

1. Introduction

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1. Introduction

Introduction

The purpose of this chapter is to present the general framework where this investigation is placed. Therefore, it will advance from general aspects of chemical sensors to the more specific details concerning gas sensors based on tungsten oxide.

This chapter is divided into four main parts. Firstly, a brief overview of chemical sensors is provided. It aims at giving a first vision of chemical sensing, as well as at classifying the different devices available at the moment. The second part will focus on gas sensors based on metal oxides. It contains a short overview of their main features as seen from a user, developer and basic scientist approach. This three-fold vision is necessary in order to make good progress in basic understanding of these devices and their applications to real world.

The third subsection examines WO_3 as a material for gas sensing applications. It will begin by highlighting the importance of this material among usual metal oxides utilised for gas detection. This is followed by a brief examination of some structural properties of tungsten oxide, with an emphasis on the crystalline structure, defects related to oxygen vacancies and surface configuration of the material. It finishes with a discussion about the detection of ammonia, hydrogen sulphide and nitrogen dioxide by WO_3 -based sensors. The importance of the detection of these gases is examined and recently published papers are briefly reviewed.

Finally, motivation and main targets of this investigation, as well as the organisation of this dissertation, are presented and argued.

1.1 Chemical sensors

According to Göpel and Schierbaum [1], 'Chemical sensors are devices which convert a chemical state into an electrical signal'. Although many authors have provided more general or specific definitions for this sort of sensors [2-6], this is probably the simplest one that best fits the purpose of this work. By 'chemical state', it must be understood different concentrations or partial pressures of molecules or ions in a gas, liquid or solid phase. If it is not specified, it is often assumed that these chemical sensors are just the primary link of the measuring chain, in other words, an interface between the chemical world and the electronics. There are two types more of small self-contained analytical systems: *Microinstruments* and *Micro-Total Analytical Systems (μ -TAS)* [7]. Microinstruments are based on molecular spectroscopy since they measure molecular properties by IR, UV, x-ray, TGA and many others. As to μ -TAS, they are small analytical systems that incorporate sampling, separation, mixing, transporting and all types of such analytical processes.

Some typical properties associated with chemical sensors, according to Stetter and Penrose [7] are:

- a sensitive layer is in chemical contact with the analyte
- a change in the chemistry of the sensitive layer (a reaction) is produced after the exposure to the analyte
- the sensitive layer is on a platform that allows transduction of the change to electric signals
- they are physically 'small'
- they operate in real time
- they do not necessarily measure a single or simple physical or chemical property
- they are typically less expensive and more convenient than an equivalent instrument for the same chemical measurements

As stated above, every chemical sensor is divided into two domains: the physical transducer and the chemical interface layer. At the chemical interface, the analyte interacts chemically with a surface, producing a change in physical/chemical properties. These changes are measured by the transducer domain, which monitors this change and generates a related electrical signal.

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One way to classify chemical sensors is by the transduction mechanism. As shown in [7], the different transduction principles and the magnitudes that can be measured are:

- Electrochemical: voltages, currents, impedance
- Mechanical: weight, size, shape
- Thermal: heat flow, heat content
- Magnetic: field strength, field detection
- Radiant: frequency, intensity

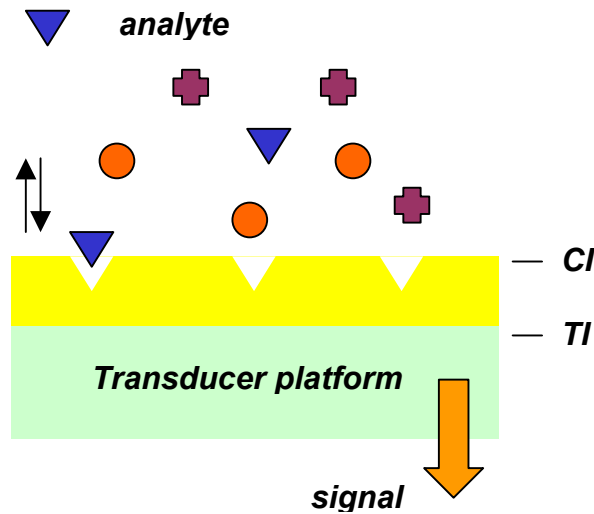


Fig. 1: Cross-section of a chemical sensor. CI indicates the chemical interface, whereas TI indicates the transducer interface (Adapted from [7]).

Besides, chemical sensors can also be arranged by the chemical reaction that occurs at the interface. This approach is very interesting since chemical parameters, such as the type of chemical reaction, equilibrium constant, kinetic parameters, will determine the sensor performance, including sensor sensitivity and selectivity.

Chemical reaction at the interface	Example
Adsorption	
Physisorption	$A[\text{gas}] + S[\text{surface site}] = AS[\text{surface}]; K_{\text{ads}}$
Chemisorption	$V_{\text{ads}} = Ae^{-dG/kT}$
Partitioning	$K = C_m / C_s$
Acid-base	$HA + KOH = H_2O + K^+ + A^-; K_a \text{ or } K_b$
Precipitation	$Ag^+[\text{aq}] + NaCl[\text{aq}] = AgCl[s] + Na^+[\text{aq}]; K_{\text{sp}}$
Ion exchange	$H^+[\text{aq}] + Na^+[\text{surface}] = H^+[\text{surface}] + Na^+[\text{aq}]; K_i$
Oxidation/reduction	$CO + 1/2O_2 = CO_2; K_{\text{rxn}}$

Table 1: Possible reactions at the chemical interface of chemical sensors (Adapted from [7]).

1.2 Properties of gas sensors based on metal oxides

Sensors using DC resistance of heated metal oxide semiconductors are members of the Electrochemical class of chemical sensors, subclass of impedance sensors. Gas sensors based on different metal oxides (SnO_2 , TiO_2 , In_2O_3 , WO_3) should be identified as different types within the 'class' of electrochemical-impedance sensors and are often called MOX sensors (from Metal Oxide sensors). In their simplest configuration, MOX sensors consist of a substrate with a heater, electrodes and a sensitive layer in contact with the electrodes.

According to Bârsan et al. [8], metal oxide sensors can be studied following three different approaches: user, developer and basic scientist.

1.2.1 User approach

There are some characteristics that make MOX sensors appealing for gas sensor users. Although highly debatable, some of them are [9]:

- Low cost, small size and easy to handle (compared to other gas sensors)
- Fast sensor response and recovery
- Robust construction and good mechanical strength
- Long operating life

On the other hand, they have some disadvantages that are still a matter of research (some of them being common to most of gas sensors):

- Poor selectivity
- Influence of humidity
- High power consumption (except micromachined-supported)

From the point of view of a user, the sensor response is usually based on the variation of the DC sensor resistance with gas pressure or concentration, although AC resistance or time-derivative of the resistance can be also measured. The typical empirical formula describing the variation of conductance (G) with partial pressure of the gas (p) for MOX sensors is [10]:

$$G = G_0 + A_1 p^\beta \quad (1)$$

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Many other empirical formulae have been proposed for the detection of certain gases, to avoid humidity interference or to compensate the drift of the sensor response [6,11-13].

1.2.2 Developer approach

Developers have optimised gas sensors either by trial and error or by a systematic research approach. The goal is to determine a parameter set so that optimised sensors can be manufactured and applied in practice for fulfilling certain tasks such as monitoring different substances in different environmental conditions [8]. Two of these parameters will be briefly described here: deposition-preparation of the sensitive layer and substrate characteristics.

