



UNIVERSITAT DE BARCELONA



Tin Oxide Gas Sensors: An Electrochemical Approach

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Como leí una vez en una tesis (y es algo que suscribo totalmente), ésta es la parte más importante de una tesis, dado que es la única que se lee todo el mundo, así que es una parte que debe ser tratada con el esmero correspondiente, y eso es lo que voy a tratar de hacer. Eso sí, todo aquél que me conozca sabrá que, si quiero ser exhaustivo en esta parte, puedo fácilmente pasarme la extensión habitual de una tesis (unas 100 o 200 páginas) sólo en ella así que, mientras que en el resto de la tesis lo que voy a tratar es de que parezca que he trabajado mucho más de lo que realmente lo he hecho, en esta parte me veo obligado a hacer un resumen y no extenderme tanto como quisiera. Ya pido perdón por anticipado por si me olvido a alguien. Prometo invitar a algo a todo aquél que no esté incluido por olvido, así que ya sabéis: todos aquellos que os creáis con derecho a figurar aquí, buscad si estáis citados directa o indirectamente, porque a lo mejor cae algo...

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“La paciencia
todo lo alcanza”

Santa Teresa de Jesús, *Versos*

“Sólo con paciencia
no se alcanza nada”

El Hombre Orquesta, *Autobiografía*

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0. Preface

0. PREFACE

0.1. Brief history of materials research

Historically, one of the keys of mankind development is the research on new materials that can improve their properties crucial in each age for the species. Thereby, after the achievement of the biped position at the beginning of the human development, the first issue for our species to survive was the research of how to use our hands, which no longer had to be used to displace us. In this way, in the Stone Age we survived thanks to the use of silex instruments to hunt and to protect ourselves from the wild animals. Afterwards, the will of new knowledgement drove to the development of agriculture and stockbreeding in the Neolithic and to the finding of metal properties and how to use them, thereby beginning the Metal Age. Since then, the most important issue of how to survive became accomplished, but knowledgement will was never fulfilled and new materials have been discovered, not only to establish our superiority with respect to other animal species, but specially to extend our capabilities and also to improve our daily life. Thus, afterwards, the main aim of mankind has been to make easier the daily life by developing new instrumentation that decreases the amount of work that we have to do to complete the same tasks. Altogether, the knowledgement of our body functionality and of the environmental nature has also been crucial for our development: this background has allowed us to live a longer life and to enjoy it in better conditions than our ancestors. All this research, originally addressed to our basic needs, has created new basic needs (for example, today we cannot imagine life without electricity or without soap). Thus, the disappearance of the need to survive increased the interest for painting, writing,...

During our evolution, science (understood as the research of new knowledgement free of subjectivity) has been always present. Nevertheless, it was not until Galileo that modern science began, as he established the fact that knowledgement must come from the experimental observation and the development of mathematical models that can explain these experimental results, thereby giving ground to the scientific method. This fact, together with the Industrial Revolution along the 19th century (for which the discovery of the great heat capacity of carbon minerals to move machines was crucial), produced that the knowledgement on the nature has increased much faster than ever, thereby approaching us to our latest wish: the knowledgement of the behaviour of everything surrounding us.

We are still far away from this wish (if we can ever fulfil it) and there is still the need to greatly increase our knowledgement in all fields of science. Within these fields, one of the most important, if not the most important, still is the development of new materials that improve in some way actual available materials. There is a great amount of scientific work concerning very different applications, including from biology to chemistry, physics or geology. One of the recent advances most publicly known is the research of knowledgement about the human genome, whose almost complete identification has only recently been achieved. The scientific research within this field searches the knowledgement of the functionality of the different human genes and their interactions to improve the human body. Certainly, thinking on the human body as a mere material is shocking nowadays but in my opinion we are not so far away from this. Our actual ethical guidelines force us to discard the genetic modification of human simply because of the physical aspect, but this is not so clear when we asked ourselves about the need to modify a gene in order to have a longer life or to have stronger muscles. If we look

to our history, the most important scientific changes have always been shocking to the generation that discovered them but they have always surpassed the ethics of the age and have created a new ethic that include them, and this will probably also happen in this case. Will this mean that in the future we will have “The Happy World” that Aldous Huxley imagined? May be??

With respect to the scientific research in more conventional materials, there is a great diversity of scientific fields and it is not the aim of this preface to describe all of them. Nevertheless, apart from the basic scientific research (always important to accomplish our late wish, that has been previously described), the main scientific activity in the field of materials is within the applied area, i.e., research in materials that could be applied in our daily life in a short period of time. Shockingly, most of this scientific work (as most of the scientific work in general) is funded by other two main driving forces of our society: the need of power and money. This is another fact in common with our whole history: all the positive discoveries have always had a negative application and, inevitably, we have always applied both sides of them. Thus, the need to win wars within our own specie give funds for the scientific research of better materials or instruments to fabricate weapons that can kill more people and are more powerful. Moreover, we have always wanted to have more money to live better and, since the establishment of capitalism at the end of the 19th century as the main economic system that rules our world, there have been funds for the research of materials that are better or similar to the existent ones but that have a lower economical cost, thereby owing the consumer to spend less money to buy the same thing, thus having more money to buy another things, and owing also the manufacturer to have a greater economical benefit for the sale of the same thing.

0.2. Why the research on SnO₂?

Tin oxide has recently received a great scientific interest because of its wide range of applications. Thus, looking only at the most recently reported applications, it has been studied as overcoat for thin film magnetic recording media overcoat [1], as transparent electrode in panels and other electrochromic devices, and also in photoelectrochemical studies and those related to the development of solar cells [2-6]. Efficiency in these applications is usually improved by suitably doping the tin oxide substrate but, once doped, newer applications are also reported, as for example doping with Sb, Cl and F increases the conductivity of tin oxide [7,8], while doped tin oxide deposited on titanium presents high overpotentials for the oxygen generation reaction, thereby giving good anodes for the electrochemical oxidation of both organic pollutants and cyanide [9]. It is also investigated as material for Li-ion batteries [10-12]

The development of the Information Society, as last step of the Electronics revolution, requires the development and improvement of devices (sensors) able to transform physical or chemical phenomena into electrical signal for further treatment using transducer systems. Thus, our society requires gas sensors for domestic, automotive and industrial applications due to the implication of gases in environmental control or dangerous emissions. So, major reasons for the need of gas sensors are monitoring of environmental pollutants and controlling their emission. At this respect, the market, based on the new regulations, demands a higher reliability in domestic and environmental gas sensors for the detection of combustible and toxic gases. For gas monitoring, different kinds of sensor systems can be used: Spectroscopic, Optical and Solid State are the three main families of gas sensors. Spectroscopic systems are those based on the direct analysis

of fundamental gas properties, such as molecular mass or vibrational spectrum; optical sensor systems are based on the measurement of the absorption spectra after light stimulation; and solid-state ones are based on the change of physical and/or chemical properties of a sensing material after gas exposure. These last changes depend on the gas-sensing material and usually involve changes in its electrical properties.

There exist a large variety of devices fulfilling some of the characteristics of ideal gas sensors. The most recently developed include: - MOSFET sensors (based on a change of the electrostatic potential), reported for the first time in 1975 by Lundström et al.[13]; - Piezoelectric sensors (based on changes of the frequency of crystal vibration upon absorption of different gases). The crystals may be made to vibrate in a bulk acoustic wave (BAW) or in a surface acoustic wave (SAW), and since frequency changes depend on the mass of the adsorbed gas and piezoelectric sensors may be coated with an unlimited number of materials, they present the best selectivity [14]; -Conducting polymer sensors have been under development since approximately 10 years ago [15]. These sensors use a conducting organic polymer as the sensing element, monitoring changes of the resistance by the adsorption of gas.

Gas sensors are also popular because of the applications of electronic noses. Electronic noses are a new concept of sensor application, which tries to mimic the human olfactory system by using an array of electronic chemical sensors with partial specificity and appropriate pattern-recognition electronics [16], using artificial neural networks. Electronic noses can be applied successfully to [17-19]: - Environmental monitoring; - Medicine applications, as an electronic nose can examine odours from human body and thus can serve to identify diseases; - Food industry, which constitutes the largest market for electronic noses, whose applications include quality assessment in food production and inspection of food quality by odour.

Among the large variety of materials used in sensors, the market is dominated by metal oxide semiconductors, usually known simply as semiconductor gas sensors (SGS). SGS detection signal is based on the change of material resistivity after gas exposure, being usually maximum at temperatures ranging from 200 to 800 °C, always depending on tested gas, the own sensor material and its doping. Thus, after Brattain and Bardeen demonstrated already in 1953 [20] that gas adsorption at the surface of Ge lead to a significant variation of the conductance, the first built structure to be used as gas sensor, making use of this phenomena, has been attributed to Seiyama (ZnO sensor) and Taguchi in 1962 [21,22], while the first SGS based on SnO₂ were developed later in 1970 by Taguchi [23]. Initially they were known as Taguchi or Figaro sensors (the inventor and the name of the company that commercialised the sensors, respectively). Since that moment SnO₂ has become the most investigated material for MOS sensors.

