Semiconducting Oxide Gas-Sensitive Resistors

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Abstract

The overall aim of this thesis is to describe the gas sensing behaviour of a wide range of metal oxide semiconductors which exhibit tremendous changes in their electrical resistance at high temperatures (typically > 300°C) upon exposure to traces (ppm) of reactive gases present in the air.

The effects of surface segregation in antimony-doped tin dioxide (Sn$_{1-y}$Sb$_y$O$_2$) on both the electrical response to water vapour and the catalytic combustion of methane in the presence of water vapour were demonstrated. Effects of microstructure, and especially particle size, on the behaviour (sensitivity and selectivity) of these compounds to carbon monoxide and methane were also demonstrated. A change in behaviour correlating with the Debye length was shown. Theoretical calculation methods were used to model surface segregation and surface defects. Antimony segregates as Sb$^{3+}$ and the complex [Sn$_n^{n''}$-O$_{n''}$] is a stable surface species. A model for gas response and surface reaction involving this complex is proposed.

The properties of solid solution series prepared by systematic cation substitution as a way of understanding the gas response mechanism linked to the surface chemistry has been examined in (CrNbO$_4$)$_x$(Sn$_{1-y}$Sb$_y$O$_2$)$_{1-x}$, Ti$_x$(Sn$_{1-y}$Sb$_y$)$_{1-x}$O$_2$, and (MWO$_4$)$_x$([Sn-Ti]O$_2$)$_{1-x}$ [with M: Mn, Fe, Co, Ni, Cu, Zn]. Effects of stoichiometry, microstructure, combustion gradient and surface segregation on gas (water, carbon monoxide, methane, propane and ammonia) sensitivity and selectivity have been observed and discussed.
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"L'homme de Science le sait bien, lui, que, sans la Science, l'homme ne serait qu'un stupide animal sottement occupé à s'adonner aux vains plaisirs de l'amour dans les folles prairies de l'insouciance, alors que la Science, et la Science seule, a pu, patiemment, au fil des siècles, lui apporter l'horloge pointeuse et le parcmètre automatique sans lesquels il n'est pas de bonheur terrestre possible."

Pierre Desproges (Vivons heureux en attendant la mort)
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Chapter 1. General Introduction

1.1. Background

Gas sensors are required for improved environmental protection, improved product performance and improved process operation. The dominant influence in recent years with regard to gas sensor development has been pressure for environmental protection, notably in the USA, and later in other countries, for vehicle pollution control, and in Japan, for flammable gas monitoring in homes and other buildings. Flammable gas monitoring in industrial plants using catalytic gas detectors has also been mandated by legislative requirements in many countries.

For the last three decades, gas sensors based either on surface characteristics or the bulk electrical properties of ceramics have been the subject of extensive research and development. The application of these sensors range from air-to-fuel ratio control in combustion processes such as automotive engines and industrial furnaces to the detection of leakage of inflammable and toxic gases in domestic and industrial environment. While the solid-state physical sensors used to measure temperature, pressure and other physical parameters have been a success commercially, their chemical analogs used to measure moderate to very low concentration of toxic gases (such as H₂, O₂, CO, NOₓ, SOₓ, H₂S, NH₃, CH₄, C₃H₈, C₂H₅OH and so on) have achieved a relative success. Ten millions sensors are sold each year mainly in the USA and mainly for domestic CO alarms. Despite their overall lack of selectivity, the semiconductor-based chemical sensors owe their popularity to their high sensitivity, simple operation, small size, and relatively simple associated electronics.

The recent emergence of concern over environmental pollution and efficiency in a variety of combustion process and of an increased awareness over a need to monitor potentially hazardous gases has stimulated substantial research and development in the field of gas sensors. Requirements to detect and monitor these gases has already led to the development of a wide variety of devices and methods, as evidenced by a large number of instruments now available commercially.
The general procedure for research on chemical sensors is summarised in Fig 1.1

As indicated on Fig 1.1., research on materials and technology of electronics interface are indispensable to the development of chemical sensors. Both must be intimately combined in every process in order to produce a superior sensor system. For the advancement of sensor research, it is crucial to establish a guiding concept concerning the construction of the sensor device and achieve exact understanding of the sensing mechanism. Otherwise, results obtained by haphazard experiments may prove to be less useful in the development of chemical sensors.

The majority of these detection and metering devices involve the application of surface or bulk chemical and physical properties of materials, and can, therefore, be called solid-state chemical sensors [1,2].

Based on the sensing principles, gas sensors can be classified in three main categories:
• The solid-electrolyte-based sensors exhibit exceptionally high ionic conductivity at high temperature (in the range of 773 to 1573 K). These materials have only one mobile species and, in the case of oxide systems based on stabilized zirconia, they find wide applications, e.g. oxygen sensors.

• The catalytic combustion sensor is a device wherein the sensing material also acts as a heater. It consists of an active alumina beads with certain amount of highly dispersed catalyst (Pt, Pd, Rh, etc.), each bead mounted on a Pt coil. When a combustible gas is admitted and heated to about 673-723 K the evolved heat of combustion of the gas results in further rise of temperature of the sensing element which in turn increases its resistance. This resistance increase is then correlated to the concentration of the inflammable gas [3].

• The semiconducting-oxide gas sensors represent the most widely studied area of solid-state sensors and are based on the principle that adsorption of foreign species on a semiconducting surface provide surface states, and the electrical properties of these surfaces change as a result of adsorption and/or reaction [4,5].

Hence, one area that has witnessed relative success in gas sensor applications, and which directly concerns this research work, is the use of gas sensitive semiconductor resistors. Commercially, metal oxide sensors have been available for many years and the dominant manufacturer is Figaro Engineering in Japan. The type of metal-oxide sensor sold by Figaro is called the ‘Taguchi Sensor’, after the developer of the SnO2 sensor [1]. Commercial design generally achieve high surface-to-volume ratios of the active semiconducting elements through the use of thin layers consisting of highly porous aggregates of loosely sintered particles. Such layers can easily be prepared by printing or painting onto a substrate a dispersion of the oxide in an appropriate vehicle and subsequently dried and fired.

The operating mechanism, which will be described in details later in this chapter, is usually the change of the semiconducting oxide conductivity in the presence of a certain ambient reducing or oxidising gases. Specifically, the most important sensing
mechanism is likely to be the reaction of the gases with adsorbed oxygen on the surface of, e.g. ZnO or SnO$_2$ semiconductors. Sintered powders or thin-films are used because surface and bulk conductivities are always measured in parallel, which for a sensitive measurement requires a large surface-to-bulk ratio. Early sensors made of ZnO and SnO$_2$ oxide semiconductors exhibited resistances strongly dependent on the ambient hydrocarbon vapor concentration [6].

Despite the low selectivity and the high operating temperature semiconducting oxide gas sensors are quite popular for qualitative monitoring of combustible gases and as leakage detectors, mainly due to their simple fabrication and low cost. Conductance, the measured parameter, is essentially the surface conductance, since it is unlikely that the conductivity will be homogeneous throughout the semiconductor oxide film which explains why only relative conductivities or resistivities are important measurable quantities. Although, as mentioned previously, the original measurements were made using ZnO, most commercial gas sensors at present make use of SnO$_2$ sensing films because they offer higher stability and high sensitivity at lower operating temperatures [7]. Other metal oxides such as WO$_3$, Fe$_2$O$_3$, and Co$_3$O$_4$, have also showed similar gas-sensitive properties. TiO$_2$ has also been used commercially as a “thin-film” sensor, but in a temperature range where defect mobility is high. The devices themselves consist of thick or thin-film resistors operating at high temperatures (100 < T < 600°C) in order to undergo fast and reversible surface reactions. Use of mixed oxides such as perovskites-type oxide for semiconductor type sensor has also been studied extensively. Some of these mixed oxides may prove to be excellent and useful sensor materials by improving the donor-acceptor level, surface-level and surface reactivity, which strongly influence the sensing characteristics of this type of sensor.

