxygen, where the electrons come directly

from the oxygen vacancies and, finally, Amalric-Popescu et al. [140] show that under evacuation at temperatures lower than 400 °C only ionosorbed oxygen species are observed, whereas at 400 °C and higher temperatures oxygen vacancies appears. These discrepancies have several reasons: the employed high temperature pre-treatments; the fact that the experiments are performed on powders and, foremost, the EPR signal is acquired at 123 K or at room temperature. One has to keep in mind that a severe drawback for EPR is the so-called exchange broadening of the signal under air (O<sub>2</sub> containing gas) stream due to magnetic interaction occurring from the collisions of oxygen molecules with adsorbed species. It limits, but not excludes the application of this method to the gas sensors investigations.

Besides oxygen, the practical use of sensors indicates water vapour as having an important role in sensing. As in the case of oxygen, here also we are missing information gained in operando. Again as for oxygen, but for different reasons, water effects are difficult to study by applying the most successful operando spectroscopic technique, id est. IR. Here, the reason is not the lack of spectroscopic signature of water-related surface species, but the overlapping between the signals coming from gaseous and surface species. In the case of DRIFT, this fact asks for a referencing that, on the one hand, eliminates the disturbance corresponding to water vapour presence but, on the other hand, makes it impossible to follow up the building of water-related surface species when the water vapour concentration increases. The referencing is made, generally, by using the spectrum of the sensor before the exposure to target gases, recorded at the same humidity. By that, only changes in the concentration of water-related surface species due to the reaction with the target gases are possible to be observed [119,126].

In case of IR transmission measurements this problem is not as dramatic as in the case of diffuse reflectance also because the weight of surface-related information is diminished; here, by decreasing the dead volume above the sensitive layer/material the influence of gaseous components can be minimized. This concept has been practically realized in operando investigations of catalysts, where the dead volume was squeezed down to  $0.12 \text{ cm}^3$  [141].

Generally, for IR spectroscopy a possible way to sort out the problem of overlapping signals from surface and gaseous water-related species could be provided by the use of modulation spectroscopy; the latter is an adequate tool to separate a weak system response from huge background absorption. The prerequisite condition is that the process under consideration enables a periodic external stimulation, case in which phase sensitive detection (PSD) is used to demodulate the periodic component. Recently, a new method of PSD was introduced without the need of a lock-in amplifier or spectrometer build-in hardware [142]. The modulated excitation (ME) can be, in general, applied to any FTIR mode (including DRIFT) because the only requirement is that the FTIR instrument acquires time resolved measurements.

When compared to the number of available phenomenological characterization techniques, the corresponding number of useful spectroscopic ones is quite low. In fact, until now just the methods based on IR spectroscopy were proven to be operando compatible. This fact strongly contrasts with the need for the type



Fig. 13. DRIFT spectra of the SnO<sub>2</sub> sensor at 200  $^{\circ}$ C in the presence of different C<sub>3</sub>H<sub>8</sub> concentrations: (a) 100 ppm; (b) 200 ppm; (c) 500 ppm; (d) 750 ppm; (e) 1000 ppm, in dry air. As a reference the spectrum of sensor at 200  $^{\circ}$ C in dry air was used.

of insight spectroscopy is supposed to provide, which is crucial for the understanding of the gas sensing with metal oxide-based gas sensors. There is an urgent demand for devising new ways to apply spectroscopic methods especially in relation to the lack of information on oxygen-related surface species in operando conditions. Until then, the way forward is probably the use of indirect approaches in which the effect of oxygen is monitored through the changes it determines on species with an IR signature in combination with phenomenological techniques. Also here the same reasoning on the use of model samples and special testing conditions, which was described at the end of the previous section, is valid. Even more for the spectroscopic techniques it is important to design model samples and to test them in ways that will allow for the gaining of relevant information (Fig. 13).

## 6. Conclusion and outlook

On the basis of the experimental techniques review that is the object of this paper, we can state that it is possible to radically improve the level of knowledge in the field of metal oxide-based gas sensors. With all limitations, described in the previous sections, one has at the moment a large set of experimental techniques that are possible to be simultaneously applied and the results of which can be synergistically combined (for a schematic representation, see Fig. 14); that will allow for qualitative improvements in both the understanding of sensing and transduction on the one side, and the development of practical sensors on the other side. For that to happen, there are a few criteria to be met:



Fig. 14. Overview of available investigation techniques.