The study of SnO₂ as gas sensing material is due to its suitable physicochemical properties as, for example, it has a high reactivity to reducing gases at relatively low operating temperatures thanks to the easy adsorption of oxygen at its surface because of the natural non-stoichiometry of SnO₂. Moreover, SnO₂ has a lower cost when compared to actual available materials for similar applications. Nowadays, the research on these materials is focused to increase their sensitivity, selectivity and stability, and one of the main issues to accomplish these issues is the presence of metals at low concentrations. Thus, the present of a certain metal on the SnO₂ surface improves the properties of the material with respect to certain gases, which are different depending on the added metal.

Moreover, the chemical state and the dispersion of the added metal on the SnO₂ surface also influence the gas sensing response of these materials.

The principle of operation of SnO₂-based SGS lies on detecting the conductivity changes experienced by the n-type material when surface chemisorbed oxygen reacts with reducing gases, such as methane or CO. In the simpler schematisation of the detection mechanism, it could be said that in clean air the conductivity is low because the conduction electrons are bound to surface oxygen, whereas in the presence of a reducing gas, electrons are no longer bound to the surface states and the conductivity increases. Therefore, the adsorption of gaseous species controls the surface and grain boundary resistance of the oxide. As gas adsorption is related to the surface of the material, polycrystalline and even nanocrystalline structures are preferred.

Nowadays, investigation is directed, rather than to new sensors, to increase the characteristics of existing sensors. Ideal sensors should present: - high sensitivity towards chemical compounds; - high selectivity (low cross sensitivity); - high stability; - low sensitivity to humidity and temperature; - high reproducibility and reliability; - short reaction and recovery time; - be robust and durable; - easy calibration; - small dimensions (portability).

Most of these properties are dependent not only on the used material, but also on the method used for its synthesis, and specially on the additives present on the material surface and the method used for their addition. The main goal of this PhD memory is to describe an original new method developed for the proper addition of catalysts to tin oxide substrate. Secondly, a first basic approach of tin oxide surface behaviour has been started to better understand the molecular mechanism of the catalytic reaction.

Chapter 1 illustrates the basic properties of tin oxide, giving special attention to the state-of-the-art of the knowledgement about gas-sensing mechanism and the properties related to it. Chapter 2 gives a brief description of the most important characterisation techniques that have been used, while chapter 3 describes the experimental procedures used within this work. Chapter 4 presents the results of the characterisation of the SnO₂-based samples, beginning with the characterisation of the undoped samples, and of the samples doped with the addition process and the metals actually more used, followed by the characterisation of samples doped with an original new addition method and finishing with the characterisation of the addition of alternative metals. A comparison of the conversion catalytic power of CO to CO₂ showed by some samples is also given. Afterwards, a discussion of the results is presented. Chapter 5 is devoted to the electrochemical study of tin oxide growth, with a methodological introduction, a results and a discussion section. Finally, the original conclusions that can be extracted from the present work and the references used along the writing of this memory will be presented.

1. Introduction

1. INTRODUCTION

Commonly, a material is selected for a defined application on the base of its intrinsic properties and, dealing with chemical processes, the materials properties can be divided into bulk properties and surface properties. Within the subject of this memory, the most important properties are those concerning the surface of the material, although we cannot forget the influence of the bulk properties. Thus, we will begin this section briefly describing the bulk properties of tin dioxide. Afterwards, we will study the influence of the surface of the material and the dopants in the catalysis and gas-sensing mechanism. Nevertheless, it must be stated that the current status of physics and chemistry are not developed enough to know clearly the effects of surface properties on gas sensitivity, and here we present the most accepted theories at the current development of the field.

1.1. Structure and main bulk properties of tin dioxide

Tin dioxide is a semiconductor material, transparent, of high chemical and mechanical stability[25]. Only one stable phase (and no metastable one) is known, which has a tetragonal arrangement of the atoms receiving the names of rutile or cassiterite.

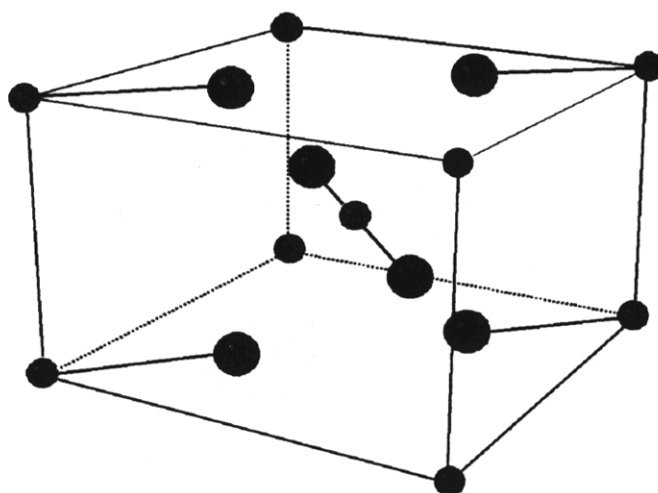


Fig. 1.1. *Unit cell of the crystalline structure of SnO₂. Bigger circles represent oxygen atoms (After [24]).*

The corresponding heat of formation is $\Delta H = 1.9 \cdot 10^3 \text{ J mol}^{-1}$, the heat capacity of the material is $C_p = 52.59 \text{ J mol}^{-1} \text{ K}^{-1}$, the density at 300 K is 6.95 g cm^{-3} and the melting point is $1630 \text{ }^\circ\text{C}$. This crystalline structure contains metal atoms in octahedral coordination and oxygen in planar three-coordination (see fig. 1.1.). Lattice parameters are $a = 4.737 \text{ \AA}$ ($a=b$ in the tetragonal structure) and $c = 3.186 \text{ \AA}$. The atomic position at 300 K in the unit cell is $(0,0,0)$ and $(1/2, 1/2, 1/2)$ for the metal and $\pm(u, u, 0)$ and $(1/2+u, 1/2-u, 1/2)$, being $u=0.387$, for the oxygen. The rest of the atoms of the unit cell can be obtained applying the rutile symmetry D_{4h}^{14} (C_{2v} , $P4_2/mnm$ point group) [25-27]. The Brillouin zone corresponding to this structure is presented in fig.1.2. [28].

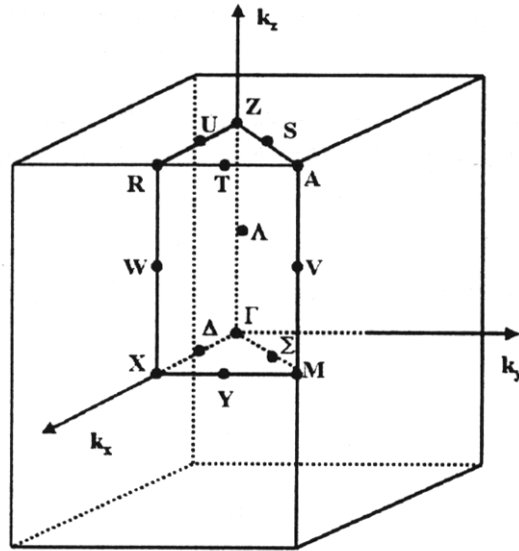


Fig. 1.2. Brillouin zone for the rutile structure (see [28]).

From the point of view of lattice dynamics, the presence of six atoms in the unit cell causes the existence of 18 branches of vibration modes, from which 3 are acoustical and 15 optical modes. Different authors [29] have calculated the correspondent dispersion relations, as seen in fig.1.3. Mathematically, the irreducible representation of phonon modes becomes:

$$\Gamma = \Gamma_1^+ \oplus \Gamma_2^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_1^- \oplus \Gamma_4^- \oplus \Gamma_5^-$$

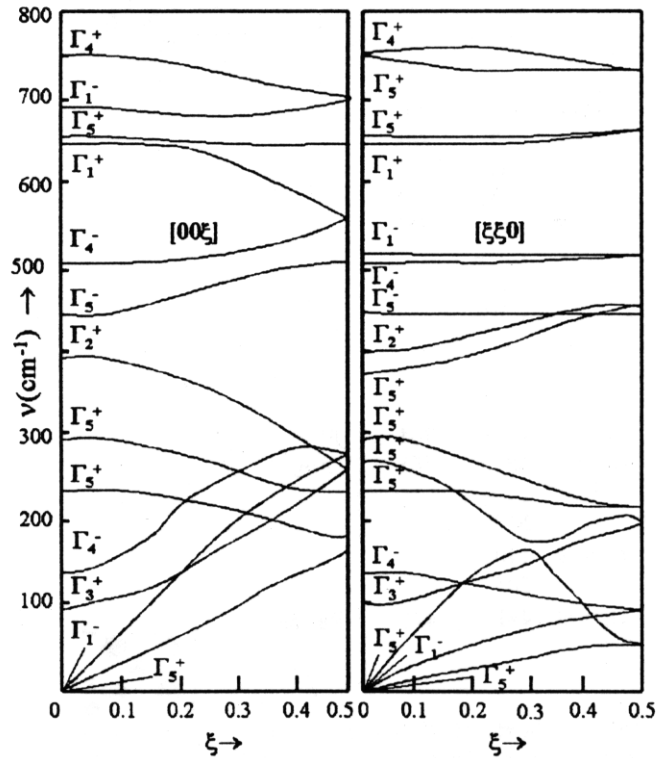


Fig. 1.3. Dispersion relations for phonons propagating along $[0,0,\xi]$ and $[\xi,\xi,0]$ directions (After [28]).