1.2. Purpose of this study

Low selectivity, poor sensitivity at low gas concentration and a lack of clear understanding of the sensing mechanisms represent some of the problems associated with semiconductor sensors, and are yet to be resolved. Against this background, the
overall aim of this thesis was twofold. Firstly, the effects of antimony surface segregation (Chapter 3.) and particle size (Chapter 4.) of well-studied undoped and antimony-doped SnO₂ materials on gas response and catalytic activity were looked into. Theoretical calculations methods were also used (Chapter 5.) with regard to understanding the defect chemistry of antimony dopant. This study should contribute to a better comprehension of the chemical and physical mechanisms involved at the solid-gas interface. Secondly, compositional substitution effects on gas response, of new materials or materials which have not been routinely used for gas-sensing applications before, have been studied. Hence, systematic solid solution substitutions (Chapter 6. and 7.) and transition metal variation (Chapter 8.) were prepared as a strategy to identify potential material selection for sensor performance enhancement.

1.3. Band theory related to gas sensing

Most semiconducting oxides in the past have been considered to behave essentially as extrinsic (or impurity type) semiconductors as the thermal promotion of electrons from the valence band (VB) to the conduction band (CB) can be neglected over the temperature range studied. The way in which surface defects influence the overall electronic properties depends on the energies of the defect levels with respect to the band edges and on their electronic occupancy. These factors are especially significant with semiconducting materials, where both bulk and surface defects provide easily ionizable carriers. Hence, the electronic energy levels in the band gap are considered as “surface states” which can be donor (D) and acceptor (A). Fig 1.2. represents the band model of a semiconductor surface. \( E_C \) is the conduction-band edge, \( E_V \) the valence-band edge, \( E_i \) the mid-gap energy and \( E_F \) the Fermi energy. Fig 1.2a. shows the energy-band model when there is no charge exchange between the surface states and the semiconductor. The equilibrium case is described by Fig 1.2b. where electrons have moved from a region of high \( E_F \), the near surface region of the semiconductor, to a region of low \( E_F \), the surface states.
Fig 1.2. Band model of a semiconductor surface showing charging of surface species.

a) no charge exchange between the semiconductor and the surface states
b) "band bending" where electrons from the surface region move to the surface states

This separation of charge leads to a double-layer potential difference, which raises the energy levels at the surface represented by $E_{CS}$ and $E_{VS}$ the band edges at the surface. When the double-layer potential difference is high enough to make $E_F$ constant, an equilibrium is established. This movement of bands near the surface is called 'band bending'.

For non-transition-metal oxides, such as SnO$_2$ mobile charge carriers at the surface (electrons and holes) can interact with adsorbed molecules and can participate in surface reactions. The flow of these free carriers toward or away from the surface can establish a potential gradient between the surface and the bulk of the material that may determine the reactivity of the surface. The electrical double layer formed in Fig 1.2b. can be of three types:

- If extra electrons are injected into an n-type semiconductor an accumulation layer develops. This double layer is a surface region where carrier concentration is higher than in the bulk, and is associated with a downward bending of the bands at the surface (see Fig 1.3a.). This could be formed by a high concentration of surface O vacancies, leaving extra holes in the surface region.
• If electrons are extracted from the conduction band of an n-type semiconductor by an acceptor surface state, a depletion layer or space charge layer (especially important in gas sensing applications) develops at the surface. Here the double layer arises between the negatively charge surface states and the positive donor ions (immobile). This might also occur if the surface is covered with adsorbed oxygen such as $\text{O}_2^-$ or $\text{O}'$, which gives an upward bending of the bands (see Fig 1.3b.). The band-bending is caused by an unequal concentration of (positive) ionized impurity centers and (negative) electrons in the space-charge region. Such a space charge may also be induced by the application of an external electric field or by the presence of a charged layer on the surface, such as adsorbed ions or electronic surface states, which act as a source and sink of electrons.

![Fig 1.3. Types of surface double layers.](image)

- An inversion layer which is of little interest in gas sensing can also develop with n-type semiconductors when a very strong oxidising agent (acceptor surface state) adsorbs on the surface.

Chemisorption of many gases can influence surface conductivity, and this phenomenon is actually responsible for the use of semiconducting oxides as sensors.
14. Molecular adsorption on semiconducting oxides

1.4.1. Types of chemisorption

The ionic nature of the oxides is responsible for a predominance of donor/acceptor, or acid/base interactions. Oxide ions act as basic sites and can interact with acceptors such as H⁺. Cation sites which are Lewis acids may interact with donor molecules such as H₂O through a combination of electrostatics (ion-dipole attraction) and orbital overlap. The involvement of lattice oxygen is also very important.

1.4.2. Adsorption mechanisms

Firstly, it is obviously necessary to distinguish between dissociative and non-dissociative or molecular adsorptions. Secondly, a distinction between the type of interaction with the surface can be made:

- weak electrostatic implying physisorption.
- donor/acceptor or acid/base which do not involve electronic carriers.
- oxidation/reduction with electron transfer implying a change of the oxidation state of an adsorbate with the capture or release of an electron.
- oxidation/reduction with oxygen transfer.

1.4.3. Electronic interactions in chemisorption

Changes in the electronic structure of the surface are frequently important in chemisorption. The band-bending and alterations in surface conductivity occurring with some semiconducting oxides form the basis of gas sensor operation. Donor/acceptor interactions result from the overlap of a filled orbital on the donor with an empty one on the acceptor. This leads to the stabilization of the filled level, which is now shared between the two halves of the combined system. As can be seen in Fig 1.4., the empty orbital acquires some corresponding antibonding character and is raised in energy.
Fig 1.4. Interaction between the filled orbital of a donor (D) and the empty orbital of an acceptor (A), giving the molecular orbitals of the combined system (D:A)

Unlike the non-degenerate s levels that form the lower part of the band in non-transition-metal oxides, the d orbitals of transition metal oxides have five-fold degeneracy in the free ions. The d orbitals of surface cations can be divided roughly into $t_{2g}$ and $e_g$. Fig 1.5. illustrates what might happen when a donor adsorbs at a surface of a $d^0$ oxide. As early transition-metal cations have relatively few d electrons (including $d^0$ oxides such as TiO$_2$), only the $t_{2g}$ orbitals are occupied, and not much interaction between these orbitals and the adsorbates should be observed. With transition metals further along the series, $e_g$ orbitals may be occupied, and shifts in energies have been observed when adsorption occur.

In the case of non-transition-metal-oxides the empty cation orbitals which are of s and p symmetry should overlap strongly with adsorbate orbitals. Because of the larger conduction-band widths found in these oxides, a picture of localised electrons on particular cations is not appropriate; rather it is better to think about free carriers. Nevertheless, donor/acceptor interactions cannot change directly the number of free carriers and alter the surface conductivity.
Fig 1.5. Resulting perturbation in orbital energies arising from the adsorption of a σ donor molecule onto a d¹ ion at the surface.