- The study should be focused on the sensor, taken as a whole. It is important to keep in mind that the overall performance is determined by the combination from all sensor parts contributions.
- The test conditions should be as much as possible the ones corresponding to the real applications. This requires a good knowledge of the latter on the basis of which the critical parameters are identified.
- The starting point for all experimental work needs to be the characterization of the sensor response (dc resistance) in the application conditions. On its basis, the issues that are of interest and, accordingly, the needed additional investigation methods can be selected.
- For the understanding of specific questions related to the sensing performance it is useful to use model samples and special testing conditions. The design criteria for the model samples and test environment should target the issue under study and try to optimize the quality of the experimental results.

It is important to note that the investigations presented in the review need to be conducted in combination with structural ones, able to provide the microscopic and morphological inputs on sensing layer/material, etc. and with the help of theoretical modeling.

Coming back to the experimental techniques presented here, we can state that the most important drawback is on the side of the spectroscopy; namely, the lack of direct operando experimental information on surface oxygen species is a very important handicap. Adapting spectroscopic techniques that will be able to provide this type of knowledge to realistic operation conditions is actually the biggest challenge we face on the experimental side.

An additional difficulty is to adapt the available technique to the new class of sensors based on individual nano-crystals (wires, bands, tubes, etc.) [53]. Besides the technological obstacles associated to this type of devices, the uncertainties related to the origin of the sensing effect are imperiously asking for appropriate investigation techniques.

#### References

- D.E. Williams, Semiconducting oxides as gas-sensitive resistors, Sens. Actuators B: Chem. 57 (1999) 1–16.
- [2] N. Barsan, M. Schweizer-Berberich, W. Gopel, Fundamental and practical aspects in the design of nanoscaled SnO<sub>2</sub> gas sensors. A status report, Fresen. J. Anal. Chem. 365 (1999) 287–304.
- [3] G. Korotcenkov, Gas response control through structural and chemical modifications of metal oxide films: state of the art and approaches, Sens. Actuators (2005) 209–232.
- [4] K. Ihokura, J. Watson, The Stannic Oxide Gas Sensor: Principle and Application, CRC Press Inc., 1994.
- [5] G. Heiland, Zum Einfluss von Wasserstoff auf die elektrische Leitfähigkeit von ZnO-Kristallen, Zeit. Phys. 138 (1954) 459–464.
- [6] A. Bielanski, J. Deren, J. Haber, Electric conductivity and catalytic activity of semiconducting oxide catalysts, Nature 179 (1957) 668–669.
- [7] T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani, A new detector for gaseous components using semiconductive thin films, Anal. Chem. 34 (1962) 1502f.
- [8] N. Taguchi, U.S. Patent 3,631,436 (1971).
- [9] http://www.figarosens.com.