| Mode | Koster not. | Deg. | Branch | Type | Calc. freq. in Γ point (cm^{-1}) | Meas. freq. (cm^{-1}) | Active | Vibration scheme in [001] direction |
|--------------|-------------|------|--------|---------------------|---|--|--------|-------------------------------------|
| Γ_1^+ | A_{1R} | 1 | 1 | Optical | 646 | 634 | Raman | |
| Γ_2^+ | A_{2R} | 1 | 1 | Optical | 398 | | | |
| Γ_3^+ | B_{1R} | 1 | 1 | Optical | 100 | 184 | Raman | |
| Γ_4^+ | B_{2R} | 1 | 1 | Optical | 752 | 779 | Raman | |
| Γ_5^+ | E_u | 3 | 7 | 1TA +3TO +3LO | $v_1^{\text{TO}}=243$ 236 $v_2^{\text{TO}}=605$ 297 $v_3^{\text{TO}}=368$ 651 $v_1^{\text{LO}}=268$ $v_2^{\text{LO}}=377$ $v_3^{\text{LO}}=750$ | 243 273 605 273 368 757 | IR | |
| Γ_1^- | A_{2u} | 1 | 3 | 1LA +1TO +1LO | $v^{\text{LO}}=687$ $v^{\text{TO}}=512$ | 704 465 | IR | |
| Γ_4^- | B_{1u} | 1 | 2 | Optical | 140 505 | | | |
| Γ_5^- | E_R | 2 | 1 | Optical | 441 | 476 | Raman | |

Fig. 1.4. Phonon modes reported in the literature at 300 K (After [24]).

Figure 1.4. summarises the properties of these modes. The inversion symmetry of the rutile structure leads to four infrared active phonons ($3\Gamma_5^+$, $1\Gamma_1^-$) and four Raman active phonons (Γ_3^+ , Γ_5^+ , Γ_1^+ , Γ_4^+).

In SnO_2 , chemical bonding is mainly governed by the linear combination of oxygen 2s and 2p orbitals with tin 5s and 5p orbitals [30]. Whole calculations are given for every point of Brillouin zone in fig.1.5. As seen, the upper valence band consists of a set of three bands (Γ_2^+ , Γ_3^+ , and Γ_5^+), and the top of the valence band is a state of Γ_3^+ symmetry. The bottom of the conduction band is Γ_1^+ , which is a 90% tin s-like state and is very similar to that for a free electron in spite of the overall ionic character of SnO_2 . Therefore the gap is $E(\Gamma_3^+ - \Gamma_1^+) = 3.6\text{eV}$ and its variation with respect to temperature is $1.2 \cdot 10^{-3} \text{ eV K}^{-1}$ between 300 and 1300 K.

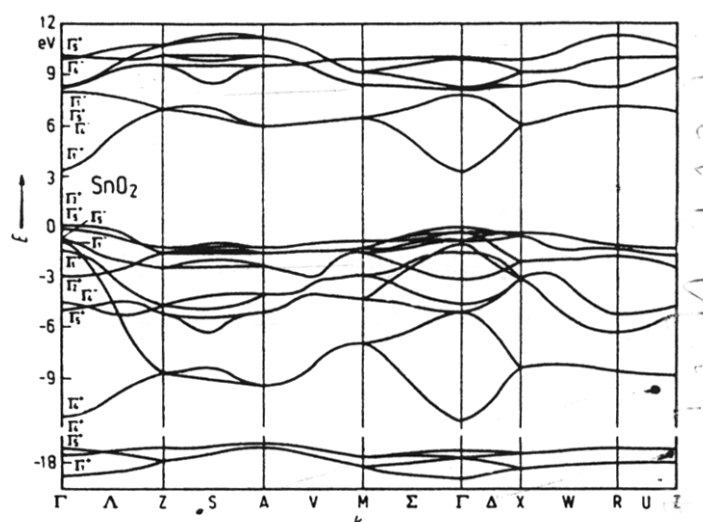


Fig. 1.5. *SnO₂ calculated band structure (see [28]).*

With respect to its chemical properties, tin oxide has a high chemical stability, as it is only attacked by hot concentrated alkalis, being this one of the reasons of the wide research done with this material.

1.2. Catalysts and gas sensors based on tin dioxide

Pure tin oxide is an n-type semiconductor due to the presence of oxygen vacancies, which electronically act as electron donors. In fact, surface sheet conductance measurements have shown how oxygen vacancies in (110) surfaces can increase the surface conductivity by more than two orders of magnitude with respect to the bulk conductivity [31]. In the same way, it is unambiguously agreed that the conductance change on exposure to gases arises mainly through a surface phenomenon on the SnO₂ grains.

Chemical sensing can be thought as composed of two parts [32]: the reception function, which recognises or identifies a chemical substance, and the transducer function, which traduces the chemical signal into an output signal. While the former is usually performed by the surface of each semiconductor particle, the whole microstructure of the active sensing element is involved in the latter.

In the framework of our chemical interest, this memory is more devoted to the former function and, more precisely, on the different factors affecting the electronic structure of the surface of the nanoparticles. The following sections are dedicated to describe it, finally giving a brief outline of the influence of the microstructure on the detection.

1.2.1. Reception function

1.2.1.1. Intrinsic behaviour of tin oxide

As has been commented above, tin oxide is an n-type semiconductor due to the existence of the native donor levels. These levels have energies of 0.03-0.034eV and 0.14-0.15eV below the conduction band edge, and are generally attributed to single and double

ionisation of oxygen vacancies [33,34], as unrelaxed vacancies are above, i.e., within the conduction band. The position of the Fermi level is fixed and would be between the conduction band edge and the intrinsic Fermi level position (that is very close to the mid of the band gap), because SnO₂ presents a negligible concentration of electronic band-gap states at their geometrically ideal surfaces.

Nevertheless, the above discussion is not valid for a polycrystalline material formed by crystallites, mainly due to two effects: the presence of grain boundaries and the own crystallite size. Thus, the areas of grain interphasing, i.e. grain boundaries, are formed by several layers of atoms displaced from their original positions, thereby allowing the coupling between the crystalline lattices of both crystals. The natural disorder of grain boundaries results in the modification of the local band structure of the material due to the appearance of interfacial energetic levels within the band gap. The origin of these levels is conditioning the behaviour as acceptor or donor levels. With respect to the influence of crystal size, it is mainly due to the fact that as grain size is reduced, the number of ideal surfaces (i.e., those with negligible band gap states) reduces as well and in the case of nanoparticles, these ideal surfaces do not exist, thereby increasing the number of unreconstructed surfaces, dangling bonds, and surface vacancies, that induce acceptor or donor levels at the grain surface.

The existence of surface or interface traps acting as acceptors or donors, each of them having a certain density of states and certain parameters of emission and capture, makes that in the thermodynamic equilibrium at each temperature, the Fermi level position is determined by this region. The charge trapped at grain boundaries or surfaces is compensated by opposite charged depletion regions surrounding them. However, a direct association between the created states, their activity, their location in the band gap and the type of defects from where they are caused can not be predicted a priori. Nevertheless, for an n-type semiconductor, in the case of grain boundaries the position of the Fermi level in the grain boundary has to be lower than the corresponding position in the bulk material just to generate the band bending of the surface.

Rigorous treatment of this situation starts with the one-dimensional Poisson's equation under depletion conditions:

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{dE}{dx} = -\frac{\rho(x)}{\varepsilon} \quad \text{Eq. 1}$$

where $\varphi(x)$ is the electrostatic potential at distance x from the surface/interface plane, ρ is the charge density at the same position and ε the dielectric constant of the semiconductor.

Then, if we consider that grain sizes are large enough to have neutral regions inside, the contour conditions $\varphi|_{x=0} = V_s$, and $\left. \frac{d\varphi}{dx} \right|_{x=W} = 0$, being V_s the barrier height and W the width of the space charge region. Under abrupt approximation the net charge density in the depletion region ($0 < x < W$) is $\rho(x) = eN_D$, being N_D the density of donor states in the bulk of the semiconductor, and by solving the Poisson's equation the width of the depletion region is given by:

$$W = \sqrt{\frac{2\varepsilon V_s}{eN_D}} \quad \text{Eq. 2}$$

and the charge per unit of area appearing in the depletion region will be given by:

$$Q_{SCR} = eN_D W = \sqrt{2\varepsilon e N_D V_s} \quad \text{Eq. 3}$$

By considering only the surface states (not considering the potential contact between two grains) and applying the charge neutrality,

$$\sqrt{2\varepsilon e N_D V_s} = Q_{ss} = e \int N_{ss}(E) f_{ss}(E, E_F) dE \quad \text{Eq. 4}$$

which gives a barrier height:

$$eV_s = \frac{Q_{ss}^2}{2\varepsilon N_D} = \frac{e^2}{2\varepsilon N_D} \left[\int N_{ss}(E) f_{ss}(E, E_F) dE \right]^2 \quad \text{Eq. 5}$$

where N_{ss} is the net surface density of charged states per energy unit and f_{ss} is the probability of occupancy of the boundary levels given by the Fermi-Dirac statistics.