Since the adsorption of molecules such as H₂O does appear to change the surface conductivity of SnO₂, their interaction with carriers must be indirect. It is believed that when electrons are bound in surface states below the Fermi level (Eₚ), interaction with the filled level of a donor could raise the energy of these states above Eₚ, releasing the electrons. An alternative possibility is that pre-adsorbed species such as O₂, which interact by redox mechanism that involve free carriers, may be displaced by the new adsorbate.

In contrast to the D/A type of interaction, the redox mechanism directly alters the electron configuration of the surface. In transition-metal oxides, reduction or oxidation of the surface by an adsorbate is expected to show up clearly as a change in population of the d levels. In ZnO and SnO₂, band-bending and changes in surface conductivity are expected. The transfer of charge to or from the surface also creates a substantial dipole, and large changes of work function can occur.
1.5. Operating mechanisms of semiconducting oxide gas sensors

Several physical processes can be involved in registering changes in the composition of a gaseous atmosphere as changes in the conductance of a semiconducting oxide. The mechanisms and models for gas sensitivity of semiconducting oxides have been explained by two different approaches [8]:

- Bulk conductance changes are, mostly, only sensitive to changes in \( p(O_2) \), and the oxide defect chemistry controls the sensor behavior as the bulk of the material tends toward equilibration with the ambient oxygen pressure.

- Changes in surface conductance involve sensing small concentration of reacting gases in the presence of ambient oxygen in air. For reactive gases in air combustion occurs on the surface of the sensor and the gas phase is not at equilibrium. The measured signals depend on diffusion and reaction conditions at or near the interface between the gas and the sensor and within the porous sensor mass.

1.5.1. The bulk conductivity mechanism

Materials that respond to changes in oxygen partial pressure at high temperature (700°C and above) are reflecting the equilibrium between the atmosphere and their bulk stoichiometry. The combustible gas, if chemically active, extracts a lattice oxygen from the metal oxide, leaving vacancies that act as donors. The oxygen from the air tends to re-oxidize the metal oxide, removing the donor vacancies. Thus, there is a competition between the oxygen removing donor vacancies and the combustible gas producing donor vacancies. The density of donor vacancies, and hence the resistance, then depends only on the concentration of combustible gas because the oxygen pressure is constant when operating in air for example.

For a non-stoichiometric oxide, such as TiO\(_2\), the electrical conductivity is related to the carrier concentration via:
where $\mu$ is the electron mobility, $n$ is the number of charge carriers and $q$ is their charge. In the presence of ambient oxygen of partial pressure $p(O_2)$, the relation giving the dependence of conductance on oxygen partial pressure can be expressed as:

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right)p(O_2)^{1/n}$$

where $T$ is the temperature in Kelvin, $E_a$ is an activation energy, $k$ is the Boltzmann's constant and the sign of $n$ depends on the charge balance in the lattice and on the stoichiometry of the reaction taking place. Thus, at a given temperature, the resistance of TiO$_2$, is a function of $p(O_2)$ alone. TiO$_2$ was first used by Ford Motor Co.[9], followed by Nissan Motor Co [10] for internal combustion engine applications.

Two factors contribute to $E_a$: the thermal activation of charge carriers into the conduction band; and the energy required to form the defect which can be directly linked to the change in number of charge carriers in the conduction band. Hence, reduction processes at the surface of a TiO$_2$ sensor produce oxygen vacancies, $V_{O}^{-}$, and titanium interstitials $Ti_{I}^{++}$. The relative importance of these defects in signal generation depends on temperature bearing in mind that oxygen vacancies dominate below 1000°C. The solid state chemistry can be described by the following reactions using the Kroger-Vink notation:

$$2Ti_{I}^{x} + O_{O}^{x} \rightarrow 2Ti_{I}^{+} + V_{O}^{+} + 1/2O_2 \quad (1.3)$$

$$2[2Ti_{I}^{+} \rightarrow Ti_{I}^{x} + e'] \quad (1.4)$$

$$O_{O}^{x} \rightarrow V_{O}^{+} + 2e' + 1/2O_2$$

Here, equation (1.3) represents the creation of a donor state, a reduced titanium atom and (1.4) represents the activation of an electron ($e'$) from the donor state to the conduction band.
1.5.2. The surface conductance effects

The second major category of gas detection for which semiconducting oxides are employed involves their use in an atmosphere of fixed partial pressure of oxygen to detect small concentrations of potentially hazardous gases. This category of metal oxides actually refers to all of the materials studied in this thesis. Conductivity changes induced in semiconducting oxides as a consequence of the presence of small concentrations (ppm levels) of reactive gases in air (large excess of oxygen) are presumed to be caused by non-equilibrium changes in surface coverage of ionized oxygen species which act as electron acceptor states at the surface. The mechanism described in section 1.5.1. can not explain this observation, since the oxygen partial pressure would not be sensibly changed under this circumstance and the materials are normally held at temperature in the range 300-500°C, where useful surface reactions proceed at sufficient rate. This mechanism seems to be controlled by surface processes which are not at equilibrium with the bulk, as there is no mobility of ionic species in the bulk. Most sensors that have so far been developed to detect reducing gases by exploiting surface reactions on semiconducting oxides have made use of tin dioxide as the active element.

1.5.2.1. Surface combustion model

Analysis of oxygen adsorption

For oxides the overall stoichiometry has a decisive influence on the surface conductivity. Oxygen vacancies left after surface reactions can diffuse toward the bulk, increasing the conductivity near the surface. Adsorbed oxygen ions act as surface acceptors, binding electrons and diminishing the surface conductivity. Fig 1.6. represents the various oxygen species relevant to surface reactions.

At room temperature the equilibrium of the \((O_2)_{ads}\) coverage with gaseous \(O_2\) is approached slowly, although the reaction is exothermic. On \(SnO_2\) reaction takes place with increasing temperature as observed from EPR studies [11]:

18
Above 450K, O$_{ads}$ ions are found to be the prevailing species. At constant oxygen coverage, the transition causes an increase of surface charge density with corresponding variations of band bending and surface conductivity.

As oxygen is adsorbed, the electrical double layer is formed in the n-type semiconductor, with the negative layer being the adsorbed oxygen, and the positive charge being the bulk donors that have given up their electrons. Thus, a potential barrier to charge transport is developed as the charge carrier density at the interface is reduced since the electrons come from ionized donors via the CB (see Fig 1.3b.). Adsorption of oxygen is inhibited as the surface charge is developed. As the total charge in the space-charge layer must equal the charge on the adsorbed oxygen, the density of electronic charges on the surface, $N_D$, can be expressed as such:

$$N_S = N_D x_o$$
where \( N_D \) is the donor density in the material assuming immobile donors, and \( x_o \) is the thickness of the space-charge layer which represents the electron depleted region. The conductivity is modelled by first solving Poisson’s equation in one dimension:

\[
d^2 \phi / dx^2 = -qN_D / \varepsilon \varepsilon_0
\]

(1.7)

where \( \phi \) is the potential relative to the bulk potential. As shown in Fig 1.3., \( \phi = 0 \) at \( x = x_o \) (in the bulk), decreasing to \( \phi_s \) at the surface. After integrating twice (1.7.) becomes:

\[
q \phi = -(qN_D / 2\varepsilon \varepsilon_0)(x_o-x)^2
\]

(1.8)

If the boundary conditions are expressed as \( \phi = 0 \) and \( d\phi / dx = 0 \) at \( x = x_o \), then at the surface \( (x = 0) \):

\[
q \phi_s = -(qN_D / 2\varepsilon \varepsilon_0)x_o^2 / 2\varepsilon \varepsilon_0
\]