- [10] http://www.fisinc.co.jp.
- [11] http://www.appliedsensors.com.
- [12] http://www.citytech.com.
- [13] http://www.microchem.com.
- [14] J. Marek, H.-P. Trah, Y. Suzuki, I. Yokomori, Sensors for Automotive Technology, VCH Weinheim, Weinheim, 2003.
- [15] T.C. Pearce, S.S. Schiffman, H. Troy Nagle, J.W. Gardner, Handbook of Machine Olfaction: Electronic Nose Technology, Wiley, 2003.
- [16] M. Batzill, U. Diebold, The surface and materials science of tin oxide, Prog. Surf. Sci. 79 (2005) 47–154.
- [17] U. Diebold, Structure and properties of TiO<sub>2</sub> surfaces: a brief review, Appl. Phys. A: Mater. Sci. Process. 76 (2003) 681–687.
- [18] V.E. Henrich, P.A. Cox, The Surface Science of Metal Oxides, University Press, Cambridge, 1994.
- [19] D. Kohl, Surface processes in the detection of reducing gases with SnO<sub>2</sub>based devices, Sens. Actuators 18 (1989) 71–113.
- [20] P.G. Harrison, A. Guest, An infrared and thermogravimetric analysis of the thermal dehydration of tin(IV) oxide gel, J. Chem. Soc. Faraday Trans. 83 (1987) 3383–3397.
- [21] S. Lenaerts, J. Roggen, G. Maes, FT-IR characterisation of tin dioxide gas sensor materials under working conditions, Spectrochim. Acta A 51 (1995) 883–894.
- [22] A. Chiorino, G. Ghiotti, F. Prinetto, M.C. Carotta, G. Martinelli, M. Merli, Characterization of SnO<sub>2</sub>-based gas sensors. A spectroscopic and electrical study of thick films from commercial and laboratory-prepared samples, Sens. Actuators B: Chem. 44 (1997) 474–482.
- [23] M.I. Baraton, L. Merhari, H. Ferkel, J.F. Castagnet, Comparison of the gas sensing properties of tin, indium and tungsten oxides nanopowders: carbon monoxide and oxygen detection, Mater. Sci. Eng. C: Biomim. Supramol. Syst. 19 (2002) 315–321.
- [24] N. Barsan, U. Weimar, Understanding the fundamental principles of metal oxide based gas sensors; the example of CO sensing with SnO<sub>2</sub> sensors in the presence of humidity, J. Phys.: Conden. Matter 15 (2003) R813–R839.
- [25] T. Sahm, A. Gurlo, N. Barsan, U. Weimar, Basics of oxygen and SnO<sub>2</sub> interaction; work function change and conductivity measurements, Sens. Actuators B: Chem. 118 (1–2) (2006) 78–83.
- [26] D. Amalric-Popescu, F. Bozon-Verduraz, Infrared studies on SnO<sub>2</sub> and Pd/SnO<sub>2</sub>, Catal. Today 70 (2001) 139–154.
- [27] M.I. Baraton, L. Merhari, Influence of the particle size on the surface reactivity and gas sensing properties of SnO<sub>2</sub> nanopowders, Mater. Trans. 42 (2001) 1616–1622.
- [28] S. Emiroglu, N. Barsan, U. Weimar, V. Hoffmann, In situ diffuse reflectance infrared spectroscopy study of CO adsorption on SnO<sub>2</sub>, Thin Solid Films 391 (2001) 176–185.
- [29] N. Barsan, U. Weimar, Conduction model of metal oxide gas sensors, J. Electroceram. 7 (2001) 143–167.
- [30] N. Barsan, Conduction models in gas-sensing SnO<sub>2</sub> layers: grain-size effects and ambient atmosphere influence, Sens. Actuators B: Chem. 17 (1994) 241–246.
- [31] R. Sanjines, V. Demarne, F. Levy, Hall effect measurements in SnOx film sensors exposed to reducing and oxidizing gases, Thin Solid Films 194 (1990) 935–942.
- [32] T. Sauerwald, D. Skiera, D. Kohl, Field induced polarisation and relaxation of tungsten oxide thick films, Thin Solid Films 490 (2005) 86–93.
- [33] X. Zhou, Y. Xu, Q. Cao, S. Niu, Metal-semiconductor ohmic contact of SnO<sub>2</sub>-based ceramic gas sensors, Sens. Actuators B: Chem. 41 (1997) 163–167.
- [34] M.R. Cassia-Santos, V.C. Sousa, M.M. Oliveira, F.R. Sensato, W.K. Bacelar, J.W. Gomes, E. Longo, E.R. Leite, J.A. Varela, Recent research developments in SnO<sub>2</sub>-based varistors, Mater. Chem. Phys. 90 (2005) 1–9.
- [35] M. Egashira, Y. Shimizu, Y. Takao, S. Sako, Variations in *I–V* characteristics of oxide semiconductors induced by oxidizing gases, Sens. Actuators B: Chem. 35 (1996) 62–67.
- [36] O.K. Varghese, L.K. Malhotra, Electrode-sample capacitance effect on Ethanol sensitivity of nano-grained SnO<sub>2</sub> thin films, Sens. Actuators B: Chem. 53 (1998) 19–23.