The synthesis and deposition of the sensing layer is obviously the most crucial part in the preparation of gas sensors. Three main groups can be distinguished: powder/slurry deposition, chemical vapour deposition (CVD) and physical vapour deposition (PVD) [8,14] (Table 2). The main difference between powder/slurry based films and CVD or PVD has traditionally been attributed to their different film thickness. While the former lead to sensitive layers of several microns of thickness (thick films), the layer thickness of the latter varies between 20 and 1000 nm. Beyond this classification, there is a fundamental difference in the microstructure of these thick and thin films. Thin films are usually very 'compact' (not porous), so the interaction with gas is limited to the external surface of the sensitive layer. On the other hand, gas can penetrate through most of thick films and so the interaction can occur throughout the whole layer. This has led to some authors argue that thick film must be more sensitive than thin films [14], since the change of conductivity is not limited to the outermost zone of the sensitive layer but to the whole layer.

Nevertheless, this classification must be carefully taken. For instance, it is well known that spin-coating techniques, which are actually using a slurry, are able to obtain 'thin films' in the sense of thickness (and the slurry can be obtained by a sol-gel process, for instance), being actually 'thick films' in terms of porosity [15]. As regards screen-printing, it must be understood that this technique is a two-step process: firstly the powder is obtained (by sol-gel, precipitation or any other method) and then a slurry based on this powder is screen printed. A more complete description of the application of these techniques to MOX sensors can be found in [16].

Regarding substrates, thick films have been typically deposited on alumina substrates provided with electrodes (usually interdigitated) and a heater. Thin films are of course deposited on flatter surfaces, i.e. silicon, what allows the use of micromachined gas sensors. However, the compatibility between powder technology and micromachined substrates have been also presented recently, what opens a new line of low power-consumption gas sensors with thick sensitive films [14, 17-20].

Powder/Slurry	CVD	PVD	
		Sputtering	Evaporation
Sol-gel	Thermal CVD	Sputtering	Molecular beam epit.
Precipitation	Plasma CVD	Reactive sputtering	Thermal evaporation
Screen-printing	Laser induced CVD	Cathode sputtering	Reactive evaporation
Dip coating	Electroless plating		Ion plating
Drop coating			Reactive ion plating
Pulverisation coating			Arc evaporation
Spin coating			Laser evaporation

Table 2: Typical deposition techniques used for the preparation of gas-sensitive materials based on semiconductors. CVD stands for Chemical vapor deposition, PVD for Physical vapor deposition. (adapted from [8,14]).

1.2.3 Basic Scientist approach

Basically, the actual gas sensing process consists of three different parts: receptor, transducer and operation mode [14]. The *receptor* is the surface of the metal oxide, where chemical species undergo adsorption, reaction and desorption. Traditionally, the adsorption of a gas species on a solid has been divided into physisorption and chemisorption. Although arguably*, a molecule is considered to be chemisorbed if there is an electronic transfer between the gas and the solid, whereas there is no transfer in the case of physisorption. Ideally, the interaction of the gaseous molecules will induce a change in the depletion layer of the metal oxide grain (see next subsection). These changes are transduced into an electrical signal depending on the microstructure of the sensitive film (the *transducer*). The porosity of the film, the grain size and the different grain intersections will determine the *output signal*, which takes into account the whole sensitive layer. This output signal is usually electric, although the measurement of the thermovoltage or of the changes in the sensor temperature is also possible. Excellent reviews providing more details can be found in [21-23]. Hereafter the attention will be focused on the role of oxygen surface species, the role played by catalytic additives and the microstructure of the sensitive film.

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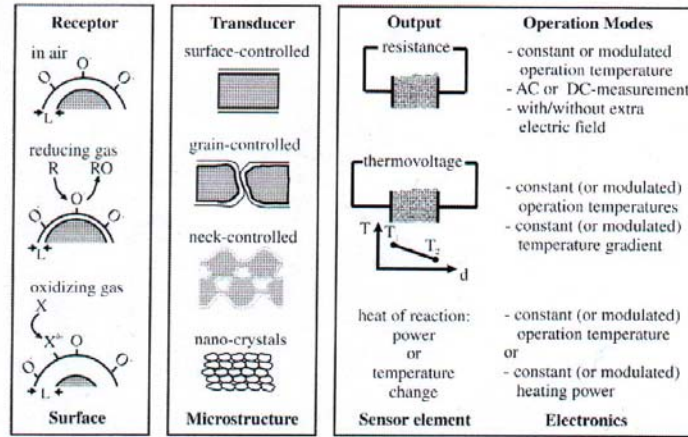


Fig. 2: Schematic view of the gas sensing elements: receptor, transducer and output signal (After [14]).

Oxygen surface species on MOX

According to Williams and Moseley [21], most target gases are detected due to their influence on the oxygen stoichiometry of the surface. Many studies have revealed that the key reaction involves modulation of the concentration of surface oxygen ions. The reactions involved in generating conductivity changes are reported to be confined to the first monolayer.

Some metal oxides, such as SnO₂, TiO₂ or WO₃, are intrinsically n-type bulk semiconductors, the stoichiometric excess of metal being due to oxygen vacancies. Under normal sensor operating conditions, the conductivity of the surface has revealed to be much less than that of the bulk. This has been attributed to the formation of surface oxygen ions that trap electrons, inducing a surface depletion layer and thus the development of Schottky barriers at interparticle contacts (Fig. 3). This barrier exercises controlling influence over the conductivity and its height ϕ_s is related to the square of the surface charge ($N_s\theta$)² by the expression:

$$\phi_s = \frac{e(N_s\theta)^2}{2\epsilon\epsilon_0 N_D} \quad (2)$$

* As a matter of fact, chemisorption can occur without electronic transfer.

where N_s is the number of surface states per unit area, θ is the fractional occupancy and N_D is the number of donor states per unit volume in the bulk. However, this straightforward model must be carefully considered since some experimental data have raised discrepancy [24].

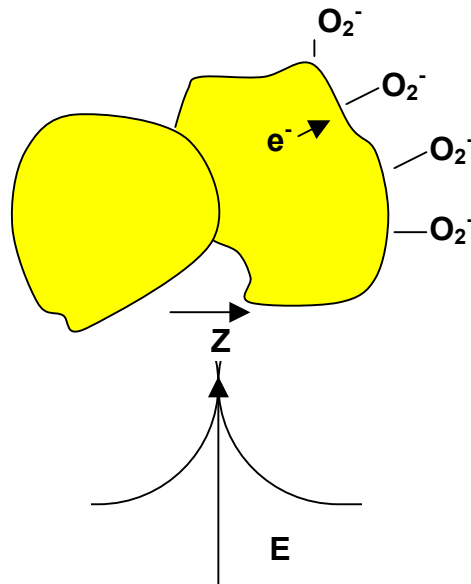


Fig. 3: Schematic diagram of the formation of interparticle Schottky barriers as a result of the trapping of charge at surface oxygen ions (here represented as O_2^-) (Adapted from [21]).

Many studies have been devoted to identify the surface oxygen species. Below about 200°C the stable surface ion is thought to be O_2^- . Between around 200°C and around 500°C the principal ion present is thought to be O^- . At temperatures above around 550°C, equilibration of lattice oxygen with the atmosphere occurs [25-27].