(1.9)

where \( \phi_s \) is the surface potential relative to the bulk. From (1.9.) and (1.6.)

\[
q \phi_s = -(qN_s / 2\varepsilon \varepsilon_0)N_D
\]

(1.10)

which gives the barrier height as a function of the density of adsorbed oxygen. Equation (1.9.) and (1.10.) form the Schottky equation. The density of carriers at the surface \( n_s \) is given by the Boltzmann factor as

\[
n_s = N_D \exp(q\phi_s)
\]

(1.11)

As described previously, the oxygen will adsorb to an equilibrium value such that the energy of the oxygen level is near the Fermi energy, which means that the Fermi energy describes the occupancy of the electrons on the \( O_2/O_2^+ \) level at an energy \( E_{O_2} \). As the concentration of \( O_2 \) represents the concentration of physically adsorbed oxygen, it should, in principle, remain constant if the oxygen pressure and temperature are constant. From Fermi statistics:

\[
[O_2^+]/[O_2] = \exp[-(E_F-E_{O_2})/kT]
\]

(1.12)

where \( [O_2^+] = N_s \), the charge concentration at the surface, and \( E_{O_2} \), is the energy level associated with the \( O_2^+/O_2 \) redox couple. From equations (1.9.) and (1.12.) an expression for \( x_o \), the thickness of the depletion layer at the surface can be obtained which can be related to the conductance change due to the layer depleted of current carriers. Hence, the conductance of a thin-film sample can be estimated by:

\[
G = \sigma(Wt/L)(1-x_o/t)
\]

(1.13)
where \(\sigma\) represents the conductivity, \(t\) the thickness, \(L\) the length and \(W\) the width assuming only one side is exposed to atmosphere. Hence, if \(x_o\) is close to \(t\), the conductance will be sensitive to \(x_o\). From Eq. 1.13. we obtain:

\[
dG / G = -dx_o/(t-x_o)
\]

(1.14.)

From (1.14.), it is clear that in the presence of a reducing agent, the value of \(N_S\) varies with the partial pressure of the agent and \(x_o\) varies with \(N_S\).

**Electrical properties of compressed powders in air**

The quantitative description of resistance for a compressed powder is very complex and a semi-quantitative approach seems to be more appropriate. The best description of conductance for sintered powder consists of grains of powder connected by ‘necks’ where the grains have fused [2]. From Fig 1.7. a semi-quantitative model for powder conduction with a pressed pellet can be derived. Each grain has a surface barrier (depletion region) at the surface which must be overcome if electron are to move from grain to grain. The activation energy is given by \(-q \mathcal{V}_S\), and if it is assumed that the surface barrier \(-q \mathcal{V}_S\) is the same for all particles, and that the variations in the contact area and number of intergranular contacts appear are expressed in the linear term \(G_o\), then from Eq. (1.14.):

\[
G = 1/R = G_o\exp(q\phi/kT)
\]

(1.15)

Sensitivity arises because electrons must overcome the barrier \(q\phi_S\), therefore, the conductance varies exponentially with the barrier height.
Typically, SnO$_2$ is a wide-band-gap (around 3.6 eV) n-type semiconductor in which the predominant charge transport is by conduction band electrons resulting from non-stoichiometry of the form SnO$_{2-x}$. In air, the surface of the oxide is populated by a variety of chemisorbed and physisorbed species such as O$_2$, H$_2$O, OH$^-$, O$_2^-$, O$^{2-}$ and O$^-$ dependent upon the conditions. The presence of such species is believed to control the electrical conductance of the oxide via their effect on the occupancy of the surface states particularly near grain boundaries which mechanisms have been discussed previously. Hence, the electrical conductance in air of the oxide in a pressed pellet form is a complex and variable function of the sample temperature. Significant hysteresis in the behaviour is observed, with strong evidence of dependence upon the sample history and upon whether the temperature is increasing or decreasing inducing morphological changes. For commercial sintered sensors made from SnO$_2$, the air conductance-temperature relationship shows much less pronounced sigmoid
behaviour and little hysteresis. Therefore, the differences between the behaviour of SnO$_2$ in sensor applications and in the pressed form can be systematically reduced by sintering in air.

The sigmoid conductance temperature characteristics obtained in Fig 1.8, which represents the resistance vs. $1/T$ of an SnO$_2$ pellets in a stream of dried air showing a pronounced difference between the first (A) and the two subsequent (B and C) temperature cycles (ramping temperature from 20°C to 700°C and back to 20°C). Once the temperature rises above 500°C in cycle (A), water is lost from the pellet, and the subsequent behaviour therefore is that of the dry material. The resistance rise in (A) above 370°C is due to the loss of water and the resistance fall on the decreasing temperature (A) cycle is due to the readsoption of water. For the B and C cycles the resistance behaviour can thus be attributed to a typical dry material.

**Fig 1.8.** In $R$ vs $1/T$ for a SnO$_2$ pellet (in synthetic dried air) ramping up temperature from RT to 700°C and back to RT.
It has been observed that regardless of the atmosphere under which the measurements are made, the activation energy in low temperature region is significantly lower than at higher temperatures. Increasingly severe pre-sintering results in higher activation energies in both temperatures regions. It has been suggested that the electrical conductance of SnO\textsubscript{2} is likely to be controlled by Schottky barriers in samples subjected to less than 24h pre-sintering at 1273 K. Under such a regime, charge transport across the intergrain boundaries may be treated as an activated process characterised by an effective activation energy related to the coverage and charge of the chemisorbed species.

**Interaction of combustible gases with adsorbed oxygen**

The oxygen coverage saturates because the adsorption rate decreases with increasing coverage, since charges have to be transferred to the adsorbate over the surface barrier. The resistance of the material is then dominated by high resistance contacts between grains. A surface-catalyzed combustion might take place when a reactive gas is present, reducing the coverage of oxygen species on the surface. This would result in a resistance decrease due to the reduction of the depletion length and the surface potential barrier height. Two equations relating the donor density \( N_D \), the charge \( q_S \) associated with oxygen surface coverage, the width of the depletion layer \( x_o \) or \( L \), and the surface barrier height \( \Delta \phi_S \) can be expressed as:

\[
L = \frac{q_S}{N_D e} \\
\Delta \phi_S = \frac{q_S^2}{2 \varepsilon \varepsilon_0 e N_D} \quad (1.16)
\]

For p-type oxides, as the current is carried by VB holes, more carriers will be generated as electrons move to the adsorbed oxygen and the conductivity will rise. Hence, any decrease in the oxygen coverage will lead to an increase in resistance as a decrease in the charge carrier concentration is observed. As such, the surface coverage of oxygen is not limited by the supply of electrons and does not result in a barrier to charge carrier transport.
Any target gas that shifts the surface oxygen concentration away from its equilibrium changes the resistance of the material. Operationally, at this stage, it is necessary to introduce the concept of classification for n-type or p-type materials (see Table 1.1).