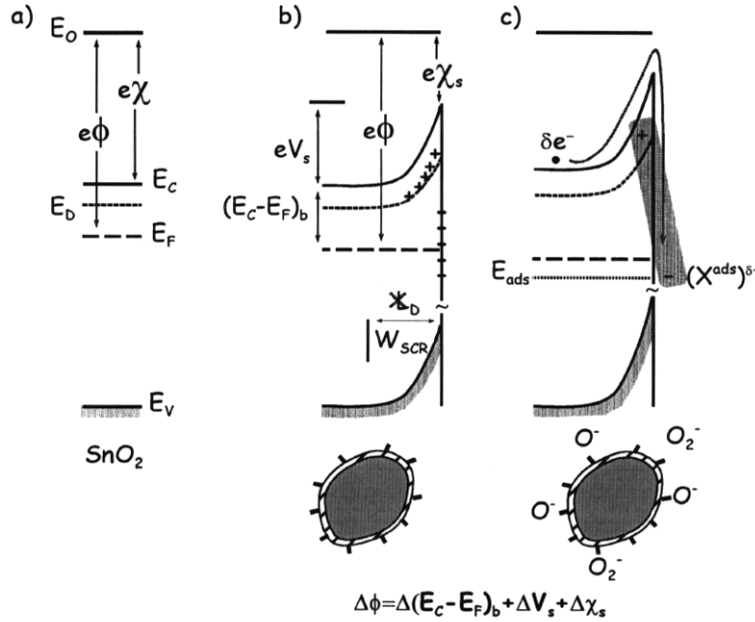


Fig. 1.6. a) Typical energy diagram of an n-type semiconductor like tin oxide. E_0 is the vacuum level, E_C and E_V the conduction and valence band edges, E_F the Fermi level position, E_D the position of the donor level, and ϕ and χ the work function and electron affinity, respectively; b) Modifications when the material is polycrystalline, when the existence of surface traps creates a depletion region and a potential barrier near the surface; c) Influence of the oxygen chemisorption, by the creation of dipoles between the chemisorbed charges and the uncompensated charges of the depletion region, that produce inter bandgap levels (After [35]).

In order to calculate the expression for the barrier height it is necessary to introduce some model for the distribution of interface/surface states, $N_{ss}(E)$. Thus, considering a density of states independent of the energetic position, $N_{ss}(E) = N_{ss}$, with $f_{ss}(E, E_F) = 0$ for $E > E_F$ and $f_{ss}(E, E_F) = 1$ for $E < E_F$, we have:

$$eV_s = \frac{e^2 N_{ss}^2 (E_F - E_V)^2}{2\epsilon N_D} \quad \text{Eq. 6}$$

Instead, if we consider a density of states localised in E , $N_{ss}(E) = N_{ss} \delta(E - E_{ss})$, $f_{ss}(E) = \left[\exp\left(\frac{E - E_F}{kT}\right) + 1 \right]^{-1}$, we have:

$$eV_s = \frac{e^2 N_{ss}^2}{2\epsilon N_D} \left[\frac{1}{1 + \exp\left(\frac{E_{ss} - E_F}{kT}\right)} \right]^2 \quad \text{Eq. 7}$$

that, for a state well below the Fermi level (it is considered that only one effective and totally filled state exists), gives the well known Schottky equation for planar geometry,

$$eV_s = \frac{e^2 N_{ss}^2}{2\epsilon N_D} \quad \text{Eq. 8}$$

This theoretical treatment can be intuitively seen in figs.1.6. and 1.7., that show how from Poisson's equation, it is deduced that the charge in the depletion regions causes curvature of the energy bands, leading to potential barriers (doubly Schottky barrier at an interface), which prevent the movement of any remaining majority free carriers from one grain to another.

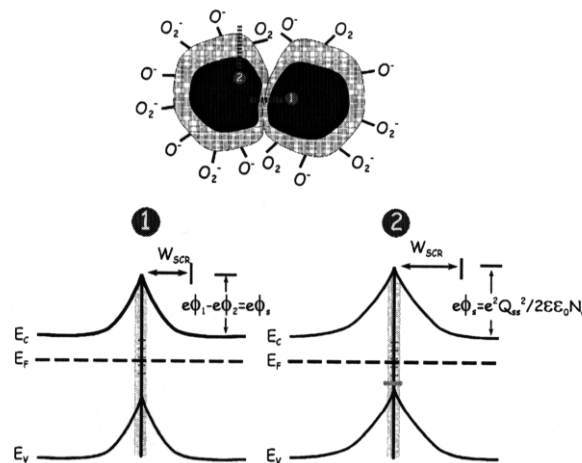


Fig. 1.7. Surface or interface traps create a potential barrier and a depletion region. Under gas adsorption, as grain boundaries are less exposed, barrier height should be different at grain boundaries and at surfaces, as shown in this figure (see [35]).

The explained scheme should be the initial step to begin the analysis of the gas sensing mechanism in SnO₂. Nevertheless, the situation is normally skipped because:

- i) the large quantity of unknowns and uncertainty of parameters,
- ii) this situation would be only important for very small grains, where the density of interface traps is not negligible because of the existence of non-perfect surfaces, and
- iii) except for the case in which the Fermi level is pinned by a large density of surface states of any type, the more realistic situation is when the surface of the grains is covered by oxygen ions that dominate the height of potential barriers, and hence, the conduction of electrons from grain to grain.

1.2.1.2. Effect of the presence of gases in contact with the tin oxide surface

If one does not consider the kinetics of the reactions taking place at the surface of the semiconductor particles, the general picture when SnO₂ is in a certain atmosphere is the same as above.

Thus, when SnO₂ is exposed to an atmosphere at moderate temperatures, two things can occur, namely, gas adsorption due to the high reactivity of the SnO₂ surface or reaction of interaction of the gas molecules with the molecules chemisorbed at the SnO₂ surface. Gas adsorption, understood as a direct chemical interaction between the gas molecules and the semiconductor surface is accompanied by charge exchange. Such interchange is interpreted from the electronic point of view as the creation of an inter-band-gap level whose occupation probability is given by the Fermi-Dirac distribution function when equilibrium is achieved. Its behaviour as acceptor or donor will depend on the type of molecule adsorbed. Thus, gases that capture electrons from the bulk of SnO₂ when they are adsorbed create acceptor levels, while gases that give electrons to the SnO₂ through the creation of an oxygen vacancy introduce donor levels. On the other hand, reaction of molecules in the gas phase with those existing already on the semiconductor surface is interpreted as the annihilation of the previously created forbidden band-gap states.

Nevertheless in most cases there is not a direct relationship between the presence of a certain gas in the ambient and the type of level created or annihilated because some intermediate reactions can occur [36]. Moreover, for a single gas molecule impinging on a modified oxide sensing surface, whether the molecule is “detected” or not depends on whether its interaction with the active sensor element is sufficiently strong and of significant duration, and it is through a statistically large number of such local events, on the atomic and molecular scale, that a collective response (macroscopic signal) is produced.

There are two types of adsorption: physisorption and chemisorption, depending on the strength of the binding. Physisorption is considered when the energy of the bond is of the order of 0.01-0.1eV, while chemical adsorption is considered when the adsorbed molecules are bound to the semiconductor with bonding energy as large as 1eV. Such difference is due to the underlying adsorptive forces, as physisorption is caused by dispersion forces, forces of electrostatic nature and electrical image forces, whereas chemisorption is based on the stronger covalent forces (overlapping between the adsorbate and adsorbent wave functions) and, hence, is connected with a partial electron transfer between adsorbent and adsorbate [37].

Thus, it is only after chemisorption that the charge displacement occurs between the gas and the semiconductor surface and, as it has been explained, this interchange of charge gives rise to a band bending in the surface region (equation 5), to a change of the surface conductivity and to a change in the electron affinity $\Delta\chi$, due to the creation of dipoles at the surface [38], i.e., to a total work function change given by (Fig. 1.6):

$$\Delta\Phi = -\Delta(eV_s) + \Delta\chi + \Delta(E_C - E_F)_{bulk} \quad \text{Eq. 9}$$

Chemisorption may also produce changes in the surface mobility, as ionosorbed molecules play an important role in electronic conduction as charged scattering centres at the surface [39].

Once the surface of the semiconductor is occupied by adsorbed molecules, new molecules trying to adsorb experience a new environment in such a way that the amount of total ions adsorbed is limited to a coverage of $\sim 10^{-2}$ - 10^{-3} monolayers for electrostatic reasons (Weisz limitation) [40]. For example, in the case of oxygen chemisorption, the positive charge appearing in the semiconductor surface as a consequence of adsorption causes a band bending of up to about 1eV and a thickness of the depletion layer of about 1 to 10 μm [36]. With growing surface density of chemisorbed oxygen, the band bending of the depletion layer increases, shifting the level of surface acceptors above the Fermi level, thus limiting the adsorption of new arriving oxygen molecules. This limitation could be overcome if acceptor levels are introduced by other gases but, because of the existence of interface traps, the Fermi level can be pinned, making the material insensitive to the adsorption of certain ions.

Thus, if the coverage of the surface of the semiconductor by chemisorbed species is θ , then the barrier height is related to the square of the surface charge $(N_{ss}\theta)^2$ through the Schottky relation (Eq. 8). In general, the coverage will be determined by the gas pressure P and there will be additional charges (Q_0) as a consequence of filled states resulting from traps at the surface/interface:

$$eV_s = \frac{e^2(Q_0 + N_{ss}\theta(P))^2}{2\varepsilon N_D} \quad \text{Eq. 10}$$

The conductivity in the surface region is then given by:

$$\sigma = \sigma_n + \sigma_p = e\mu_n n_{bulk} e^{-eV_s/kT} + e\mu_p p_{bulk} e^{eV_s/kT} \quad \text{Eq. 11}$$

Although holes can be neglected in the bulk conductivity, their contribution to surface conductivity when a high density of negative ions are absorbed may not be negligible, as with the increase of the height of the surface barrier, the hole contribution increases as well, while the electron term decreases [41]. Such conditions can occur in an oxygen or other oxidising gas rich ambient or with low concentration of reducing gases.