- [37] E. Traversa, Ceramic sensors for humidity detection: the state-of-the-art and future developments, Sens. Actuators B 23 (1995) 135–156.
- [38] R. Lalauze, N. Bui, C. Pijolat, Interpretation of the electrical properties of a SnO<sub>2</sub> gas sensor after treatment with sulfur dioxide, Sens. Actuators 6 (1984) 119–125.
- [39] V.I. Filippov, A.A. Terentjev, S.S. Yakimov, Electrode structure effect on the selectivity of gas sensors, Sens. Actuators B: Chem. 28 (1995) 55–58.
- [40] S. Capone, P. Siciliano, F. Quaranta, R. Rella, M. Epifani, L. Vasanelli, Moisture influence and geometry effect of Au and Pt electrodes on CO sensing response of SnO<sub>2</sub> microsensors based on sol–gel thin film, Sens. Actuators B: Chem. 77 (2001) 503–511.
- [41] S. Capone, M. Epifani, L. Francioso, S. Kaciulis, A. Mezzi, P. Siciliano, A.M. Taurino, Influence of electrodes ageing on the properties of the gas sensors based on SnO<sub>2</sub>, Sens. Actuators B: Chem. 115 (2006) 396– 402.
- [42] H. Gourari, M. Lumbreras, R. Van Landschoot, J. Schoonman, Electrode nature effects on stannic oxide type layers prepared by electrostatic spray deposition, Sens. Actuators B: Chem. 58 (1999) 365–369.
- [43] T.P. Huelser, H. Wiggers, F.E. Kruis, A. Lorke, Nanostructured gas sensors and electrical characterization of deposited SnO<sub>2</sub> nanoparticles in ambient gas atmosphere, Sens. Actuators B: Chem. 109 (2005) 13–18.
- [44] M. Schweizer-Berberich, N. Bârsan, U. Weimar, J.R. Morante, W. Göpel, Eurosensors XI, Warsaw, Poland, 1997, pp. 1377–1380.
- [45] P. Montmeat, R. Lalauze, J.-P. Viricelle, G. Tournier, C. Pijolat, Model of the thickness effect of SnO<sub>2</sub> thick film on the detection properties, Sens. Actuators B: Chem. 103 (2004) 84–90.
- [46] J. Kappler, A. Tomescu, N. Barsan, U. Weimar, CO consumption of Pd doped SnO<sub>2</sub> based sensors, Thin Solid Films 391 (2001) 186–191.
- [47] W. Schmid, N. Barsan, U. Weimar, Sensing of hydrocarbons and CO in low oxygen conditions with tin dioxide sensors: possible conversion paths, Sens. Actuators B: Chem. 103 (2003) 362–368.
- [48] A. Gurlo, N. Barsan, U. Weimar, Mechanism of NO<sub>2</sub> Sensing on In<sub>2</sub>O<sub>3</sub> Thick Film Sensors as Revealed by Simultaneous Consumption and Resistivity Measurements, in: J. Sanisteir, P. Ripka (Eds.), Eurosensors 16, vol. 1, Prague, Czechia, 2002, pp. 571–572, ISBN 80-01-02576-4.
- [49] M. Bauer, The influence of geometry and electrical fields on the performance of tin dioxide gas sensors, PhD Thesis in preparation (2002).
- [50] M. Bauer, N. Barsan, K. Ingrisch, A. Zeppenfeld, I. Denk, B. Schumann, U. Weimar, W. Goepel, Influence of measuring voltage and geometry of the sensing layer on the characteristics of thick film SnO<sub>2</sub> gas sensors, in: Proceedings of the 11th European Microelectronics Conference, 1997.
- [51] G.K. Reeves, H.B. Harrison, Obtaining the specific contact resistance from transmission line model measurements, IEEE Electr. Dev. Lett. 3 (1982) 111–113.
- [52] U. Hoefer, K. Steiner, E. Wagner, Contact and sheet resistances of SnO<sub>2</sub> thin films from transmission-line model measurements, Sens. Actuators B: Chem. 26 (1995) 59–63.
- [53] E. Comini, Metal oxide nano-crystals for gas sensing, Anal. Chim. Acta 568 (2006) 28–40.
- [54] N. Barsan, M. Schweizer-Berberich, W. Göpel, Fundamental and practical aspects in the design of nanoscaled SnO<sub>2</sub> gas sensors: a status report, Fresen. J. Anal. Chem. 365 (1999) 287–304.
- [55] J.H. Werner, Electronic Properties of Grain Boundaries in Polycrystalline Semiconductors I, Springer-Verlag, Berlin, 1985.
- [56] S.R. Morrison, The Chemical Physics of Surfaces, Plenum Press, New York, 1990.
- [57] J.F. McAleer, P.T. Moseley, J.O.W. Norris, D.E. Williams, B.C. Tofield, Tin dioxide gas sensors, J. Chem. Soc. Faraday Trans. 1 84 (1988) 441–457.
- [58] S.M. Sze, Physics of Semiconductor Devices, John Wiley & Sons Inc., 1981.
- [59] M. Ramzan, R. Brydson, Characterization of sub-stoichiometric tungsten trioxide (WO<sub>3</sub>-x) using impedance spectroscopy, Sens. Actuators A 118 (2005) 322–331.
- [60] A.C. Bose, P. Balaya, P. Thangadurai, S. Ramasamy, Grain size effect on the universality of ac conductivity in SnO<sub>2</sub>, J. Phys. Chem. Solids 64 (2003) 659–663.