Table 1.1. Classification of semiconducting oxide materials

<table>
<thead>
<tr>
<th></th>
<th>Oxidizing conditions (increase of oxygen)</th>
<th>Reducing conditions (decrease of oxygen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance rises</td>
<td>Resistance falls</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance falls</td>
<td>Resistance rises</td>
</tr>
</tbody>
</table>

As mentioned previously any adsorbed oxygen species will pick up electrons to form O$_2^-$, O$^{2-}$ or O'. Thus, if the current is carried by valence-band holes (p-type conductivity) there will be more charge carriers as electrons move to the adsorbed oxygen and the conductivity will rise. On the other hand if the current is carried by conduction-band electrons (n-type conductivity) fewer carriers will be generated and the conductivity will fall. The initial adsorption of oxygen on an n-type material leads to high resistance and its removal by reducing gas lowers the resistance. Hence, overall, the choice of semiconducting materials for gas sensors relies mainly on n-type materials rather than p-type, which are relatively unstable because of their tendency to easily exchange lattice oxygen with air.

The chemical steps involved in the oxidation of combustible gas such as CO by adsorbed oxygen can be very complex. The dependence of conduction on gas partial pressure of metal oxide gas sensors has been expressed as follows:

$$
\sigma \propto p(R)^\beta
$$

where $p(R)$ is the partial pressure of the combustible gas $R$, and typically $0<\beta<1$.

The response model to a non-equilibrium gas mixture has been expressed as the dependence of the surface state occupancy, $\theta$, on $p(R)$.

Based on electron-spin resonance studies, the active adsorbed species appears to be O$^-$, which are believed [13] to be more active than O$_2^-$. Experimentally [14,15], it has been observed that on SnO$_2$, ZnO and TiO$_2$ at high temperature the catalytically
active O\textsuperscript{-} form becomes dominant. At moderate oxygen pressure O\textsuperscript{-} becomes the dominant species at 150\degree C for SnO\textsubscript{2}, 180\degree C for ZnO and 400\degree C for TiO\textsubscript{2} [16]. Hence, for these materials, a gas sensor will probably be possible only for temperatures above those listed. Until now, for these three oxides no low-temperature (room temperature) sensors have been reported, apart from surface-modified forms (e.g. SnO\textsubscript{2}-Pt) for which the response mechanism is different [17].

In the case of an n-type semiconducting oxide, such as SnO\textsubscript{2}, the chemistry taking place at the surface can be modeled by two main reactions. A simple model for a catalyst-free surface has been described in [18]. In the first reaction, atmospheric oxygen becomes chemisorbed to the surface consuming electrons

\[ \frac{1}{2}O_2 + e^- \xleftrightarrow[k_i^o]{k_i^{-1}} O^- (ads) \]  

(1.18.)

The ionosorption of oxygen results in a decrease in conductivity whose largest effect is observed at contacts between grains of sintered powder (grain boundaries). The reducing gas, R, present in the ambient air produces a counter reaction

\[ 2R + O^- (ads) \xrightarrow{k_2^o} 2RO + e^- \]  

(1.19.)

where e\textsuperscript{-} is a conduction electron. The reducing gas removes the chemisorbed oxygen, frees up an electronic carrier and raises the conductivity of the sensor. These two irreversible reactions which act in opposite directions eventually reach a steady-state.

The fractional surface coverage \( \theta \) of ionised oxygen species and the total rate of combustion can be expressed as such:

\[ \theta = k_1p^{1/2}(O_2)/[k_{-1} + k_1p(O_2) + k_2p^2(R)] \]  

(1.20.)

rate = \( k_2\theta p^2(R) \)

A condition for sensitivity to the partial pressure of the combustible gas is then:

\[ k_1p(O_2) \ll k_2 \text{ and } k_{-1} \ll k_2p(R)^2 \]  

(1.21.)

which means that the rate of combustion is fast in comparison with the rates of adsorption and desorption. Although this model seems to describe the observed response well enough, it clearly oversimplifies the surface chemistry mechanisms.
1.5.2.2. Model for conductivity

Some materials show p-type response to some reducing gases and n-type to others, and some materials can show a change in sign of response with increasing concentration of the reducing gas. These effects have been observed by systematic substitution into the lattice of complex oxides. Assuming a small enough grain size, a low enough bulk donor density and a surface acceptor state density high enough that the grain are fully depleted of conduction electrons, a simple model has been developed by Williams and Moseley [19]. It is demonstrated that the conductivity goes through a minimum with increasing surface density of acceptor states. The model rationalises the observed pattern of response behaviour to different gases by different materials: a systematic change in response pattern with change in the volume density of electron-donor states in the solid is predicted. The conductivity variation has been conventionally interpreted [8] as follows: the charge transport seems to be controlled by Schottky barriers at grain junctions. The barrier arises as a consequence of electron transfer from bulk donor states to surface acceptor states, usually formulated as chemisorbed oxygen species. Nevertheless, a ‘surface-trap limited’ conductivity could be observed if the bulk donor density was low enough which would result in grains fully depleted of conduction electrons. The consequences of this condition are described below.

Hence, if $N_S'$ is the acceptor state density per unit area, $D$ the average radius of gas-exposed domains of the solid, then the acceptor state density per unit volume of the solid, $N_S$ is

$$N_S = (3/r)N_S'$$

(1.22.)

Complete depletion of the grain would arise if $N_D \ll N_S$, where $N_D$ is the bulk donor density. Taking into account the equilibrium between gaseous oxygen and surface oxygen ions, the Debye length, or depletion layer thickness, $L$, can be calculated. The surface coverage and depletion layer thickness reach a limit, $L$, as the surface potential develops and further adsorption of oxygen is inhibited. As stated previously $L$ can be expressed as such:

$$L = \left(\frac{2\varepsilon\varepsilon_0 k_B T}{e^2 N_D}\right)^{1/2}$$

(1.23.)
The condition for complete depletion of the grains can now be written

\[ L > D \]  \hspace{1cm} (1.24.)

Considering the surface-trap-limited case the carrier concentration can be determined by:

1) ionization of surface acceptors

\[ S^- \rightarrow S + e' \]

\[ K_1 = N_c \exp(-\Delta E_s / k_B T) = (1 - f_s)n / f_s \] \hspace{1cm} (1.25.)

\[ \Delta E_s = \text{surface acceptor ionisation energy} \]

\[ f_s = \text{fraction of surface acceptors with trapped electrons} \]

2) ionization of donors

\[ D \leftrightarrow D^+ + e' \]

\[ K_2 = N_c \exp(-\Delta E_D / k_B T) = f_D n / (1 - f_D) \] \hspace{1cm} (1.26.)

\[ \Delta E_D = \text{donor ionization energy} \]

\[ f_D = \text{fraction of donors ionized} \]

3) thermal excitation of carriers from the valence band

\[ X \leftrightarrow h^* + e' \]

\[ K_3 = N_c \exp(-\Delta E_G / k_B T) = pn \] \hspace{1cm} (1.27.)

\[ \Delta E_G = \text{band gap} \]

\[ N_c = \text{density of states at conduction band edge} \]

\[ n \text{ and } p \text{ are the concentration of electrons and holes respectively} \]

4) conductivity

\[ \sigma = \mu_e en + \mu_p e p \] \hspace{1cm} (1.28.)

\[ \mu_e \text{ and } \mu_p = \text{electron and hole mobilities respectively} \]

\[ e = \text{electron charge} \]

5) charge balance

\[ p + f_D N_D = f_S N_S + n \] \hspace{1cm} (1.29.)