In most cases, however, the hole contribution is negligible. If, in addition, the grains forming the polycrystalline SnO_2 are large enough to consider that they are formed by a surface depletion region and a neutral interior one, conductance can be considered dependent only on the surface conductivity of electrons, and may be described by [42]:

$$G = G_0 e^{-eV_s/kT} \quad \text{Eq.12}$$

where G_0 is a factor which includes the bulk intragranular conductance and geometrical effects. Under real atmospheric conditions barrier height depends on the temperature and partial pressure of oxygen and reducing gases, $eV_s = eV_s(T, p_{O_2}, p_R)$ [43], as indicated in eq. 10. In this way, it is usual to find in the literature dependencies of the conductivity on the partial pressure of gases, mainly of oxygen. By using the charge transfer model Clifford proposed a theoretical model [44], connecting the partial pressure P_x of the gas phase with the concentration of physisorbed species X_{phys} and applying the mass-action law to the catalytic surface reaction,



succeeding in describing from a uniform point of view the numerous power laws for the conductivity which are experimentally observed:

$$\sigma \propto A e^{-E_A/kT} P_x^{-1/m} \quad \text{Eq. 14}$$

where E_A is the activation energy which represents the sensitivity of the electrical conductivity to the temperature changes and $1/m$ represents the sensitivity of the conductivity to the changes in the partial pressure of the gas x [45].

1.2.1.3. Temperature effects on SnO₂

Temperature has pronounced effects on the sensitivity of SnO₂ gas sensors, as it influences the physical properties of semiconductors (change of the free carrier concentration, Debye length,...), but also because every reaction taking place at the surface of the semiconductor, as well as the most probable species adsorbed and, hence, the reaction sites, are temperature dependent. So, temperature specially affects those properties related to the processes occurring at the surface of the sensor. For example, adsorption and desorption processes are temperature activated processes, as well as surface coverage by molecular and ionic species, chemical decomposition, reactive sites, ... In this way, dynamic properties of the sensors such as response and recovery time and the static characteristics of the sensor depend on the temperature of operation [46], and a temperature for which the sensitivity of a Semiconductor Gas Sensor (SGS) is maximum is always observed.

As has been discussed, because of the natural non-stoichiometry of SnO₂, it presents an n-type character. Therefore the species who tend to trap electrons from the semiconductor are those who are easily adsorbed. This implies that, under usual operating conditions (understood as an ambient such as synthetic air (79% N₂ + 21% O₂), in which some small quantity of other gas is introduced and certain humidity conditions), the surface of SnO₂ is mainly covered by oxygen and water species. So, the oxygen available as well as the different species resulting from water are crucial for the understanding of the operating behaviour.

Thus, adsorbed oxygen species transform at the surface of an oxide according to the general scheme $O_{2\text{ ads}} \rightarrow (O_{2\text{ ads}})^{\cdot-} \rightarrow (O_{\text{ads}})^{\cdot-} \rightarrow (O_{\text{lattice}})^{2-}$, in which they are gradually becoming richer in electrons. At room temperature all the forms are adsorbed, being the coverage of the species at the surface restricted by Weisz limit [40]. In fact, at room temperature, the equilibrium of the $(O_{2\text{ ads}})^{\cdot-}$ coverage with gaseous O_2 is approached slowly. With increasing temperature $(O_{2\text{ ads}})^{\cdot-}$ converts to $2(O_{\text{ads}})^{\cdot-}$ by taking one electron from the bulk, thereby causing (at constant oxygen coverage) an increase of surface charge density with corresponding variations of band bending and surface conductivity. According to Yamazoe et al. [47], oxygen desorbs with a maximum temperature of desorption as physisorbed O_2 at 80 °C, as $O_2^{\cdot-}$ at 150 °C and $O^{\cdot-}$ or O^{2-} at 520 °C, while at temperatures higher than 600 °C the thermal reduction of the SnO_2 occurs and lattice oxygen is desorbed. Thus, $(O_{\text{ads}})^{\cdot-}$, which is a very reactive specie, is the dominant specie in the case of tin oxide for temperatures between 423 and 933 K, while the O^{2-} species are highly unstable and do not play much role in determining the sensitivity. In fact, this is the least stable form of oxygen in the gas phase, and becomes stabilised only in the crystal lattice by the electric field created by its neighbouring actions, i.e., by the Madelung potential of the lattice. The net effect of surface states (coming either from adsorption of oxygen molecules or from crystal structure defects) is, when a high concentration of surface states is present, a pinning of the Fermi level within the bandgap.

However, a gaseous species, which apparently has nothing to do with such a redox process, can also affect the electric resistance, as typically exemplified by the case of water vapour adsorption because of the dissociative adsorption of water.

Water can be adsorbed in two states: molecular water, H_2O (physisorption), and hydroxyl groups, $\text{OH}^{\cdot-}$ (chemisorption). Adsorption of water vapour always produces a large increase in electronic conductivity in SnO_2 . This is because the chemisorbed hydroxyl groups are bound to tin atoms and the remaining hydrogen ions reduce the oxygen atoms, creating donors for tin dioxide. Thus, analysis of results of research [48-50], which studied the ceramic tin oxide behaviour in humid atmosphere, has shown that the basic processes responsible for the observed alterations of conductivity with temperature are the transition $O_2 \rightarrow O^{\cdot-}$ ($T > 150$ °C), $O_2^{\cdot-}$ desorption ($T > 150$ °C), water loss ($T = 280$ - 440 °C) and $O^{\cdot-}$ desorption ($T > 520$ °C) from SnO_2 . The specifics of such conductivity vs. temperature behaviour may be explained taking into account that the desorption of water in molecular form is at $T = 20$ - 100 °C (with a maximum at 110 °C, and not complete desorption until 150 °C), dissociative chemisorption of H_2O is at $T > 160$ °C and desorption of $\text{OH}^{\cdot-}$ groups begins at 250 °C but not entirely finishes until evacuation at 500 °C [47], with a maximum at 400 °C. Nevertheless, the mechanism of water is still under investigation.

Thus, there are different possible temperature-dependent elementary steps of molecular recognition with semiconductor gas sensors that have to be optimised for the specific detection of a certain molecule. These steps firstly involve the low-temperature surface reactions. Examples are adsorption and catalytic reactions at active sites (the latter involving intrinsic point defects, such as oxygen vacancies, and/or extrinsic point defects, e.g., segregated metal atoms) and similar reactions at grain boundaries or at three-phase boundaries (e.g., at metallic contacts or at surface metallic clusters). All of these reactions involve adsorbed negatively charged molecular ($O_2^{\cdot-}$) or atomic ($O^{\cdot-}$) oxygen species as well as hydroxyl groups ($\text{OH}^{\cdot-}$) at different surface sites. These steps secondly involve the high-temperature bulk reactions between point defects in the SnO_2 crystal and oxygen (O_2) in

the gas phase. The key for the controlled operation of such sensors is the careful adjustment of the operation temperature, since conduction changes upon exposure to different gas components usually show different maxima as a function of temperature. The necessary reversibility of the sensor response under steady-state or constant-flow conditions requires that all of the involved reactions are thermodynamically or kinetically controlled. For low-temperature sensor operation, the surface concentration of adsorption or reaction complexes must be unequivocally given by the temperature and the partial pressures in the gas phase. For high-temperature operation this requires that the bulk defect equilibrium adjust the concentration of doubly charged oxygen vacancies in the oxygen sublattice of tin dioxide and the segregation distribution of dopants at the surface and interfaces. Many of these reactions lead to a change of the electron concentration and hence to a change of the partial electronic conductances at the surface, in the bulk, at contacts or at grain boundaries.

So, it is clear that when a gas is introduced in the ambient atmosphere, its reactivity will depend on the species adsorbed and the state of the surface is evidently gas dependent. In general, most target gases are detected via the influence that they have on the oxygen stoichiometry of the surface. In this way, CO for example can reduce the surface of SnO₂ taking oxygen chemisorbed and, thus, giving electrons to the bulk of the semiconductor, decreasing barrier height and increasing surface conductance. In this case CO₂, the reaction product, leaves the surface and returns to the gas phase, and the CO chemisorption is the rate-limiting step. On the other hand, reactions between the surface oxygen ions and hydrocarbons or hydrogen generally produce water vapour as one of the reaction products, thus changing completely the surface of the semiconductor and taking active part in the chemisorption processes [51].

It is evident that gas detection with SGS can not be completely explained by only taking into account the charge transfer occurring at the surface of the semiconductor. Charge transfer only explains the situation in equilibrium and surface reactions have to be considered for a detailed understanding of the response to different gases. Indeed, it has been demonstrated that in porous sensors besides reactivity, diffusivity of gases or more precisely, difference in diffusivity between a target and oxygen gas, is an important factor determining the sensitivity of the sensor [52]. This makes the sensing properties of SGS (especially thick films) to be dependent on the molecular size of the sensed gases and of temperature, as all diffusion mechanisms are highly temperature dependent.