- [61] G. Martinelli, M.C. Carotta, L. Passari, L. Tracchi, Study of the moisture effects on SnO<sub>2</sub> thick films by sensitivity and permittivity measurements, Sens. Actuators B: Chem. 26 (1995) 53–55.
- [62] G. Ghiotti, A. Chiorino, G. Martinelli, M.C. Carotta, Moisture effects on pure and Pd-doped SnO<sub>2</sub> thick films analyzed by FTIR spectroscopy and conductance measurements, Sens. Actuators B: Chem. 25 (1995) 520–524.
- [63] A. Labidi, C. Jacolin, M. Bendahan, A. Abdelghani, J. Guérin, K. Aguir, M. Maaref, Impedance spectroscopy on WO<sub>3</sub> gas sensor, Sens. Actuators B: Chem. 106 (2005) 713–718.
- [64] L. Chen, S.C. Tsang, Ag doped WO<sub>3</sub>-based powder sensor for the detection of NO gas in air, Sens. Actuators B: Chem. 89 (2003) 68–75.
- [65] B.W. Licznerski, K. Nitsch, H. Teterycz, T. Sobański, K. Wiśniewski, Characterisation of electrical parameters for multilayer SnO<sub>2</sub> gas sensors, Sens. Actuators B: Chem. 103 (2004) 69–75.
- [66] Z. Ling, C. Leach, R. Freer, NO<sub>2</sub> sensitivity of a heterojunction sensor based on WO<sub>3</sub> and doped SnO<sub>2</sub>, J. Eur. Ceram. Soc. 23 (2003) 1881–1891.
- [67] A. Ylinampa, V. Lantto, S. Leppavuori, Some differences between Au and Pt electrodes in SnO<sub>2</sub> thick-film gas sensors, Sens. Actuators B: Chem. 14 (1993) 602–604.
- [68] P. Montmeat, R. Lalauze, J.P. Viricelle, G. Tournier, C. Pijolat, Model of the thickness effect of SnO<sub>2</sub> thick film on the detection properties, Sens. Actuators B: Chem. 103 (2004) 84–90.
- [69] J. Tamaki, N. Yamazoe, Adsorption behaviour of CO and interfering gases on SnO<sub>2</sub>, Surf. Sci. 221 (1989) 183–196.
- [70] N. Yamazoe, New approaches for improving semiconductor gas sensors, Sens. Actuators B: Chem. 5 (1991) 7–19.
- [71] J.W. Gardner, A non-linear diffusion-reaction model of electrical conduction in semiconductor gas sensors, Sens. Actuators B: Chem. 1 (1990) 166–170.
- [72] J.W. Gardner, A diffusion-reaction model of electrical conduction in tin oxide gas sensors, Semicond. Sci. Technol. 4 (1989) 345–350.
- [73] J.W. Gardner, Intelligent gas sensing using an integrated sensor pair, Sens. Actuators B: Chem. 27 (1995) 261–266.
- [74] M. Hausner, J. Zacheja, J. Binder, Multi-electrode substrate for selectivity enhancement in air monitoring, Sens. Actuators B: Chem. 43 (1997) 11–17.
- [75] F. Hossein-Babaei, M. Orvatinia, Analysis of thickness dependence of the sensitivity in thin film resistive gas sensors, Sens. Actuators B: Chem. 89 (2003) 256–261.
- [76] S.-S. Park, J.D. Mackenzie, Thickness and microstructure effects on alcohol sensing of tin oxide thin films, Thin Solid Films 274 (1996) 154–159.
- [77] S.M.A. Durrani, E.E. Khawaja, M.F. Al-Kuhaili, CO-sensing properties of undoped and doped tin oxide thin films prepared by electron beam evaporation, Talanta 65 (2005) 1162–1167.
- [78] G.G. Mandayo, E. Castaño, F.J. Gracia, A. Cirera, A. Cornet, J.R. Morante, Strategies to enhance the carbon monoxide sensitivity of tin oxide thin films, Sens. Actuators B: Chem. 95 (2003) 90–96.
- [79] X. Vilanova, E. Llobet, J. Brezmes, J. Calderer, X. Correig, Numerical simulation of the electrode geometry and position effects on semiconductor gas sensor response, Sens. Actuators B: Chem. 48 (1998) 425– 431.
- [80] D.E. Williams, K.F.E. Pratt, Theory of self-diagnostic sensor array devices using gas-sensitive resistors, J. Chem. Soc. Faraday Trans. 91 (13) (1995) 1961–1966.
- [81] G.G. Mandayo, E. Castano, F.J. Gracia, A. Cirera, A. Cornet, J.R. Morante, Strategies to enhance the carbon monoxide sensitivity of tin oxide thin films, Sens. Actuators B: Chem. 95 (2003) 90–96.
- [82] M. Liess, Electric-field-induced migration of chemisorbed gas molecules on a sensitive film—a new chemical sensor, Thin Solid Films 410 (2002) 183–187.
- [83] E.H. Hall, On a new action of the magnet on electrical current, Am. J. Math. 2 (1879) 287–292.
- [84] R.S. Popovic, Hall-Effect Devices: Magnetic Sensors and Characterization of Semiconductors, Adam Hilger, Bristol, 1991.
- [85] R.S. Popovic, Hall Effect Devices, Institute of Physics Publishing (IOP), Bristol, Philadelphia, 2004.