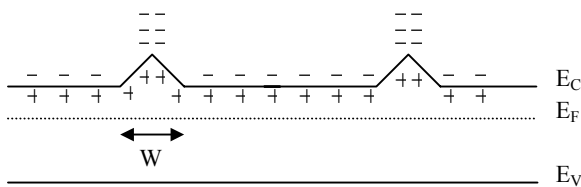


Fig. 4: Energy band representation of an n-type semiconductor crystalline with a grain boundary width W . Negative charge in the conduction band and positive charges in the energy gap are due to the oxygen vacancies.

In the case of n-type metal oxides, since the electrons come from ionised donors via the conduction band, the charge carrier density at the interface is thereby reduced and a potential barrier to charge transport is developed (Fig. 4). As the

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surface charge is developed, the adsorption of further oxygen is inhibited, the adsorption rate slows down because charge must be transferred to the adsorbate over the developing surface barrier and the coverage saturates at a very low value. At the junction between the grains of the solid, the depletion layer and associated potential barrier lead to high-resistance contacts, which dominate the resistance of the solid. The resistance is then sensitive to the coverage on the surface of adsorbed oxygen ions and any factor that changes this, will change the resistance. For instance, in the presence of a reactive gas, a surface-catalysed combustion might occur and the surface coverage of adsorbed oxygen ions might be decreased and the resistance would correspondingly decrease as a consequence of the reduction in the surface potential barrier height and depletion length. The surface barrier height ϕ_s , the depletion layer width d_{sc} , the charge Q_s associated with oxygen surface coverage and the donor density N_D in the solid are related:

$$d_{sc} = \frac{Q_s}{N_D e} \quad (3)$$

However, the processes of surface catalysis and electrical response are not necessarily always connected, since, for a surface reaction to give an electrical response, there must be some coupling with the charge carrier concentration. This can be expressed in the case of surface oxygen species by the model



from which theoretical expressions for the gas concentration dependence of conductance can be derived. For instance, Clifford [28] proposed that conductivity σ should depend on partial pressure P_x of a gas phase following:

$$\sigma \propto A e^{-E_A/kT} P_x^{-1/m} \quad (6)$$

where E_A is the activation energy, which represents the dependence of electrical conductivity on temperature, and $1/m$ accounts for the dependence of conductivity on gas partial pressure. Interestingly, when O^- species are involved, the parameter m is supposed to take a value of 2.

Catalytic additives on MOX sensors

The addition of an appropriate amount of metal additives has been shown to improve the detection of various kinds of gases via the enhancement of the sensor response and a decrease of the temperature of maximum sensor response. A decrease in response time and a better selectivity are also claimed to be achievable by using these additives.

The use of additives on metal oxides is evidently related to the use of supported metal/metal oxides in catalysis. In this field, the main target is to enhance the reaction rate of the gases. On the other hand, in the field of metal oxide sensors, this higher rate of reaction must be translated into an electrical signal; otherwise no advantage for gas sensing is taken from catalysing the reaction.

It is accepted that metal additives can lead to two different sensitisation mechanisms: chemical sensitisation and electronic sensitisation [29]. In the first case, the promoting effect is due to the ability of noble metals* to activate inflammable gases by enhancing their spill-over, so that they react with oxygen adsorbates more easily. Besides, the supply of oxygen can be enhanced by the presence of these catalytic additives, at the surface of which oxygen molecules from the gas phase can be easily dissociated and oxygen atoms migrate through spill-over effect to the surface of the metal oxide. In this way, the additive exerts a sort of *remote control* on the catalytic and sensing properties of the metal oxide.

On the other hand, the electronic sensitisation is associated with oxidised metal additives. The addition of fine particles of some metals to n-type metal oxides usually results in a rise of the base resistance in air. There is a decrease in the electron concentration in the oxide surface layer, which corresponds to an increase of the space-charge depth as a result of the electron transfer from the metal oxide to the metal loaded onto its surface. When the metal surface is covered with oxygen adsorbates at elevated temperatures in air (i.e. the metal is oxidised), the oxygen adsorbates extract electrons from this metal, which in turn extracts electrons from the metal oxide, leading to a further increase in the space-charge depth. Consumption of oxygen adsorbates on the metal, in addition to those on the metal oxide surface, by reaction with flammable gases, causes the enhanced sensitivity. In this case,

* *The name of noble metals comes from the fact that they are mainly found in nature in their pure metallic state. This is not a scientific category and thus it is not clear which metals can really be called noble metals, although it is generally accepted that Pt, Pd and Au are the typical ones.*

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therefore, the promoting effect arises mainly from the change in the oxidation state of the loaded material.

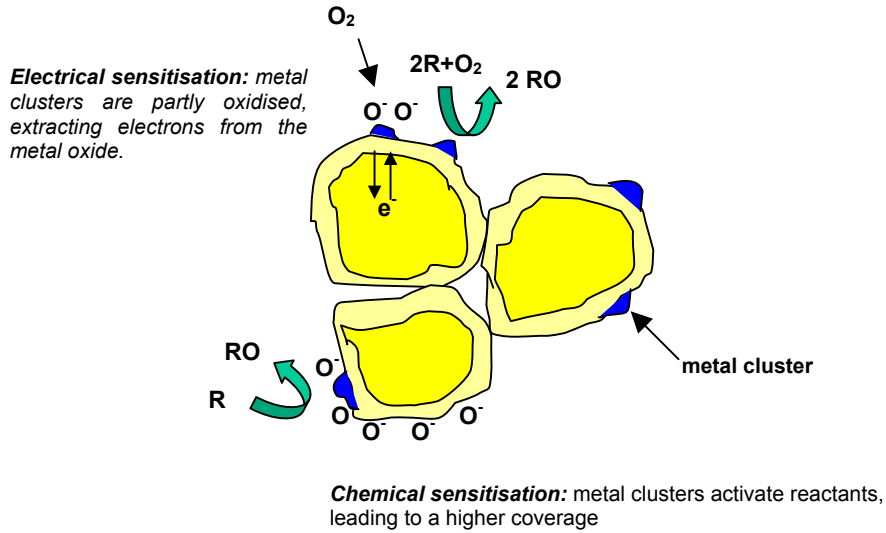


Fig. 5: Catalytic additives on MOX sensors. Top: Electrical sensitisation - oxidation state of metallic clusters depend on ambient gases). Bottom: Chemical sensitisation - metallic clusters promote the activation of gaseous species (Adapted from [9]).

Microstructure of the sensitive film

Broadly speaking, two different microstructures of the sensitive film can be described for MOX gas sensors: compact layers (where the interaction of the gases take place mainly at the geometric surface, often obtained by the so called thin film techniques) and porous layers (where the interior volume is also accessible to the gas, being obtained by most thick film techniques and RGTO, *Rheotaxial growth and thermal oxidation* [30]). As displayed in Fig. 2, the transducer mechanism in thin films is usually surface-controlled. On the other hand, transduction in porous films is highly dependent on grain size and the formation of different necks between grains.

Finally, in the case of porous films, it is necessary to consider the effects of reaction and diffusion within the microstructure: the composition of the gaseous medium within the porous structure is spatially variable as a consequence of the surface-catalysed decomposition of the gas being detected. Hence, there is a spatial variation of conductivity

through the structure. This is reflected in the measured conductance in a complex way dependent on the geometry of the electrodes. Williams and Pratt have revealed how the parameter m (Eq. 6) is highly dependent on the microstructure of the sensitive film, including this effect of diffusion [31].