1.2.1.4. Influence of the introduction of additives

In order to modify or control the surface properties of the SnO₂, introduction of noble metal additives is usually performed. The most important effects of noble metal addition are the increase of the maximum sensitivity and the rate of response, as well as the lowering of the temperature of maximum sensitivity [32, 69-71]. All these effects arise as a consequence of the promoting catalytic activity when loading with noble metals. A great amount of additives have been studied (see some examples in table 1), being Pd and Pt the most used.

| Additives | Gases |
|--------------------------------------|--|
| CaO | Odour [53] |
| CeO ₂ | Methane [54] |
| La ₂ O ₃ | CO ₂ [55] |
| Pd | CO, CH ₄ [56,57] |
| Pt | CO [57,58] |
| ThO ₂ | CO, trimethylamine [59] |
| Metals of the III group (Ga, Al, In) | Nitrogen oxides [60] |
| Bi ₂ O ₃ | CO [61] |
| Os | CH ₄ [62] |
| Cd | EtOH, H ₂ [63] |
| Rh | Acetaldehyde [64] |
| Au | CO [65] |
| Ag | H ₂ , H ₂ S, propane [66-68] |

Table 1. Summary of some reported additives for tin oxide and the gases to which they present good sensitivity.

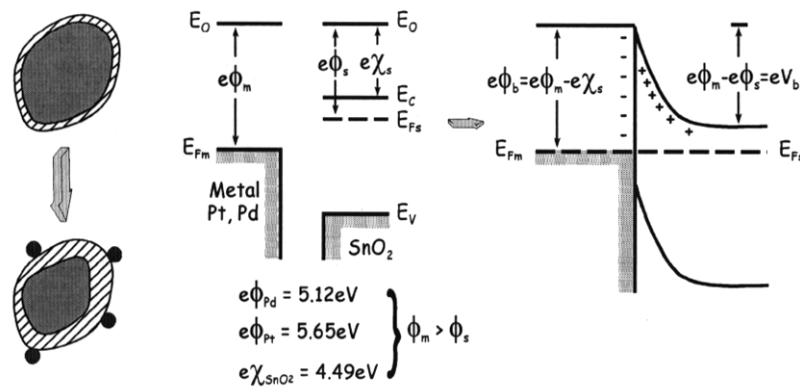


Fig. 1.8. Effects of noble metal introduction. It is observed that, after contact of the semiconductor and the metal, a Schottky barrier appears as a consequence of the different work functions (After [35]).

Thus, in general, under noble metal loading it is expected that it forms clusters at the surface of SnO₂, such as those observed in the case of Pt [72,73] and in the case of Pd [74,75]. Depending on the noble metal deposited, the loading and the interacting gas, these clusters will be in metallic or oxidised forms. In any case, the contact of the additive with the semiconducting oxide creates a barrier that is fully characterised by the electron affinity of the semiconductor, the work function of the metal and the density of surface states of the semiconductor that are located inside the energy band gap (fig. 1.8). All of these three contributions create a Schottky barrier through the formation of a depletion region in the semiconductor surface in contact with the cluster. Eventually, the surface states created by the presence of the additive can pin the Fermi level of the semiconductor to that of the additive.

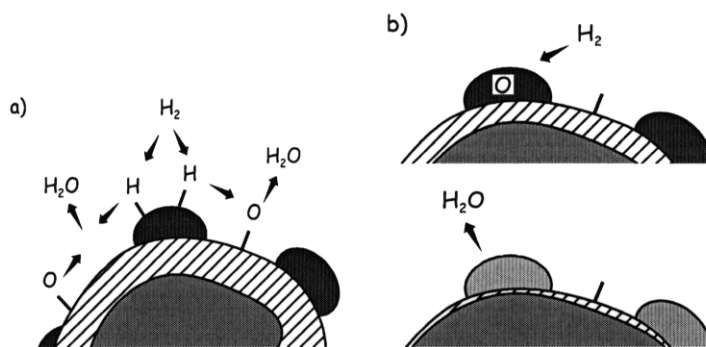


Fig. 1.9. Scheme of: (a) Chemical sensitisation mechanism; (b) Electronic sensitisation mechanism (see [35]).

Two mechanisms have been proposed to explain the observed results of the influence of additives on tin oxide [32,76] (fig. 1.9):

- i) **Chemical sensitisation:** According to it, the action of the additive is in general two-fold [77]: a) the metallic cluster presents a higher sticking coefficient to gases than the semiconductor and b) on the cluster, nearly all the gas molecules are dissociated, being the dissociation products spilt over the semiconductor support. Thus, it generally consists in the adsorption on the catalyst followed by diffusion from the catalyst to the support. Because the activation energy for desorption is much higher than for diffusion, the support can act as source of reactant supply, although the opposite case or both can also occur. Moreover, normally the support is assumed to be catalytically inactive, but not always.

It is evident why selectivity and lowering of the operation temperature are obtained by this mechanism. In the case of, for example, H₂, oxides are not very active for hydrogen activation, but the gas is activated by the deposited metal and the activated fragments (H) migrate to the semiconductor surface by spill-over mechanism, thereby reacting with the adsorbed oxygen. In this way, reactions that occur on the oxide surface and need hydrogen can proceed at lower temperatures, and are favoured over reactions that do not consume hydrogen. This type of mechanism occurs for example in Pt-loaded tin oxide, where Pt is known to remain in metallic form under most reaction conditions.

- ii) **Electronic sensitisation:** In this, there is an electronic interaction between the added particles and the semiconductor through the space charge created in the semiconductor by the presence of the surface clusters. Additives at the surface of the semiconductor act as receptors while the semiconductor acts as a transducer of the changes taking place at the surface under gas adsorption. This type of sensitisation has so far been observed in SnO₂ elements impregnated with Ag, Pd and Cu, which form stable metal oxides when exposed to air. The electronic interactions actually appear between the metal oxides and SnO₂ and disappear when the oxides are converted to metals (Ag and Pd) or a sulphide (CuS). Thus, the oxidation state of the particles changes in contact with a gas, inducing the corresponding change in the electronic state of the semiconductor.

The evolution of the chemical state of the additive would depend, in any case, of the present gases, which can infer a dynamic behaviour to the catalyst. As example it can

be considered the dissociative adsorption of CH₄ on Pd supported catalysts. While methane is known to adsorb dissociatively on supported and unsupported Pd metal [78], it does not adsorb on oxygen-covered Pd [79]. Indeed, it seems that the dissociative adsorption of CH₄ on Pd is progressively inhibited by the presence of adsorbed oxygen [80], the sticking coefficient for dissociative adsorption decreasing linearly with increasing oxygen coverage. Nevertheless, Pd is an additive widely used for CH₄ detection.

With Pd and Pt on tin oxide, one of the possible explanations for the process with respect to CO is as follows: (i) At low temperatures ($T < 100$ °C) the rate of CO and oxygen adsorption is high, and the room temperature is enough for the activation of the CO oxidation on the metal additive surface, leading to an electronic exchange between the additive and tin oxide matrix. The sample response, the magnitude and the growth rate of the conductivity under CO are maximum and the response time is minimum. (ii) By increasing the temperature, the desorption rate increases, and the superficial migration of the oxygen and the reactants at the tin oxide surface becomes possible, corresponding to a chemical sensitisation by spillover effect. The response time grows and the conductivity curve does not reach the saturation value during a cycle under CO. (iii) By increasing the temperature further, the oxidation of CO becomes possible on all the surface of tin oxide. The area of the working surface increases and, as well as in the case of low temperatures, the saturation value is quickly reached. Owing to the prevalence of desorption processes over adsorption ones, the quantity of adsorbed CO in this temperature range is smaller, leading to a diminution of the conductance. In the case of Pd (i) is predominant, while in the case of Pt is (ii).

In spite that the above mechanisms are the most accepted ones to explain most of the investigations, some authors propose other mechanisms to explain their results. Thus, for example, it has been claimed that under certain conditions for the distribution and size of the metallic clusters, tunnelling occurs between the discrete islands [81], dominating the normally considered thermoionic emission carrier transport. Other authors consider that, in some cases, the effect that the depletion region created by the presence of additives at the surface of the semiconductor has on decreasing the effective grain size is more relevant [82]. Finally, it has also claimed that improved response to gas with noble metal loading can arise mainly through the interaction of the gas molecules with the electron states introduced near the valence band edge by the additive, i.e., via the control of the population of such states and the consequent change of the band bending [83].

Probably, all the above mechanisms are present at the same time and several factors determine their activity, thereby establishing which mechanism may be dominant in each case. Thus, in general, for a given additive, its distribution through the support and loading will have important effects on the device response in addition to that arising from the nature of the catalytic material itself [83,84]. Indeed, it has been observed that the maximum gas sensitivity depends, for a given metal additive, even on the loading method (fixation, impregnation, metal evaporation,...) [85] and that the general response is influenced not only by the chemical state of the catalyst but also by its crystalline structure [86,87]. On the other hand, the temperature of operation of the sensor can also determine the real function of the additive as, for example, spill- over can only occur at certain temperatures, which may depend on the gas.

1.2.2. Sensor design of semiconductor gas sensors

The first step in sensor design is evidently to select the active material, sensor configuration and the mode of operation. By sensor configuration one can understand thick, thin film, geometry of the sensor and shape and location of the heater and electrodes [88], as well as material for the heater and electrodes [89-91]. The mode of operation can be mainly DC or modulated (transient). The first is the usual method, while the second is used to take advantage of the rate of some reactions. The connection of the sensor in hybrid integrated circuits or in a sensor array is a part of the entire system design.