- [86] J.W. Orton, M.J. Powell, The Hall effect in polycrystalline and powdered semiconductors, Rep. Prog. Phys. 43 (1980) 1263–1307.
- [87] K. Seeger, Semiconductor Physics: An Introduction, Springer, 1999.
- [88] J.L. Brousseau, H. Bourque, A. Tessier, R.M. Leblanc, Electrical properties and topography of SnO<sub>2</sub> thin films prepared by reactive sputtering, Appl. Surf. Sci. 108 (1997) 351–358.
- [89] M. Ippommatsu, H. Ohnishi, H. Sasaki, T. Matsumoto, Study on the sensing mechanism of tin oxide flammable gas sensors using the Hall effect, J. Appl. Phys. 69 (1991) 8368–8374.
- [90] C. Terrier, J.P. Chatelon, J.A. Roger, Electrical and optical properties of Sb:SnO<sub>2</sub> thin films obtained by the sol–gel method, Thin Solid Films 295 (1997) 95–100.
- [91] J.W. Hammond, C.C. Liu, Silicon based microfabricated tin oxide gas sensor incorporating use of Hall effect measurement, Sens. Actuators B: Chem. 81 (2001) 25–31.
- [92] M. Epifani, A. Forleo, S. Capone, F. Ouaranta, R. Rella, P. Siciliano, L. Vasanelli, Hall effect measurements in gas sensors based on nanosized Os-doped sol-gel derived SnO<sub>2</sub> thin films, IEEE Sens. J. 3 (2003) 827–834.
- [93] R.Y. Korotkov, A.J.E. Farran, T. Culp, D. Russo, C. Roger, Transport properties of undoped and NH<sub>3</sub>-doped polycrystalline SnO<sub>2</sub> with low background electron concentrations, J. Appl. Phys. 96 (2004) 6445– 6453.
- [94] D. Manno, G. Micocci, A. Serra, M. Di Giulio, A. Tepore, Structural and electrical properties of In<sub>2</sub>O<sub>3</sub>–SeO<sub>2</sub> mixed oxide thin films for gas sensing applications, J. Appl. Phys. 88 (2000) 6571–6577.
- [95] V.F. Korzo, V.N. Cherniaev, Electrophysical properties of indium oxide pyrolothic films with disordered structure, Phys. Status Solidi (A) Appl. Res. 20 (1973) 695–705.
- [96] M.C. Carotta, A. Giberti, V. Guidi, C. Malagù, B. Vendemiati, G. Martinelli, Materials Research Society Symposium Proceedings, Vol. 828, 2005, pp. 173–184.
- [97] J.H.W. De Wit, G. van Unen, M. Lahey, Electron concentration and mobility in In<sub>2</sub>O<sub>3</sub>, J. Phys. Chem. Solids 38 (1977) 819–824.
- [98] M. Di Giulio, D. Manno, G. Micocci, A. Serra, A. Tepore, Sputter deposition of tungsten trioxide for gas sensing applications, J. Mater. Sci.: Mater. Electron. 9 (1998) 317–322.
- [99] D.J. Smith, J.F. Vetelino, R.S. Falconer, E.L. Wittman, Technical Digest-IEEE Solid-State Sensor and Actuator Workshop, 1992, pp. 78– 81.
- [100] T.H. Kwon, J.Y. Ryu, W.C. Choi, S.W. Kim, S.H. Park, H.H. Choi, M.K. Lee, Investigation on sensing properties of ZnO-based thin film sensors for trimethylamine gas, Sens. Mater. 11 (1999) 257–267.
- [101] A. Oprea, E. Moretton, N. Bârsan, W.J. Becker, J. Wöllenstein, U. Weimar, Conduction model of SnO<sub>2</sub> thin films based on conductance and Hall effect measurements, Sens. Actuators B: Chem. 111–112 (2005) 572–576.
- [102] W. Göpel, Chemisorption and charge transfer at ionic semiconductor surfaces: implications in designing gas sensors, Prog. Surf. Sci. 20 (1985) 9–103.
- [103] K.D. Schierbaum, R. Kowalkowski, U. Weimar, W. Göpel, Conductance, work function and catalytic activity on SnO<sub>2</sub>-based gas sensors, Sens. Actuators B: Chem. (1991) 205–214.
- [105] A. Gurlo, M. Sahm, A. Oprea, N. Barsan, U. Weimar, A p- to n-transition on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-based thick film sensors studied by conductance and work function change measurements, Sens. Actuators B: Chem. 102 (2004) 291–298.
- [106] T. Sahm, A. Gurlo, N. Barsan, U. Weimar, L. Madler, Fundamental studies on SnO<sub>2</sub> by means of simultaneous work function change and conduction measurements, Thin Solid Films 490 (2005) 43–47.
- [107] J. Mizsei, Vibrating capacitor method in the development of semiconductor gas sensors, Thin Solid Films 490 (2005) 17–21.
- [108] T. Doll, A. Fuchs, I. Eisele, G. Faglia, S. Groppelli, G. Sberveglieri, Conductivity and work function ozone sensors based on indium oxide, Sens. Actuators B: Chem. 49 (1998) 63–67.