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1.3 Why bother about tungsten oxide?

1.3.1 Tungsten oxide among metal oxides for gas detection

Since Seiyama and Taguchi used the dependence of the conductivity of ZnO on the gas present on the atmosphere for gas sensing applications [32,33], many different metal oxides have been proposed for gas detection. Generally speaking, these oxides can be divided into binary oxides and more complex oxides, being the former much more common in gas sensing applications.

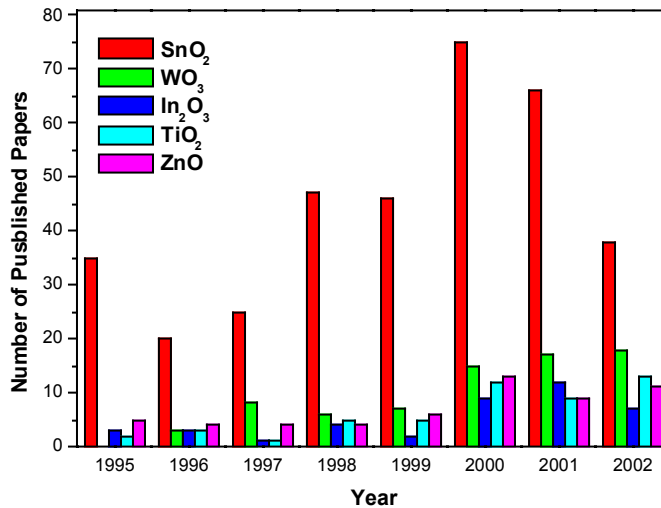


Fig 6: Comparison of the papers published on gas sensors based on SnO₂, WO₃, In₂O₃, TiO₂ and ZnO*.

Among binary metal oxides, tin dioxide (SnO₂) is the one that has received by far more attention since Taguchi built the first tin oxide sensor for Figaro Sensors in 1970 [34]. This is probably due to its high reactivity to many gaseous species. However, this characteristic has also revealed as a lack of selectivity, and thus investigation on other metal oxides has been considered necessary. Besides, developers of electronic noses have experimented with arrays of different sizes that may include around ten MOX sensors [35], apart from other types of chemical sensors. The use of different MOX sensors is highly recommended in order to increase the amount of information. Fig. 6 displays the number of published

papers* belonging to different metal oxides for gas sensing applications. It is evident that tin oxide receives clearly more attention than the rest. However, the number of papers where tungsten oxide is used for gas sensing applications has been increasing during recent years, leading this material to be the second MOX most studied for gas sensing applications.

1.3.2 Structural properties of tungsten oxide

Tungsten trioxide exhibits a cubic perovskite-like structure based on the corner sharing of WO_6 regular octahedra, with the O atoms (W atoms) at the corner (centre) of each octahedron [36] (Fig. 7). The crystal network can also be viewed as the results of alternating disposition of O and WO_2 planes, placed normally to each main crystallographic direction. This structure is also found in rhenium trioxide structure (ReO_3), from which

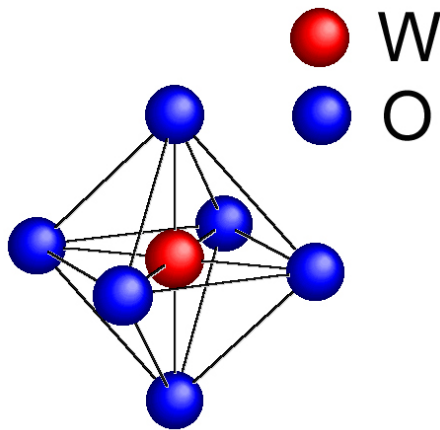


Fig. 7: Schematic model of crystalline WO_3 in the undistorted cubic phase. The unit octahedron presents the tungsten atom at the centre and 6 equivalent oxygen atoms at the corners.

takes its common name (ReO_3 -structure). This structure is in itself rather uncommon. However, since it forms the base of perovskites (one of the most important ternaries), it has in fact chief importance.

Actually, the symmetry of tungsten oxide is lowered from the ideal ReO_3 structure by two distortions: tilting of WO_6 octahedra and displacement of tungsten from the centre of its octahedron [37]. Variations in the details of these distortions give rise to several phase transitions. In fact tungsten trioxide adopts at least five distinct crystallographic modifications between absolute zero and its melting point at 1700°K. When the temperature is decreased from the melting point, the crystallographic symmetry for WO_3 changes in the sequence: tetragonal-ortorhombic-monoclinic-triclinic-monoclinic. Most of the transitions appear to be first order, and they often display large hysteresis in the transition temperatures. A summary of these transitions is given in Table 3.

* The number of papers has been evaluated using the database Science Citation Index with a typical search of (WO_3 OR (tungsten oxide) OR (tungsten trioxide)) AND (gas sensor).

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It is interesting to notice that, as suggested by Table 3 and confirmed experimentally in [45], the coexistence of triclinic and monoclinic phases in WO_3 at room temperature is common.

Electrical and optical characteristics of tungsten trioxide are dependent on the crystalline structure. Saljie and Viswanathan found the resistivity to decrease from approximately 2.0 to 0.2 Ω -cm upon heating from 293 to 1123°K [46]. The optical band gap (2.58 eV at room temperature) is found gradually decrease and become increasingly diffuse as the temperature is raised to 773°K [47].

The identification of these phases, mainly by X-ray diffraction and Raman spectroscopy, has been reported in [43,45,48,49]. A summary of other main features is provided in Appendix 1.

<i>Phase</i>	<i>Symmetry</i>	<i>Space</i>	<i>Z</i>	<i>Temperature range (°K)</i>	<i>Reference</i>
α - WO_3	Tetragonal	P4/nmm	2	1010-1170	[38]
β - WO_3	Orthorombic	Pmnb	8	600-1170	[39]
γ - WO_3	Monoclinic	P2 ₁ /n	8	290-600	[40,41]
δ - WO_3	Triclinic	P1	8	230-290	[42,43]
ε - WO_3	Monoclinic	Pc	4	0-230	[44]

Table 3: Known polymorphs of tungsten trioxide (Adapted from [36]).

Another point worth noting is that the tungsten trioxide structure is likely to host several kinds of defects. One of the most elementary defects, as in most metal oxides, is the lattice oxygen vacancy, where an oxygen atom is absent from a normal lattice site. In many d^0 oxides of Ti, V, Nb, Mo and W this sort of point defects are largely eliminated by the formation of crystallographic shear phases. In the case of WO_3 , the removal of oxygen causes the appearance of these crystallographic shear planes into the crystal along the [1m0] direction [50]. This leads to the formation of a family of WO_{3-x} compounds (see Appendix 1). From an electronic point of view, an oxygen vacancy causes the increase of the electronic density on the metallic (W) adjacent cations, leading to the formation of donor-like states slightly below the edge of the conduction band of the oxide, which acquires semiconducting properties [51]. A clearer picture of this effect will be provided after presenting the experimental results in Chapter 3.