The improvement of SnO₂ gas sensor, as well as of any other SGS, passes in most cases through the optimisation of the material. Indeed, material properties have influence in almost all the properties of the sensor, including sensor sensitivity, stability, speed of response, etc. As sensing is a surface process, it is directly related to the surface properties. Therefore an important goal is to control the semiconductor surface, up to now done usually via the introduction of additives promoting some catalytic activity. In addition, additives can sometimes modify the temperature of maximum sensitivity, which is very important if lowers, mainly in increasing stability and selectivity. In fact, depending on temperature and partial pressures, sensors may be designed with their principle based upon physisorption, chemisorption, surface or bulk defect reactions [38].

1.2.2.1. Thin and thick film SGS

Being gas detection mainly a surface process, the first and probably most important characteristic of a SGS comes from the distinction between thin and thick film SGS. In general, a SnO₂ thin film is formed by finely dispersed particles of very small size very densely packed, forming a quasi-continuous layer. On the contrary, a thick SnO₂ film is composed of poorly bounded grains of variable sizes. It is evident that the last structure presents a higher effective surface area for gas adsorption and, hence, larger changes of resistance are expected under the adsorption of different gases. On the other hand, depending on the temperature, the degree of filling of the surface states of the semiconductor by the gas molecules and other characteristics of the system, the adsorbed molecules can leave back in the gas phase if overcome some potential barrier determined usually as the heat of adsorption [92]. Therefore, the larger is the effective surface area, the lesser will be the rate through which the steady state is obtained. As a first approximation and according to what is intuitively expected, this implies that thin film gas sensors will have a higher speed of response, because in thin films gas molecules are adsorbed only at the surface of the entire structure. Nevertheless, it is only true if gas does not try to penetrate into the film. In this case, an initial rapid response takes place, but the sensor does not reach a stable value of the resistance because of the difficulty of gas diffusion imposed by the structure of the film. On the other hand, in thick films, gas follows different percolation paths through the entire thickness of the film. As the injection of electrons from the surface crystallites to the conduction band can be fast, speed of response would be limited by the gas diffusion into the grain boundaries [93] and thus by thickness [94].

In general, although thick film gas sensors present a higher power consumption, they are more robust, less susceptible to contamination and more sensitive. Thick film technology offers important advantages such as high productivity and automation, the time required to pass from prototypes to products being very short. Although hybrid integrated

circuits can be done by using thick film technologies, current tendencies in commercial sensors are focussed in the increased of the integration of the sensors, using the maximum number of steps compatible with typical semiconductor processes and reduce power consumption. Both in most cases imply the use of thin film technologies.

In thick film technology, the fabrication of the sensor can be performed by the obtention of a SnO₂-based paste, which is painted or printed on a cylindrical or planar Al₂O₃ substrate, or by pressing and sintering pellets. Thin film technology uses techniques such as sputtering or electron beam evaporation to deposit a thin and polycrystalline film of SnO₂ onto an electrically and thermally insulating substrate. In the case of thin films a different densification of the film can be obtained by using different deposition techniques, whilst thick films are always porous bodies or layers.

1.2.2.2. Microstructure of the film and grain size effects

Important factors in the transduction process include the microstructure of the sensing surface, the chemical interactions occurring on the surface and the operating temperature. The microstructure of a sensor material is important for two reasons: First, microstructure affects the distribution of adsorption sites. Second, microstructure will affect electrical transport properties.

If it is possible to decrease the crystallite size of tin dioxide particles to a sufficiently small value, the gas sensitivity would be increased, as it was observed that the gas sensitivity of tin dioxide-based elements was inversely proportional to the crystallite size, behaviour that can be extended to other materials. Moreover, since tin dioxide sensors are usually operated at temperatures above 200 °C in the presence of oxygen, their long-term stability requires thermodynamically or kinetically stabilized interface structures.

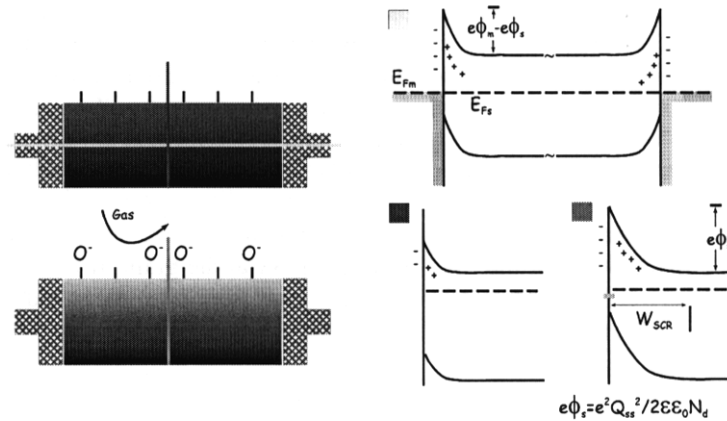


Fig. 1.10. Gas detection in a densely packed thin film. The energy band diagram both in the absence of gases and in an oxygen rich atmosphere is represented (see [35]).

In a densely packed thin film (fig. 1.10), under gas adsorption a depletion region near the surface appears. In this case the behaviour of the conductance is that of a bulk trap limited conductance in a layer of variable width (film thickness-width of the SCR), in which the activation energy for conductance would be the donor energy E_D [95]. Depending on the coverage by chemisorbed species and film thickness, the whole film can be depleted of electrons. In this case, conductance is surface trap limited, i.e., the conductance is determined by the equilibrium between conduction band states and surface

states. The activation energy for the conductance would be the surface state energy E_S [95]. In this case, conductance is directly affected by surface reactions.

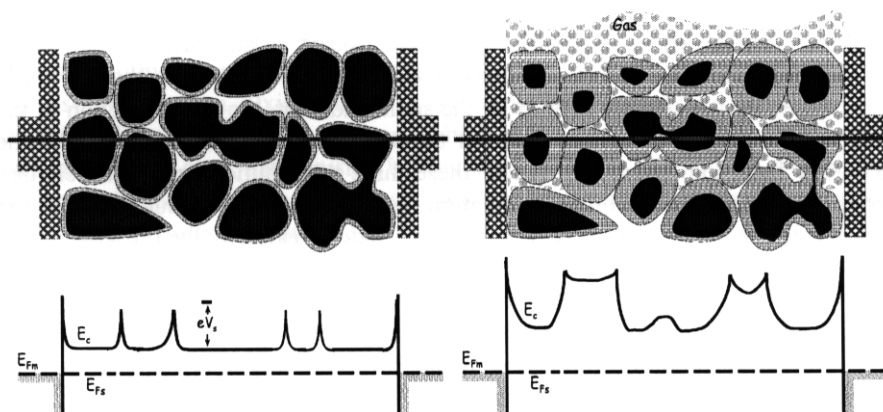


Fig. 1.11. General scheme of a porous sensor containing both grain boundaries and necks in the absence of gases (left) or in the presence of oxygen (right) (After [35]).

The case of a porous body (thick film) is qualitatively different (fig. 1.11). The porous body is formed by low-resistance paths through the bulk of the crystallites, alternating with higher resistance constrictions at the points of contact. Several cases may be considered depending on the microstructure of the film [95], being film formed by grains interconnected by grain boundaries the typical situation described in thick films. In it, the bulk of each grain can be considered neutral such that an ohmic behaviour is expected. At grain boundaries charge is trapped from the ambient and depletion regions develop. The conductivity would be limited by charge transport across Schottky barriers by thermoionic emission, or less usually, by tunnelling. The activation energy for conductance would be the barrier height and would be directly affected by the charge and fractional coverage of the surface species and, hence, a function of the composition of the gaseous atmosphere, because barrier height is determined by the square of the surface charge (eq. 5 and 10).

Resulting from the different grain size and shape of the particles forming the porous film and from the different number of neighbouring particles in contact with a certain particle (coordination number), one expects that the measured conductance is determined by a network of barriers differing in their height [96-99], i.e., the conductance is generally affected by the percolation mechanism, which depends on the barrier-height distribution and on the average coordination number of the network.

Thus, it seems that the limiting step controlling the overall mobility has to be sought at the grain boundaries. The tunnelling of the potential barrier is the main responsible process for the transport mechanism at the grain boundaries.

It is important to note that, for very small particles, grain boundary traps can themselves give rise to a completely depleted grain. In this case the boundary conditions applied to solve the Poisson's equation are no longer valid, because there is not any neutral region in the grain and thus, conductance is not dependent upon barrier height but on excitation from grain boundary traps. In the limit, for very small particles, the solution of the Poisson's equation with the adequate boundary conditions would result in a flat band

condition at which conductivity is determined by the difference between the conduction band edge and the Fermi level position [100]:

$$\sigma = \sigma_0 e^{-[E_c - E_F]_{\text{bulk}}/kT} \quad \text{Eq. 15}$$

The flat band condition occurs when nanoparticle size is lower than $2W_{\text{SCR}}$, where W_{SCR} is the width of the space charge region in the grain.