- [109] D. Koziej, N. Barsan, V. Hoffmann, J. Szuber, U. Weimar, Complementary phenomenological and spectroscopic studies of propane sensing with tin dioxide based sensors, Sens. Actuators B: Chem. 108 (2005) 75– 83.
- [110] T. Maekawa, K. Cai, K. Suzuki, N. Dougami, T. Takada, M. Egashira, Compensatory methods for the odor concentration in an electronic nose system using software and hardware, Sens. Actuators B: Chem. 76 (2001) 430–435.
- [111] G. Mueller, A. Friedberger, P. Kreisl, S. Ahlers, O. Schulz, T. Becker, A MEMS toolkit for metal-oxide-based gas sensing systems, Thin Solid Films 436 (2003) 34–45.
- [112] http://www.aca-berlin.de/operando/lectures schedule.pdf.
- [113] B.M. Weckhuysen, Snapshots of a working catalyst: possibilities and limitations of in situ spectroscopy in the field of heterogeneous catalysis, Chem. Commun. (2002) 97–110.
- [114] B.M. Weckhuysen, Determining the active site in a catalytic process: Operando spectroscopy is more than a buzzword, Phys. Chem. Chem. Phys. 5 (2003) 4351–4360.
- [115] I. Jimenez, M.A. Centeno, R. Scotti, F. Morazzoni, J. Arbiol, A. Cornet, J.R. Morante, NH<sub>3</sub> interaction with chromium-doped WO<sub>3</sub> nanocrystalline powders for gas sensing applications, J. Mater. Chem. 14 (2004) 2412–2420.
- [116] F. Morazzoni, C. Canevali, N. Chiodini, C. Mari, R. Ruffo, R. Scotti, L. Armelao, E. Tondello, L.E. Depero, E. Bontempi, Nanostructured Ptdoped tin oxide films: sol-gel preparation, spectroscopic and electrical characterization, Chem. Mater. 13 (2001) 4355–4361.
- [117] J.J. Benitez, M.A. Centeno, C. Louis Dit Picard, O. Merdrignac, Y. Laurent, J.A. Odriozola, In situ diffuse reflectance infrared spectroscopy (DRIFTS) study of the reversibility of CdGeON sensors towards oxygen, Sens. Actuators B: Chem. 31 (1996) 197–202.
- [118] J.J. Benitez, M.A. Centeno, O.M. Merdrignac, J. Guyader, Y. Laurent, J.A. Odriozola, DRIFTS chamber for in situ and simultaneous study of infrared and electrical response of sensors, Appl. Spectrosc. 49 (1995) 1094–1096.
- [119] S. Harbeck, A. Szatvanyi, N. Barsan, U. Weimar, V. Hoffmann, DRIFT studies of thick film un-doped and Pd-doped SnO<sub>2</sub> sensors: temperature changes effect and CO detection mechanism in the presence of water vapour, Thin Solid Films 436 (2003) 76–83.
- [120] O. Safonova, T. Neisius, B. Chenevier, I. Matko, M. Labeau, A. Gaskov, Proceedings of the 13th International Congress on Catalysis, France, 2004.
- [121] S. Sharma, N. Sharan, U. Kiyoshi, Yusuke, Mössbauer studies on tinbismuth oxide CO selective gas sensor, J. Appl. Phys. 71 (4) (1992) 2000–2005.
- [122] J. Trimboli, M. Mottern, H. Verweij, P.K. Dutta, Interaction of water with titania: implications for high-temperature gas sensing, J. Phys. Chem. B 110 (2006) 5647–5654.
- [123] A. Marsal, M.A. Centeno, J.A. Odriozola, A. Cornet, J.R. Morante, DRIFTS analysis of the CO<sub>2</sub> detection mechanisms using LaOCl sensing material, Sens. Actuators B: Chem. 108 (2005) 484–489.
- [124] R. Pohle, M. Fleischer, H. Meixner, Infrared emission spectroscopic study of the adsorption study of the adsorption of the oxygen on gas sensors based on polycrystalline metal oxide films, Sens. Actuators B 78 (2001) 133–137.
- [125] R. Pohle, M. Fleischer, H. Meixner, In situ infrared emission spectroscopic study of the adsorption of H<sub>2</sub>O and hydrogen containing gases on Ga<sub>2</sub>O<sub>3</sub> gas sensors, Sens. Actuators B 68 (2000) 151–156.
- [126] D. Koziej, N. Barsan, K. Shimanoe, N. Yamazoe, J. Szuber, U. Weimar, Spectroscopic insights into CO sensing of undoped and palladium doped tin dioxide sensors derived from hydrothermally treated tin oxide sol, Sens. Actuators B: Chem. 118 (1–2) (2006) 98–104.
- [127] M. Wallin, H. Grönbeck, A.L. Spetz, M. Skoglundh, Vibrational study of ammonia adsorption on Pt/SiO<sub>2</sub>, Appl. Surf. Sci. 235 (2004) 487– 500.
- [128] M.I. Baraton, L. Merhari, Determination of the gas sensing potentiality of nanosized powders by FTIR spectrometry, Scripta Mater. 44 (2001) 1643–1648.
- [129] R. Pohle, Technische Universitet München, München, 2000.