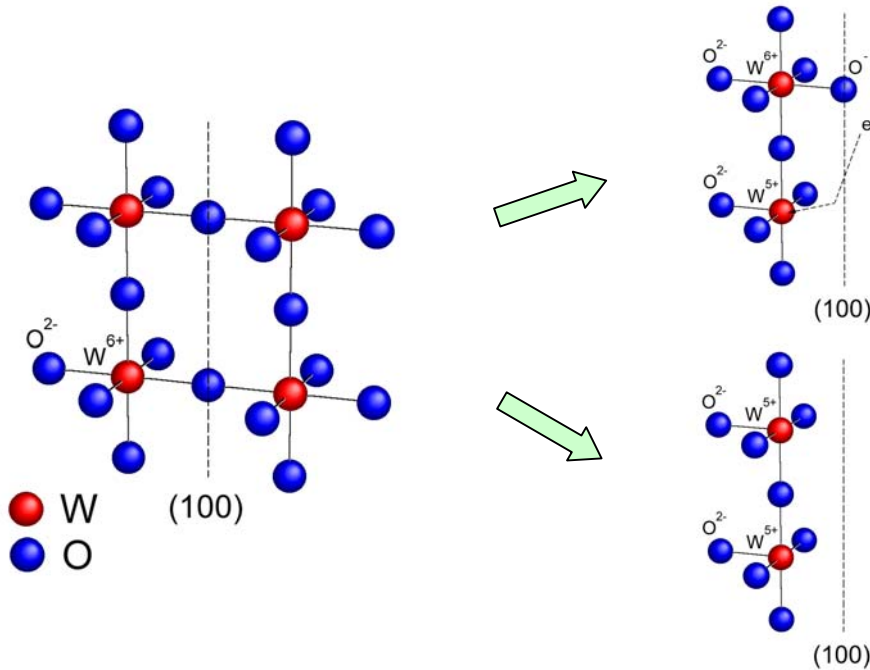


Fig. 8: Structural model of the WO_3 grain surface. Left panel: idealised WO_3 structure with the (100) fracture planes shown. Right panel: two possible states of the grains surface: in both cases the formation of the reduced tungsten ions W^{5+} is required by the neutrality condition (Adapted from [52]).

Finally, it is important to point out that in this work, superficial properties of tungsten oxide are of paramount importance, since that is where gas interaction occurs. This important point is sometimes overlooked in many papers concerning MOX gas sensors, where bulk properties are extensively reported and little attention is paid at the surface of the material. The way to progress from the above-explained crystalline structure and the surface has been proposed by Kuzmin et al. [52]. If a crack along the (100) crystallographic plane is considered, two different situations can be present on the surface of tungsten oxide. In the first one, half of the tungsten atoms remain in the valence states $6+$ and are connected to the terminal oxygen ions giving one of their electron to the nearest tungsten ion which transforms into the W^{5+} state. This situation occurs at the free surface of WO_3 single crystals and was directly observed by an STM technique [52]. Moreover, this observations suggest the shortening of the terminal $W^{6+}-O^-$ bond to the value about 1.6 \AA that is close to the value of the $W=O$ bonds in tungsten hydrates (see Appendix 1). In the second situation, all tungsten atoms at the surface change their valence state to $5+$, and the surface is represented by a $W^{5+}O_2$ terminal layer. In both cases, the surface W^{5+} sites react with the

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oxidising atmosphere of air, leading presumably to a formation of the W^{6+} -OH bonds in a humid ambience.

1.3.3 Gas sensors based on tungsten oxide

In recent years, at least three research groups have devoted a great deal of their investigation to tungsten oxide for gas sensing applications: the Department of Materials Science and Technology of the Kyushu University (Prof. Yamazoe), Departments of Physics and Chemistry of Materials, University of L'Aquila (Prof. Santucci) and the Laboratory for Surface Science and Technology of the University of Maine (Prof. Vetelino and Prof. Lad). Besides, there have been many other contributions from several other groups, what has led tungsten oxide to be highly appreciated in the field of MOX gas sensors.

In practice, these publications have been showing that tungsten trioxide is an interesting material for the detection of mainly three gases: ammonia, hydrogen sulphide and nitrogen dioxide. Investigations indicate that, sensor response of tungsten oxide to these gases can be, at least, as good as the sensor response exhibited by tin oxide, if not higher. Moreover, tungsten oxide has revealed as low sensitive to carbon monoxide and hydrocarbons, what makes it more interesting for the detection of these gases.

Gas	8-hour Exposure		15-minute Exposure	
	ppm	mg/m ³	ppm	mg/m ³
Ammonia (NH ₃)	25	17	35	24
Hydrogen sulphide (H ₂ S)	10	14	15	21
Nitrogen Dioxide (NO ₂)	3	6	5	9

Table 4: Occupational Exposure Standards 2000 of the UK Health and Safety Executive

Ammonia

Ammonia is a chemical made by both man and nature. The amount of ammonia produced every year by man is very small compared to that produced by nature every year. However, when ammonia is found at a level that may cause concern, it is usually produced either directly or indirectly by man. It is a colourless gas with a very sharp odour. The odour is familiar to most people because ammonia is used in smelling salts, household cleaners and window cleaning products [53].

Ammonia is very important to animal and human life. It is found in water, soil, and air, and is a source of much-needed nitrogen for plants and animals. Most of the ammonia in the environment comes from the natural breakdown of manure and dead plants and animals.

Eighty percent of all man-made ammonia is used as fertiliser. A third of this is applied directly as pure ammonia. The rest is used to make other fertilisers that contain ammonium. Ammonia is also used to manufacture synthetic fibres, plastics, and explosives. Many cleaning products also contain ammonia.

Outdoors, you may be exposed to high levels of ammonia in air from leaks and spills at production plants and storage facilities, and from pipelines, tank trucks, rail cars, ships, and barges that transport ammonia. Higher levels of ammonia in air may occur when fertiliser is applied to farm fields. After fertiliser is applied, the concentration of ammonia in soil can be more than 3000 ppm; however, these levels decrease rapidly over a few days. Indoors, you may be exposed to ammonia while using household products that contain ammonia. Some of these products are ammonia cleaning solutions, window cleaners, floor waxes, and smelling salts. You can also be exposed to ammonia at work because many of the cleaning products there also contain ammonia. Farmers, cattle ranchers, and people who raise chickens can be exposed to ammonia from decaying manure. Some manufacturing processes also use ammonia.

Yamazoe et al. [54-58] proposed that Au-catalysed WO_3 is an excellent sensitive material for ammonia detection. Their sensors have usually a thick-film sensitive layer based on WO_3 powder, obtained by a pyrolytic route [54]. This group has analysed the influence of the thickness of the sensitive layer [55], the addition of many different additives [57] and the interference of NO on ammonia sensor response [58]. Their Au-loaded WO_3 exhibited excellent sensing properties to NH_3 in air at 450°C , being able to detect 5 ppb of ammonia in air. The authors attribute their high sensor response to the fact that small particles of Au are dispersed on the surface of WO_3 grains and oxygen is adsorbed on these particles and on the interface between Au and tungsten trioxide [56]. The adsorbed oxygen, especially that located on the interface, traps electrons and thus forms an electron-depleted layer. This oxygen species are consumed by ammonia, resulting in a relaxation of the depletion layer.

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Meixner et al [59], using a thin-film gas sensor, have also confirmed that tungsten oxide has proved to be the most suitable material for ammonia detection. Finally, Llobet et al [60] built drop-coated WO_3 sensors on silicon substrates, showing the compatibility of thick film with new silicon technologies. A summary of these and other papers is provided in Table 5.