Using the previous equations:

\[ n^4 + n^3 \left[ N_S + K_1 + K_2 \right] + n^2 \left[ K_2 (N_S - N_D) + K_2 K_1 - K_3 \right] \\
- n \left[ K_3 K_2 + N_D K_3 K_1 + K_3 K_1 \right] - K_1 K_3 K_3 = 0 \] \hspace{1cm} (1.30.)

which can be simplified since the assumption is that \( N_S \gg N_D \), \( n \) is small and as generally \( K_3 \ll K_1 \ll K_2 \).
\[ n^2 K_2 N_S - n N_D K_2 K_1 \approx 0 \]

i.e.

\[ n \approx K_1 N_D / N_S \quad (1.31) \]

and

\[ p = K_2 N_S / K_1 N_D \]

The conductivity can then be expressed in terms of the surface acceptor state density, using equation (1.28.) and (1.31.)

\[ \sigma / e = \mu_e K_1 N_D / N_S + \mu_p K_2 N_S / K_1 N_D \quad (1.32.) \]

Change in the surface acceptor state density could be caused by the effect of the non-equilibrium process of interaction, with the surface, of the gas present at low concentration in the air. Thus, the conductance type (n or p) and the magnitude of response can be determined by the relative concentration of donor and acceptor states. Selectivity tends to occur under conditions where the material is in a transition zone between n-type and p-type behavior, where the variations in concentration of surface oxygen species has little effect on the conductivity and where the effect of specific surface coordination reactions might be observed. Indeed early work made predictions that around the transition from n- to p-type behaviour there should be changes in sign of response with increasing gas concentration, or improved specificity of response, or a distinction between responses, which were not mediated by adsorbed oxygen and those that were. These predictions will be tested in the present work (chapter 6. 7. and 8.), and a formalism will be developed to derive some further insight from the results.
1.6. What Parameters Affect the Selectivity and the Sensitivity of the Gas Response?

The two main problems with most semiconducting oxide gas resistors are their poor sensitivity at low gas concentration and mainly their lack of selectivity. Thus, most metal oxides appear to respond to a wide spectrum of reducing gases, thereby making difficult to assign the signal to a particular gas of interest in a mixture of several. The question is, therefore, whether by choice of oxide materials or some other means, selectivity can be enhanced. Many methods have been tried to solve this problem such as the use of:

- filters where only the gases of interest can reach the sensor while the others are adsorbed [20].
- thermal cycling of the sensor element [21].
- promoters and catalysts such as Pt, Pd [22] and Pd/Au [23].

In this work the effects of microstructure and stoichiometry, combustion gradients, surface segregation on gas response have been explored as well as systematic cation substitution in solid solution compounds as a route to understanding the surface chemistry mediating the selectivity and the sensitivity of the gas response.

1.6.1 Microstructure

As previously mentioned, a gas to be detected is adsorbed on the surface or may react with the reactive surface oxygen of the semiconducting oxide. This induces a change in the surface space layer, which is then converted into a change in electrical resistance of the polycrystalline elements. The gas recognition is carried out through the surface chemical processes, or, more specifically the adsorption sites or reaction sites play the role of receptor for gases.

On the other hand, the physical processes associated with the transport of electrons are responsible for the conversion of such an interaction to the electrical resistance change. This propriety is controlled not only by the semiconductive properties of the oxide but also by the microstructure of the element such as the grain size of the
particles relative to the Debye length and the geometry of the connection between particle [24].

Hence, so far the surface chemical processes have been investigated thoroughly, but the processes concerned with transducer function (by opposition with receptor function associated with gas recognition) have not been very well studied due to the complexity of practical polycrystalline elements. A characteristic change in behavior of electrical resistance at critical crystallite size, has been observed and interpreted [25] as the formation of an electron-depleted charge layer on the particles. The proportion of space charge region in each particle decreases with increasing $D$, since the thickness ($L$) of the space charge layer is kept constant. The critical value of $D$ has been assumed to be related to a stage where $D = 2L$. For $D > 2L$, the depletion is not so much dependent on the particle size and takes place on the surface only. On the other hand, for $D < 2L$ where the whole region of the particles is depleted of electrons, the degree of depletion will be mitigated sharply as $D$ increases.

To try to understand these phenomena, one must look into the microstructure of polycrystalline elements. The geometry of contacts between particles is important as the phenomenon is related to electron transport. Hence, it has been showed that necks form between particles. A model described in Fig 1.9. consisting of a large number of necks and a small number of direct grain boundary contacts has been widely accepted.

Three cases have been differentiated:

- $D < 2L$ (grain control). Each particle is included in the space charge region. Electron transport inside the particle becomes dependent on the surface effect.

- $D = 2L$ (neck control). Each channel is narrow enough to be resistive to the electron conduction. The neck size-dependent sensitivity is due to fact that the resistance of the materials is controlled by the resistance of the necks, which are in excess compared to the grain boundary contacts.
• $D >> 2L$ (grain boundary control). The resistance at grain boundary contacts determines the whole resistance which leads to a gas sensitivity independent of $D$.

![Diagram showing grain boundary control (open neck) and neck control (closed neck)](image)

**Fig 1.9.** Model for conductance accounting for the grain size effects. Unshaded part shows core region (low resistivity), while the shaded region indicates space charge region (high resistivity)

### 1.6.2. Temperature

The temperature is an important factor because some gas (e.g., alcohols or CO) are easier to oxidise than others (e.g., CH$_4$ and alkanes). Thus, a low temperature would induce selectivity toward alcohols or CO, and a high selectivity towards CH$_4$.

### 1.6.3. Combustion Gradients

Regardless of the mechanism proposed for a gas response of the conductance, it is clear that, at the elevated temperature necessary to observe such a response, a surface-catalyzed combustion of the gas being measured occurs. The sensor response, determined by the gas composition in the vicinity of the sensor surface, is dependent
upon the relative rates of diffusion in the gas phase and chemical reaction on the surface [26]. It has been suggested [27] that the effect of combustion on sensor response is dependent upon the rate of combustion and reaction of the gas within the porous pellet. Differences in the surface-catalyzed reaction rates of gases might, therefore, be exploited to give a selective gas response [8].

Thus, the porous body would contain on its outside a combustion zone which would become narrower as the temperature increases. This implies that the combustion of the gas results in a concentration gradient [8] within the sensor and that if the combustion rate is high enough, all the gas is burnt in a thin outer shell of the device. Hence, if the rate of the surface combustion reaction is approximated as

\[ \text{rate} = kp_{\text{gas}} \]  

(1.33.)

then, the diffusion profile will have a characteristic dimension (reaction depth).

\[ x \approx \left( \frac{D'}{k} \right)^{1/2} \]  

(1.34.)

where \( D' \) represents the effective diffusion coefficient (the diffusivity) of the gas within the porous structure.

Although the combustion process occurs only on the surface, if the pore size is small enough and the surface area is great enough, it effectively takes place throughout the volume. Hence, the effect of the profile of gas concentration developed is to divide the sensor element into two parts: the exterior part where the conductance changes in response to changes in the ambient gas concentration and the interior part which is ineffective since the gas concentration is very low. It has been observed [28] that in a porous sensor layer, a diffusion profile with a characteristic reaction depth could be established. This diffusion profile is controlled by the pore structure of the material. A less reactive gas would reach the center of the pellet and cause conductivity changes, whereas a reactive one would have little effect, burning on the outside. It was then proposed that it would be possible to promote selectivity in the response for a less reactive gas over one that is more reactive.
1.6.4. Composition

In order to address the problem of selectivity enhancement by the choice of oxide materials, an experimental programme was carried out [27] to investigate the response of several hundred different oxides to a range of gases. Discussing this, it has been pointed out [2] that although the gas-sensing phenomenon appears to be intimately connected with the occurrence of a surface-catalysed combustion, the notion of selectivity in a gas sensor is different to that of the apparently related notion of selectivity in a catalyst. For a catalyst, selectivity means a bias in favor of a particular product, often in a complex mixture of potential reactants, whereas for a gas sensor selectivity refers to a bias in favour of a particular reactant.