- [130] K.W. van Every, P.R. Griffiths, Characterization of diffuse reflectance FT-IR spectrometry for halogenous catalyst studies, Appl. Spectrosc. 45 (1991) 347–359.
- [131] T. Pagnier, M. Boulova, A. Galerie, A. Gaskov, G. Lucazeau, In situ coupled Raman and impedance measurements of the reactivity of nanocrystalline SnO<sub>2</sub> versus H<sub>2</sub>S, J. Solid State Chem. 143 (1999) 86–94.
- [132] O.V. Safonova, T. Neisius, A. Ryzhikov, B. Chenevier, A.M. Gaskov, M. Labeau, Characterization of the H<sub>2</sub> sensing mechanism of Pdpromoted SnO<sub>2</sub> by XAS in operando conditions, Chem. Commun. (2005) 5202–5204.
- [133] N. Yamazoe, J. Fuchigami, M. Kishikawa, T. Seiyama, Interactions of tin oxide surface with O<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>, Surf. Sci. 86 (1978) 335–344.
- [134] S. Saukko, U. Lassi, V. Lantto, M. Kroneld, S. Novikov, P. Kuivalainen, T.T. Rantala, J. Mizsei, Experimental studies of O-2-SnO<sub>2</sub> surface interaction using powder, thick films and monocrystalline thin films, Thin Solid Films 490 (2005) 48–53.
- [135] S.C. Chang, Oxygen chemisorption on tin oxide: correlation between electrical conductivity and EPR measurements, J. Vac. Sci. Technol. 17 (1980) 366.
- [136] M. Che, A.J. Tench, Characterisation and reactivity of mononuclear oxygen species on oxide surfaces, Adv. Catal. 31 (1982) 40–42.
- [137] D. Koziej, N. Barsan, U. Weimar, J. Szuber, K. Shimanoe, N. Yamazoe, Water-oxygen interplay on tin dioxide surface: implication on gas sensing, Chem. Phys. Lett. 410 (2005) 321–323.
- [138] T. Itoh, M. Toshiteru, K. Atsuo, In situ surface-enhanced Raman scattering spectroelectrochemistry of oxygen species, Roy. Soc. Chem. Faraday Dis. 132 (2006) 95–109.
- [139] C. Canevali, Surface reactivity of SnO<sub>2</sub> obtained by sol-gel type condensation: interaction with inert, combustible gases, vapour-phase H<sub>2</sub>O and air, as revealed by electron paramagnetic resonance spectroscopy, J. Mater. Chem. 7 (1997) 997–1002.
- [140] D. Amalric-Popescu, J.M. Herrmann, A. Ensuque, F. Bozon-Verduraz, Nanosized tin dioxide: spectroscopic (UV–vis, NIR, EPR) and electrical conductivity studies, Phys. Chem. Chem. Phys. 3 (2001) 2522–2530.

- [141] F. Thibault-Starzyk, J. Saussey, In Situ Characterization of Catalysts, American Scientific Publishers, San Diego, 2004.
- [142] D. Baurecht, I. Porth, U.P. Fringeli, A new method of phase sensitive detection in modulation spectroscopy applied to temperature induced folding and unfolding of RNase A, Vibr. Spectrosc. 30 (2002) 85–92.

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