<i>Material</i>	<i>Sensitive layer</i>	<i>Concentration range</i>	<i>Sensor response (R_{AIR}/R_{NH_3}) (Temp., Concentration)</i>	<i>Year / Reference</i>
$WO_3: Au$	Powder - dip coat.	5 ppb-50 ppm	~40 (50 ppm, 450°C)	1992 [54]
WO_3	Sputtering	10 ppm	~1.1 (300°C)	1995 [61]
WO_3	Sputtering	1-27 ppm	~10 (1ppm)	1995 [59]
WO_3	Drop-coating	10-1000 ppm	~6 (1000ppm- 300°C)	2000 [60]
$WO_3: Mg$	Powder - dip coat.	30 ppm	7.65 (350°C)	2000 [57]
$WO_3: Zn$			5.06	
$WO_3: Mo$			10.1	
$WO_3: Re$			9.46	
WO_3	Sputtering	1-50 ppm	~4 (50ppm, 300°C)	2001 [62]
WO_3	Powder/drop-coat.	25 ppm	~1.11 (400°C)	2003 [63]
WO_3	Sputtering	100 ppm	~7 (400°C)	2003 [64]

Table 5: Selected publications on NH_3 gas sensors based on WO_3 .

As a result of these works, WO_3 appears to be a promising material for the detection of ammonia. Some additives have been identified as suitable to enhance sensor response. However, the specific reactions that occur on tungsten oxide have not been completely explained. This point is of special interest since, as will be shown in Chapter 4 and 5, ammonia can suffer many different reaction paths that may affect the sensor response. Besides, the interference of humidity, as well as the role played by additives, merit further investigation.

Hydrogen sulphide

Hydrogen sulphide occurs naturally in crude petroleum, natural gas, volcanic gases, and hot springs [53]. It can also result from bacterial breakdown of organic matter or produced by human and animal wastes. Other sources are industrial activities, such as food processing, coke ovens, craft paper mills, tanneries, and petroleum refineries. Hydrogen sulphide is a colourless, flammable gas under normal conditions. It is commonly known as hydrosulphuric acid, stink damp and sewer gas. It smells like rotten eggs and people can smell it at low levels (less than 1 ppb).

Hydrogen sulphide is released primarily as a gas and can spread in the air. When released as a gas, it will form sulphur dioxide and sulphuric acid in the atmosphere. Hydrogen sulphide remains in the atmosphere for about 18 hours. In some instances, it may be released as a liquid waste from an industrial facility. You can be exposed by crude petroleum, natural gas, volcanic gases and hot springs. You can also be exposed at work if you work in the petroleum refining, petrochemical, or natural gas industry; food processing; wastewater treatment; coke oven plants; tanneries; or pulp and paper mills. A small amount of hydrogen sulphide is produced by bacteria in your mouth and gastrointestinal tract and by enzymes in your brain and muscle.

The group of Prof. Vetelino and Prof. Lad have carried out most of their research with tungsten oxide sensors for hydrogen sulphide detection. Unlike the group of Prof. Yamazoe, they have mainly investigated pure tungsten oxide, although paying attention to more characteristics than just sensor response, such as mobility [65], film microstructure [66] and stoichiometry [67]. These authors have concluded that activated 500 Å Au-doped WO₃ films have been found to be stable, sensitive and selective sensing elements [65]. Their films showed no ageing effects and were sensitive to 1 ppb of hydrogen sulphide at 200°C. The authors argue that, in the case of their WO₃-sputtered sensitive films, post-deposition annealing of the films to 400°C in air induced film crystallisation, an increase in surface roughness and a decrease in film conductivity. This crystallisation process markedly improved the sensitivity and response of the WO₃ films to hydrogen sulphide [66]. In [67], the authors explain that differences in response behaviour to H₂S gas between films containing the tetragonal versus the monoclinic phase suggest that oxygen vacancy and charge transport mechanisms are dependent on film microstructure.

Other papers have investigated the introduction of noble metals such as Au, Pd, Pt [65,68,69], although little attention has been paid to understanding the effect of these additives. Finally, Lantto et al. [70,71] have examined in detail the effect of tungsten trioxide crystalline structure on sensor response to H₂S, revealing that a tetragonal phase leads to an extremely high sensor response to this gas at room temperature.

From the preceding cited literature it is clear that pure tungsten trioxide is a suitable material for hydrogen sulphide detection. Connections between sensitive film microstructure, crystalline structure and sensor response have been established. Besides, some noble metals have revealed as suitable to increase sensor response. However, present

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understanding of the reaction occurring on tungsten oxide is limited. As in the previous case of ammonia, the interference of humidity and the role played by additives need further investigation.

<i>Material</i>	<i>Sensitive layer</i>	<i>Concentration range</i>	<i>Sensor response (R_{AIR}/R_{H_2S}) (Temp. Concentration)</i>	<i>Year / Reference</i>
<i>WO₃</i>	powder/pellet	10-200 ppm	~2 (200ppm-200°C)	1990 [72]
<i>WO₃:Au</i>	sputtering	0.5ppb-100ppm	~30 (100ppm, 200°C)	1993 [65]
<i>WO₃</i>	gas evaporation	100 ppm	7.7 (280°C)	1994 [68]
<i>WO₃:Pd</i>			9.7 (170°C)	
<i>WO₃:Pt</i>			9.9 (220°C)	
<i>WO₃</i>	sputtering	4 ppm	~10 (200°C)	1995 [66]
<i>WO₃</i>	gas deposition	1-10 ppm	~10000 (10 ppm,200°C)	2001 [70]
	powder/printing		~1000 (10 ppm,200°C)	
<i>WO₃</i>	sputtering	20 ppm	~ 500 (250°C)	2001 [67]
<i>WO₃:Pt</i>	sputtering	0.2-50 ppm	~ 1000 (50 ppm, 220°C)	2002 [69]
<i>WO₃:AuPt</i>			~ 40	
<i>WO₃:Au</i>			~ 20	
<i>WO₃</i>	powder/drop-coat.	25 ppm	34.11 (200°C)	2003 [63]
<i>WO₃:Au</i>	sputtering	104.8 ppm	~ 50 (250°C)	2003 [73]

Table 6: Selected publications on H₂S gas sensors based on WO₃.

Nitrogen dioxide

Nitrogen oxides are a mixture of gases that are composed of nitrogen and oxygen. Two of the most toxicologically significant nitrogen oxides are nitric oxide (NO) and nitrogen dioxide (NO₂); both are non-flammable and colourless to brown at room temperature. Nitric oxide is a sharp sweet-smelling gas at room temperature, whereas nitrogen dioxide has a strong, harsh odour and is a liquid at room temperature [53]. Nitrogen oxides are released to the air from the exhaust of motor vehicles, the burning of coal, oil, or natural gas, and during processes such as arc welding, electroplating, engraving, and dynamite blasting. They are also produced commercially by reacting nitric acid with metals or cellulose.

Nitrogen oxides are used in the production of nitric acid, lacquers, dyes, and other chemicals. Nitrogen oxides are also used in rocket fuels, nitration of organic chemicals, and the manufacture of explosives. Nitrogen oxides are broken down rapidly in the atmosphere by reacting with other substances commonly found in the air. The reaction of nitrogen dioxide with chemicals produced by sunlight leads to the formation of nitric acid, which is a major constituent of acid rain. Nitrogen dioxide also reacts with sunlight, which leads to the formation of ozone and smog conditions in the air we breathe. Small amounts of

nitrogen oxides may evaporate from water, but most of it will react with water and form nitric acid. When released to soil, small amounts of nitrogen oxides may evaporate into air. However, most of it will be converted to nitric acid or other compounds.