1.6.4.1. Solid Solution Substitutions

Solid solutions are very common in crystalline materials. A solid solution is basically a crystalline phase that can have variable composition. In substitutional solid solutions, the atom or ion that is being introduced directly replaces an atom or ion of the same charge in the parent structure. For a range of substitutional solid solutions to form, there are certain requirements that must be met. Firstly, the ions that replace each other must have the same charge. Secondly, the ions that are replacing each other must be fairly similar in size. Furthermore solid solution formation is very dependent on the temperature, and for oxide systems extensive solid solutions often form at high temperatures whereas at lower temperatures these may be more restricted or practically non-existent.

Certain materials properties such as conductivity and ferromagnetism have often been modified by changing the composition in such a way that solid solutions form, which can be used in designing new materials with specific characteristics. In systems that exhibit complete ranges of solid solutions, it is essential for the two end-member phases to be isostructural. The reverse is not necessarily true, however, and because two phases are isostructural does not imply that they form solid solutions with each other.
It has been shown [27] that for a series of transition-metal tantalates (FeTaO₄ and MTa₂O₆, M = Co, Ni, Cu) the temperature of maximum response varied with the transition-metal cation. Substitutions in barium stannates onto the tin sites increased the resistivity and decreased the magnitude of gas response and the range of gases that responded. Systematic cation substitution in solid-solution compounds materials as a way of understanding the gas response mechanism linked to the surface chemistry has been previously looked into in Cr₂₋ₓTiyO₂₋ₓ [28,29], BaₓFeₓNb₁₋ₓO₃₀ [30] and FeNbO₄-CrNbO₄-TiO₂ [31]. The effects of substitution have simply been understood as a consequence of a decrease in bulk donor concentration. Over a particular range of bulk donor concentration, where the behavior is changing from n-type to p-type, the conductivity has been observed to be relatively insensitive to changes in the surface acceptor concentration and, consequently, to the presence of gases in the atmosphere.

1.6.4.2. Dopant Concentration

To be of any interest for gas sensing applications the electrical resistivity of the metal oxides prepared needed to be < 10⁹ Ω.cm⁻¹ at room temperature with the instruments used. The conductivity of extrinsic semiconductors may be accurately controlled by monitoring the concentration of the dopant. Material with desired values of conductivity may therefore be designed. Further more solid-state doping can alter the density and type of majority charge carriers dramatically.

If a new transition metal ion is introduced into a material, the carrier density will change due to substitutions which will force a valency change in order to maintain the electroneutrality of the system. Hence, if for example, Sb⁵⁺ is substituted into SnO₂, Sn⁴⁺ species will be partly reduced to Sn²⁺ as a way to obtain the charge balance. If we consider the system Sn₁₋ₓSbxO₂, there will be two oxygen sites associated with every Sn site. As an Sn site may be occupied by Sn or Sb, each Sb introduces a positive charge resulting in a reduction from Sn⁴⁺ to Sn²⁺ for two Sb. Using the Kroger-Vink notation this can be expressed as such: (SnSnₓ (SnSn⁴⁺)SnSn⁴⁺)SnSn⁴⁺SbSbO₁₋₂. The Sn(II) species (SnSn⁴⁺) acts as an electron-donor state, causing the resistivity to fall.
1.7. Computational Methods

1.7.1. Introduction

Computational methods are now a central technique in solid state science. The field has changed qualitatively in recent years with the focus moving from reproduction of experimental data to detailed predictive calculations on highly complex systems. Computational solid state chemistry employs the full range of techniques available to the computational chemist and solid state physicist. The programmes used for this thesis employ simulations which are based on an effective potential which subsumes knowledge of electronic structure into a numerical or analytical function describing the variation of the total energy of the system with the positions of the nuclei. Such potentials may be used in energy minimisations and in Monte Carlo and molecular dynamics simulations. The first allows a determination of minimum energy for surfaces, sorbed molecules, defects and crystals, but is limited by the lattice static approximation. The second allows ensemble averages and their variation with temperature to be studied and the third yields full dynamical detail albeit for a limited time period. The simulation methodologies are now well established and the crucial factor limiting progress concerns the accuracy of the inter-atomic potentials.

Theoretical modelling of structure is especially important in the context of defects and surfaces because of the difficulties involved in experimental structure determination. Theoretical models may be divided into two broad classes:

- Those based on a quantum-mechanical calculation of the total energy
- Those using a parameterised interaction potential between ions

Such potentials may be empirically based, but the distinction between the two classes of theory is not absolute, because parametrised models sometimes use inter-ionic potentials derived from quantum mechanics. For all these calculations the goal is to predict the most stable structure by finding the atomic configuration which minimises...
the total energy. Nowadays, advances in computational power combined with efficient and accurate codes are now making serious \textit{ab initio} calculations, using either local-density or Hartree-Fock formalisms which make it possible to treat systems with many structural parameters.

The qualitative success of the ionic model suggests a parametrised scheme for calculation, using an inter-ionic potential that includes long-range Coulomb and short-range repulsive components. These ions have to be treated as polarisable entities in order to obtain accurate data. The most fully developed model in this field is the shell model, since the ionic polarisability is incorporated by simulating each ion as positively charged core, connected to a negative shell by a spring. Both the distribution of charge between the core and the shell, and the force constant of the spring, are treated as parameters whereas the total (core+shell) charge is the normal ionic one. Other parameters are responsible for the short-range forces (overlap repulsion plus dispersion), and a full parameter set may be obtained by fitting various properties of the ideal bulk solid such as: elastic, vibrational and dielectric properties, possibly supplemented (especially for short-range forces) by an appropriate quantum-mechanical calculation. Once the parameters are known, the energy of any configuration of ions may be calculated.

Further more the importance of crystal surfaces and interfaces in many phenomena such as, corrosion, catalysis, and electrode processes has stimulated theoretical and experimental studies. Computer simulation techniques analogous to those used in studying the defect and bulk properties of solids can be applied to the calculation of the properties of both defect and perfect surfaces. Modern experimental techniques such as LEED, ion scattering etc. have renewed interest in the structure of perfect surfaces. Hence, theoretical simulations can play a role in trying to interpret the experimental data. Usually, calculations can bring information on the stable ionic configuration at the surface and calculate the basic thermodynamic properties, such as surface energy, that are difficult to determine reliably by experiment. Calculations on the perfect surface are necessary precursors to investigations into the defect structure including surface irregularities such as point defect properties, adsorption and surface segregation of bulk impurities. Static lattice calculation of this type can be related to
the thermodynamic properties and structure of the crystal at absolute zero temperature if we neglect the zero point vibration. Calculations of properties at higher temperature strictly require inclusion of the dynamical effects.

Nevertheless, there is an important limitation to these calculations. It must generally be assumed that ions do not change in electronic configuration, and that other electronic effects can be neglected. Unusual species such as $O^-$ which may be common on surfaces are not easy to treat, and so far for these reasons the types of defect configuration that have been treated are rather limited.