The other situation in thick films, less common, is when the film is formed by grains interconnected by necks: in this case, surface states corresponding to the gas species adsorbed cause a depletion zone extending to a certain depth. The conductivity would be largely that of the undepleted layer in the centre of the neck and would be determined by activation of electrons from donor states in the bulk (bulk-trap limited regime with activation energy E_D), and would be affected by the gaseous atmosphere through changes in the effective channel width only. In this case, electrons will move through a channel formed inside each neck from grain to grain. If the neck is closed, the depletion zones from the two surfaces overlap, leaving a higher-resistance ohmic path through the centre. In this case the conductance would be determined by activation of electrons from surface states into the conduction band (surface-trap-limited regime with activation energy E_S), and would be directly affected by the influence of the gaseous atmosphere on the occupancy of the surface states. In fact, the closed-neck structure has an activation energy related directly to the surface states and, hence, dependent, for example, on the main species of oxygen chemisorbed. The controlling mechanisms (open or closed neck) would be determined by the microstructure of the film as well as for the gas concentration. The change as a consequence of gas adsorption from an open neck configuration to a closed neck one would give rise to a pronounced effect on conductivity and, thus, to the best microstructure to measure sensitivity.

Several authors [32,101-104] have reported the existence of two regions of sensitivity depending on grain size. It has been shown that for large grain sizes, where conductivity is dominated by grain boundary contacts, sensitivity is practically independent of grain size. On the other hand, for very small sizes, where mainly necks control conductivity, sensitivity is strongly dependent of nanoparticle size. In this region sensitivity increases with the decrease of the grain size. This effect is usually attributed to the high dependence of electron transport at any place inside the particle under a surface effect such as gas adsorption. The depletion of electrons by gas adsorption makes to pinch-off the individual grains and produces a considerable increment of resistance. Nevertheless, due to the dispersion of sizes of the nanoparticles forming the sensor, this pinch-off does not occur in all the particles simultaneously and this is why sensitivity changes rapidly but not suddenly.

1.2.2.3. Techniques for the synthesis of tin oxide

As has been previously discussed, both the technique used for the preparation of tin oxide and the way that the catalysts are added are crucial for the sensing behaviour of the material. Thus, in this section we will give a brief description of the some techniques for the preparation of tin oxide, that determine whether it is obtained as powder, thin or thick film, the grain size, ... and, in the next section, some ways of catalyst addition will be

described. As we are not exhaustive, a reader interested in more details is referred to some reviews on gas sensors [105-108].

→ **Sol-gel [109,110]:** It usually consists on the precipitation of tin hydroxide from an aqueous solution where a high pH is reached by the addition of some compound, usually ammonia. Afterwards, an annealing process is used to obtain tin oxide.

→ **CVD and spray pyrolysis [111-114]:** These techniques are suitable for the direct preparation of films, and not powders as in sol-gel. They basically consist on the spraying of a solution of tin(IV), usually as chloride, on a suitable substrate. The spraying process is usually done in an air atmosphere and the substrate is heated in order to form the tin (IV) oxide film.

→ **Sputtering [115-117]:** It basically consists on the formation of a tin (IV) oxide film by the sputtering of a heated substrate from a evaporated metallic tin or tin (IV) oxide target in a controlled oxygen atmosphere. The temperature of the substrate (100-150 °C) is usually not as high as in CVD (400-500 °C).

→ **Rheotaxial Growth and Thermal Oxidation (RGTO) [118,119]:** This technique is a two-step process in which the first step consists on the evaporation of metallic Sn onto substrates heated above the melting temperature of Sn ($T_s \approx 290$ °C > $T_m = 232$ °C). In this situation, the evaporated Sn tends to cluster into small spherical droplets that do not touch each other. In a second step, the Sn droplets are oxidised by thermal annealing in air at temperatures of the order of 500-700 °C, thereby forming polycrystalline SnO₂ films.

→ **Pulsed laser deposition [120,121]:** The tin oxide film is formed by physical vapour deposition of tin oxide from tin oxide pellets that are focused with a pulsed laser in controlled atmosphere.

→ **Hydrothermal method [122]:** It consists on the immersion of a substrate in an aqueous solution of tin hydroxide at temperatures above 100 °C for several hours.

Temperature is another parameter that affects the crystallinity and size of nuclei. In film deposition techniques there is a minimum temperature of formation of tin dioxide and, in general, an increase of deposition temperature increases the crystallinity of the deposited film. But the study of defects becomes especially important in surface because different thermal treatments lead to different vacancy scenarios.

1.2.2.4. Techniques for the addition of catalysts

In the case of the techniques for the addition of catalysts, they define the dispersion of the additive, but also the chemical features that it has. Here, we will briefly describe the most used addition techniques, together with their most important features and a brief description of the electroless technique, that is the one used within this work.

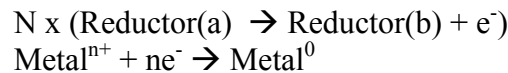
→ **CVD, spray pyrolysis and sputtering:** Described in the tin oxide synthesis, they are also used to add catalysts. Thus, in the case of CVD or spray pyrolysis, the additive is usually added either in the same tin solution used for the obtention of the tin oxide film (when homogeneous bulk doping is desired) or in a solution that is

sprayed after the tin oxide formation (for surface doping). In the case of sputtering, bulk doping with a constant dopant concentration may be achieved by using the corresponding targets. Surface doping is possible by subsequent evaporation of metals.

→ **Ion implantation [115,120,123]:** In it, the catalysts are added using a bombardment of high energy (100-200 keV) ions. This technique allows the control of the doping level throughout all the bulk of the substrate by just varying the bombardment energy. Nevertheless, this energy induces changes in the substrate (defects,...).

→ **Impregnation [57,124]** basically consists on the evaporation of an aqueous solution of the metal. The solution is stirred together with powders of the semiconductor oxide and it is usually evaporated to dryness, thereby precipitating the metal salt by supersaturation of the solution. Thus, without annealing, the oxidation state is that of the metal salt used as precursor.

→ **Electroless** is a technique introduced by Brenner and Riddell [125,126] that is based on a spontaneous electrochemical reaction. Thus, when a metal salt of the catalyst is mixed with a solution of a proper reductor, the metal is reduced from the oxidation state present in the salt, arriving to the metallic state if all the conditions have been optimised. The reduction of the metal is possible because the reductor is oxidized. The overall scheme is as follows:



This reaction can take place in an aqueous solution stirred together with powders of semiconductor oxide, and there is no need to heat the solution if the reductor is properly chosen. In this case, the catalyst is mainly in the metallic state when no annealing has been applied.

1.2.2.5. Definition of sensitivity in SGS

As has been discussed throughout this section, when SnO₂ gas sensors are in contact with gases, there is a change in the conductivity of the semiconductor. Whatever be the origin of such changes, they are monitored in a real sensor through changes in the resistance, which is used to define sensor sensitivity.

Sensitivity is defined by the resistance (or conductance) change when the sensor is exposed to a certain concentration *c* of gas as:

$$S = \frac{\partial R}{\partial c}$$

Nevertheless, the most used parameter is the gas sensor response, which is the resistance (or conductance) change when the sensor is exposed to a certain with respect to the resistance that the sensor presents in a reference gas, usually air or synthetic air. The most usually used expressions for an n-type gas sensitive material like SnO₂ are:

$$S = \frac{R_{air}}{R_{gas}}$$

for oxidising gases like NO₂, and:

$$S = \frac{R_{gas}}{R_{air}}$$

for reducing gases like CO. In this way sensitivity should be always larger than 1.

In general, it is observed that resistance changes rapidly with increasing concentration of a target gas in air and slowly after some certain concentration is present in the ambient. So, a small quantity of uncontrolled gas in the chamber or at the surface of the sensor can produce a large error in the measurement of gas response.

1.3. The use of electrochemistry in gas-sensing

When looking at the previous sections, it is obvious that gas-sensing is based on the exchange of majority carriers (electrons or holes) between the sensing material and the gas to be detected. Electrochemistry is the field of chemistry that studies the reactions in which electrical charges are exchanged, so its relationship with the field of gas sensing should be straightforward from this point of view.

Moreover, as has been previously discussed, the gas-sensing mechanism is at present not fully understood, mainly because of the great number of parameters involved in each case: parameters related to the base material (preparation, annealing,..), the additives (dispersion, chemical state,...) and the composition of the atmosphere in contact with the material. So, in order to fully understand the mechanism involved in gas sensing, all these parameters must be exactly controlled.

In SGS, semiconductors (as, for example, SnO₂) are the base materials used for gas-sensing. In this way, semiconductor electrochemistry must be a good tool to understand the gas-sensing mechanism, as it is a well-developed field. Thus, terms as “depletion”, “space charge layer”, and so on, that are used in the above discussion as the base for the understanding of the gas-sensing mechanism, are the same as those used in semiconductor electrochemistry. Thus, the reader are referred to some reviews [127-134] to have a deeper understanding of the electrochemistry of semiconductors and its relationship with gas sensors. In fact, several kinds of electrochemical gas sensors have been studied and there exist commercial electrochemical gas sensors [135-137]

It is with this last aim that an electrochemical section has been included in this work. In it, we have begun a study that has the aim to stablish the gas sensing mechanism and the influence of the different parameters in it. As few systematic works has been recently done in this field, the work has had to begin studying the electrochemical oxidation of tin in an inert deareated electrolyte. This study must be the starting point of a systematic study, as it allows us to understand the oxidation/reduction behaviour of tin and tin oxides, including tin dioxide and, as has been previously discussed, it is the charge transfer from or to the tin dioxide the basis of the gas-sensing mechanism.