The general population is primarily exposed to nitrogen oxides by breathing in air. People who live near combustion sources such as coal burning power plants or areas with heavy motor vehicle use may be exposed to higher levels of nitrogen oxides. Households that burn a lot of wood or use kerosene heaters and gas stoves tend to have higher levels of nitrogen oxides in them when compared to houses without these appliances. Nitric oxide and nitrogen dioxide are found in tobacco smoke, so people who smoke or breathe in second-hand smoke may be exposed to nitrogen oxides. Workers employed in facilities that produce nitric acid or certain explosives like dynamite and trinitrotoluene (TNT), as well as workers involved in the welding of metals may breath in nitrogen oxides during their work.

Yamazoe et al. [74,75] published some of the earlier papers on tungsten trioxide applied to NO₂ detection (actually NO and NO₂), considering the influence of grain size on sensor response.

<i>Material</i>	<i>Sensitive layer</i>	<i>Concentration range</i>	<i>Sensor response (R_{AIR}/R_{H2S}) (Temp. Concentration)</i>	<i>Year / Reference</i>
<i>WO₃</i>	Powder - dip coat.	0-200 ppm	97 (80 ppm,300°C)	1991 [74,75]
<i>WO₃</i>	Evaporation powd.	0.4-100 ppm	~20 (100ppm,350°C)	1996 [76]
		0.2-5 ppm	71 (5ppm, 200°C)	[77]
<i>WO₃</i>	Powder - printing	100 ppm	~200 (100°C)	1999 [84]
<i>WO₃/TiO₂</i>	Powder - printing	1-30 ppm	~200 (30ppm,350°C)	1999 [85]
<i>WO₃</i>	Evaporation powd.	10-30 ppm	~8 (30ppm,300°C)	2000 [86]
<i>WO₃</i>	Dip-coating	10-25 ppm	~300 (25ppm,20°C)	2002 [87]

Table 7: Selected publications on NO₂ gas sensors based on WO₃.

More recently, the group of the University of L'Aquila has focused on thin-films of WO₃ for NO₂ detection. They have considered the microstructural effects of the sensitive layer [76-77], cross-sensitivity [78], surface morphology [79] and influence of superficial oxygen vacancies [80]. Apart from these works, this group has contributed with more fundamental works on structural properties of WO₃ [81]. Their mastery of preparation and study of their sensitive films have recently leaded them to publish a very interesting visualisation of

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connection between annealing parameters, operating temperature and their effects on sensitivity, stability and microstructure [82].

According to them, in order to achieve a small grain size, the paramount factor is the annealing temperature, rather than the annealing time. Actually, kinetic solid-state sintering models have highlighted the exponential dependence of the rate of crystal growth with the sintering temperature, compared with only a linear dependence with sintering time [83]. Since sensor response is reported to decrease with increasing grain size, the authors propose to fix the annealing temperature at the crystallisation temperature of the material (300°C in the case of WO_3).

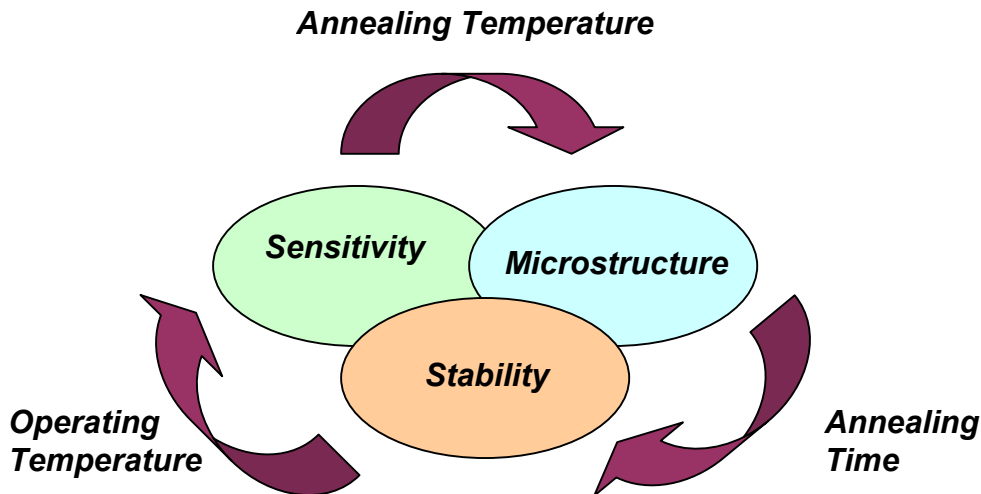


Fig. 9: Visualisation of the role played by annealing temperature, annealing time and operating temperature (factors) on microstructure, sensitivity and stability for WO_3 thin films. (Adapted from [82]).

On the other hand, these authors claim annealing time has a positive effect in improving the long-term stability of the sensor. During annealing, an adjustment of the surface or grain boundary defects to their equilibrium state takes place, being this process time-dependent. Long annealing times are required if low annealing temperatures are chosen.

Finally, there is always an optimum operating temperature that corresponds to the highest reaction rate of the gas. However, the operating temperature must always be lower than the annealing temperature to achieve stability. If this optimum temperature is over the crystallisation temperature, annealing temperature must be risen and thus sensitivity will not be at their maximum.

1.4 Motivation, objectives and organisation

As already noted, tungsten oxide-based gas sensors are of high interest at the moment because of their good sensing properties to ammonia, hydrogen sulphide and nitrogen dioxide. However, despite the high number of published papers, there are still a number of points that need further improvement. First of all, the present understanding of the specific reactions of ammonia and hydrogen sulphide on the surface of tungsten oxide is rather limited (those of nitrogen dioxide have received much more attention and have been intensively investigated by the group of l'Aquila for WO_3 and by many other research groups for other MOX sensors, especially SnO_2 [16]). Understanding these reactions is a key point in the development of more selective sensors, as well as an important achievement from the scientific point of view. In order to improve our knowledge on this matter, it is necessary to pay attention to those techniques that can give us information about the superficial reactions that occur on the surface of the sensing material. This is actually the first step in chemical sensing and its study and connection with sensor response has not been always examined in detail. As a matter of fact, it is rather surprising that in the field of catalysis, which is actually the source of MOX sensors, these kinds of *real condition* techniques are intensively used, whereas they are not a common investigation tool among many gas-sensor groups.

Some other obscure points concerning tungsten oxide sensors are the role played by additives and the interference role played by water. To the moment, only noble metals (Pt, Pd and especially Au) have been considered to enhance sensor response of WO_3 -based gas sensors. Although these additives have been successfully used for many years on many MOX sensors, they can lead to rather unselective devices, especially if they activate oxygen species. As to humidity, although some works have dealt with its influence on nitrogen dioxide sensor response, there is not yet available data about its influence on the detection of ammonia and hydrogen sulphide by tungsten oxide.

Finally, most of the papers concerning WO_3 are based on thin films of this material. It has been often argued that these thin films are compatible with silicon substrates and thus low-power consuming devices can be built, as a contrast with powder and their traditional highly consuming alumina-based devices. This is not true anymore, as cited above. Nowadays there are techniques to obtain thick-films on micromachined sensors. Since these porous films are supposed to be much more sensitive than compact thin films and powders

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can be submitted to high-temperature annealing before film deposition to stabilise them, obtaining sensitive materials in the form of powders is again of paramount importance.

The first objective of this study was to synthesise pure and catalysed WO_3 nanocrystalline powders. As reported above, only one chemical route (the pyrolysis of ammonium paratungstate) had been explored in the field of MOX sensors to obtain nanocrystalline WO_3 powders before the beginning of the present investigation, to the best of our knowledge. For this work, nanocrystalline tungsten trioxide was prepared following a soft chemistry route, classified as a sol-gel route by some authors, from tungstic acid (Chapter 2). This route has been applied in different fields like catalysis but it had never been used before for gas sensing applications. A preliminary study showed that this route was able to obtain tungsten oxide with comparable crystallite sizes and structural properties closer to monocrystalline WO_3 than the pyrolytic route, as well as higher sensor response to NO_2 under the same test conditions [88]. However, it was not the purpose of this dissertation to make a comparison of these two routes but it is focused on the properties of nanocrystalline WO_3 powders obtained from tungstic acid.

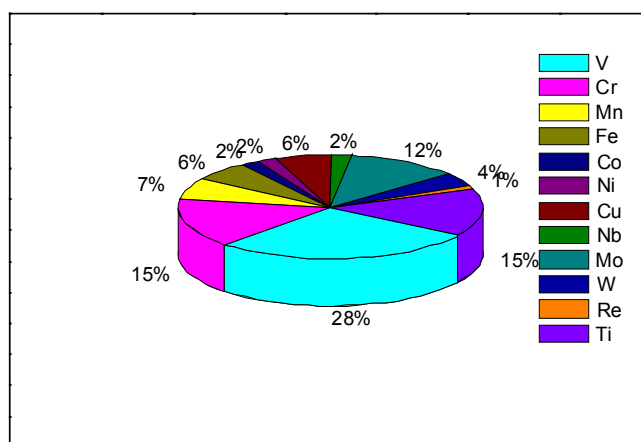


Fig. 10: Overview of the importance of copper, vanadium and chromium in supported metal oxide catalysis, based on the number of published papers in the period 1967-2000 (Adapted from [96]).

The additives chosen to improve sensor response were copper, vanadium and chromium. These are transition metals and, as indicated above, only noble metals had been investigated

before the beginning of this work in WO₃-based sensors. These additives were chosen due to their reportedly high catalytic activity in ammonia and hydrogen sulphide (see [89-92] and references therein) and their extensive use on supported catalysis (see Fig. 10). Since their electron work function is higher than the electron affinity of WO₃* and they are easily oxidised, they could induce electrical sensitisation, at least, to the WO₃ particles. Compared to noble metals, it can be argued that most noble metals activate oxygen species by the spill-over effect, what can be rather unselective. On the other hand, if metal centres are oxidised, there will be well-defined metal-oxygen bonds that can be broken differently depending on the reactive molecule. Besides, their precursor chemicals are usually cheaper than those of noble metals are.

This study also aims at evaluating the structural properties of the obtained materials. It is well known how important is to control and investigate the fundamental properties of the sensing materials in order to understand and improve the performance of sensor devices. This goal can only be achieved if a *multitechnique* approach is followed, as many conclusions can only be reached with the aid of more than one characterisation technique. Therefore, X-ray Diffraction (XRD), Raman spectroscopy, Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Electron Paramagnetic Resonance (EPR) and Diffuse Reflectance Infrared Spectroscopy (DRIFTS) have been applied to this investigation (Chapter 2). Firstly, pure nanocrystalline WO₃ powders are analysed in Chapter 3. The main parameter investigated was the influence of annealing treatments on the structural properties. Structural and spectroscopic properties of catalysed WO₃ are reported in the second part of Chapter 3. In this case, the emphasis was on the characterisation of catalytic centres by XPS and EPR, rather than on bulk WO₃. It is interesting to point out that the use of EPR is not very common in the field of additive characterisation in MOX sensors. Nevertheless, recent papers have shown that this technique can give a tremendous amount of information of not only additives' state, but also of fundamental sensing mechanisms of MOX sensors [93,94].

This study also evaluates evaluate the sensing properties of thick-film gas sensors based on the previously presented powders (Chapter 4). The target gases are ammonia, hydrogen sulphide and nitrogen dioxide. Typically, sensors were evaluated at different working

* The electron affinity of WO₃ is 3.33 eV, whereas the work functions of Cu, V and Cr are 4.6, 4.3 and 4.5 eV, respectively. (Actually, it is the work function of WO₃ what should be lower than the metals' work functions to have a depleted layer in tungsten oxide, but it obviously depends on the position of the Fermi Level, i.e. the amount of oxygen vacancies or donor impurities on WO₃).

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temperatures under one concentration of the target gas in dry air. Once suitable working temperatures were found, sensor responses to different concentrations of that gas, as well as influence of humidity, were evaluated. The aim was basically two-fold: to evaluate the influence of two different annealing temperatures, different additives introduction and humidity on sensor response, and to select the most suitable material and operating conditions, from those tested, for each gas. The emphasis is very much on ammonia and hydrogen sulphide detection than on nitrogen dioxide, since additives were selected to improve sensor response to these reducing gases.

This study also attempts to understand the specific reactions that occur on the surface of tungsten oxide by applying *real condition* characterisation techniques (Chapter 5). By *real condition* it must be understood that the temperature and gas ambience of the sample was controlled and that it was as similar to operating conditions of the sensor as possible. It is often argued that traditional characterisation techniques, although being able to give valuable information, are not so useful in the field of gas sensors unless they are performed under *real* atmosphere and temperature conditions. These studies, which are standard in the field of catalysis, are not so common for gas sensors, though. Two techniques have been selected: DRIFTS and Temperature Programmed Desorption (TPD). As regards DRIFTS, only the interaction of ammonia and WO_3 -based powders was investigated. This technique has revealed as excellent to understand the interaction of this gas with metal oxides (see [90] and references therein) and, to the best of our knowledge, it has not been applied to gas sensing with tungsten oxide. Hydrogen sulphide and nitrogen dioxide DRIFTS studies are not reported since they require some experimental conditions far from those used in gas sensing (high gas pressure and low temperature). As to TPD, it has received more attention in the field of MOX sensors (see [95] and references therein), although it has been scarcely applied to tungsten oxide. TPD has not been applied to nitrogen dioxide since it requires concentrations over 2 orders of magnitude higher than common concentrations in gas sensing.

Finally, this study seeks to combine the information obtained from these different sources in order to contribute to the understanding of gas sensors based on WO_3 (Chapter 6).

To sum up, the main objectives of this investigation are:

- to synthesise nanocrystalline powder of pure and Cu,V, and Cr-catalysed WO_3 ; to analyse the structural properties of WO_3 and their evolution with annealing temperature; to investigate the chemical state of additives on WO_3 particles (Chapter 3).
- to test thick-film sensors under ammonia, hydrogen sulphide and nitrogen dioxide ambiances; to test the influence of humidity on the detection gases cited above; to identify the best sensing elements and operating conditions for each gas (Chapter 4)
- to study the application of controlled ambience and temperature techniques to the characterisation of the reactions of ammonia and hydrogen sulphide on WO_3 (Chapter 5).
- to understand the influence of the structural properties, additive state and chemical reactions and species on sensor response of WO_3 -based gas sensors (Chapter 6).

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