1.7.2. MARVIN (Minimisation and Relaxation of Vacancies and Interstitials for Neutral Surfaces) Program

1.7.2.1. Introduction

MARVIN [32] is a program used to model 2-dimensional surfaces and interfaces and which performs an energy minimisation calculation at 0 K. The programming language for MARVIN is "C". There are several types of simulations that can be performed with this program which include the prediction of surface structure, docking of molecules on surfaces, crystal morphologies, atomic force microscopy (AFM) imaging process and neutral clusters (see Fig. 1.10.).
2.4.2.2. Theoretical Model

MARVIN uses a small finite number of atoms that are duplicated in two dimensions instead of treating the infinite crystal surface as an infinite number of atoms. The simulation cell is the basic component of the program and has planar 2D periodic boundary conditions parallel to the interfaces. The 2D lattice vectors are used to generate the surface by being applied to the coordinates of each atom within the small finite cell as can be seen in Fig 1.11.

The coordinate system has been chosen such as the z axis is normal to the surface. The cell can be divided into lots of blocks, which are split into two regions (I and II). Each of the atoms can be formed of more than one particle. Thus, in region I the atoms are relaxed until there is zero force on each of them whereas those in region II are kept fixed rigid to reproduce the potential of the bulk lattice on region I.
Fig 1.11. Schematic of the MARVIN simulation model. The simulation cell is repeated infinitely in the x and y directions. The region I atoms are allowed to relax whilst those in region II are kept fixed.

The total energy of the system which is the most important quantity that MARVIN calculates represents the total energy that is minimised for static lattice calculations, and the gradient of the total energy is used for dynamics and the more sophisticated minimisation algorithms. It can be defined as the energy of the entire region I structural units, which interact with themselves, all the region II structural units and the periodic images of both regions. The contribution to the total energy can be divided into terms depending upon the number of atoms needed to determine the interaction. Hence, for each atom, the energy $E_a$ can be expressed as:

$$E_a = \frac{1}{2} \sum_b U_{(ab)}^{(2)} + \frac{1}{3} \sum_{bc} U_{abc}^{(3)} + \frac{1}{4} \sum_{bcd} U_{abcd}^{(4)} + \text{higher order terms} \ldots$$  \hspace{1cm} (1.35.)

Where $abcd$ are indices for all the atoms in the system, and $U_{ab...}^{(N)}$ is the interaction energy of order (N) between atoms ab..... The fraction before each summation is to account for the double counting of interactions. The total energy is the sum of all the $E_a$'s. Considering the two-body terms it possible to understand how these sums are
affected by the boundary conditions imposed by the program. The energy of each atom in region I is given by:

\[ E_a = \frac{1}{2} \sum_{b}^{N_{at}} \sum_{I} U_{ab}^{(2)} (r_{ab} + 1) \]  

(1.36.)

Where I represents the sum over all the 2-D lattice vectors and \( N_{all} \) denotes the sum over “all” of the other atoms in the 2-D cell. This equation assumes that the two body potentials depend upon the vector defining the relative position of the two atoms. The two-body potentials used in MARVIN only depend upon the magnitude of the atom \( a, b \) separation. Since the total energy is what the program has to calculate, equation (1.36.) has to be expanded by summing \( E_a \) over all the region I atoms.

\[ E_{total} = \sum_{a}^{N_1} E_a = \frac{1}{2} \sum_{I}^{N_1} \sum_{a}^{N_1} \left[ U_{ab}^{(2)} (I_{ab}) + \sum_{b=0}^{N_{at}} U_{ab}^{(2)} (r_{ab} + 1) \right]. \]  

(1.37.)

For simplicity \( r_{ab} \) is shorthand for \( r_a - r_b \) and \( I_{ab} \) means the \( I=0 \) is not included in the sum. The general meaning of the equation (1.37.) is that each atom interacts with a periodic plane of atoms b. The term \( U_{ab}^{(2)} \) is the two-body interaction of an atom with its periodic images. The second part of equation (1.37.) can be split into 2 parts, where the first part is over all the region I ions and the second part is over all of the region 2 ions.

\[ 1/2 \sum_{b=0}^{N_{at}} U_{ab}^{(2)} (r_{ab} + 1) = \sum_{b=0}^{N_{at}} U_{ab}^{(2)} (r_{ab} + 1) \]  

(1.38)

The last term in the sum is the boundary interaction energy.

\[ E_{boundary} = \sum_{I} \sum_{a}^{N_1} \sum_{b}^{N_1} U_{ab}^{(2)} (r_{ab} + 1). \]  

(1.39)

The total energy computed by the program is the energy of region I ions in the “infinite” crystal surface or interface.

For ionic crystals the largest contribution to the energy is electrostatic. Actually, this is not completely true since the electrostatic energy is attractive and holds the crystal together, whilst the short range repulsive energy keeps the crystal from collapsing. The balance between these two forces keeps the equilibrium. Unlike the short range forces that go as \( r^{-6} \) or faster, the electrostatic potential is proportional to \( r^{-1} \) and is conditionally convergent. In 3-D systems the Ewald method is used to speed the
convergence. In MARVIN a derivation that is appropriate for 2-D slabs [33,34] is
used.

Expanding equation (1.41.) for just the coulomb interaction.

\[ E_{\text{Madelung}} = \frac{1}{2} \sum_{a}^{N_i} q_a \sum_{b}^{N_i} q_b \left( \frac{1}{|r_a - r_b + 1|} \right) \quad (1.40.) \]

Where q is the charge on atom (or ion core or shell depending upon the model being
used), and l is the sum over lattice vectors. However, this sum is conditionally
convergent and can be rewritten as,

\[ E_{\text{Madelung}} = \frac{1}{2} \sum_{a}^{N_i} q_a q_b U_{ab}^{\text{Madelung}}. \quad (1.41.) \]

Where

\[ U_{ab}^{\text{Madelung}} = U_{ab}^{\text{Reciprocal}} + U_{ab}^{\text{Real}}. \quad (1.42.) \]

Heyes [34] demonstrated that

\[ U_{ab}^{\text{Reciprocal}} = \pi / A \{ [-2z_{ab} \text{erf}(Gz_{ab}) - 2 \exp(-Gz_{ab}^2) / \pi^{1/2} G \]
\[ + \sum_{k=0}^{\infty} \exp(ik \cdot r_{ab}) / |k| [\exp(|k|z_{ab}) \text{erfc}(|k| / 2G + Gz_{ab}) \]
\[ + \exp(-|k|z_{ab}) \text{erfc}(|k| / 2G - Gz_{ab})] \} \quad (1.43.) \]

and

\[ U_{ab}^{\text{Real}} = \sum_{l} \text{erfc}(G|r_{ab} + 1|) / |r_{ab} + 1| \quad (1.44.) \]

where \( z_{ab} \) is the vertical separation between ions a and b perpendicular to the surface,
\( k \) are the 2D reciprocal lattice vectors and \( A \) is the surface area of the simulation cell.
The Gaussian weighting factor, \( G \), determines how the sum is divided between real
and reciprocal space and was chosen to minimise the number of terms in the sums:

\[ G = (\pi / A)^{1/2} \quad (1.45.) \]

These expressions can be directly incorporated into equation (1.37.) to produce the
total Coulombic energy with one small correction. The reciprocal sum for an ion
interacting with its own images will include a self-interaction term which is removed
by subtracting \( 2^{1/2}/AG \) for each region I particle. Most potentials for oxides and
halides are based on the assumption of the fully ionic model [35] with ionic
polarisability treated by the shell model of Dick and Overhauser [36], in which an ion
is modelled by a massive (charge \( X \), mass \( M \)) core connected by an isotropic harmonic
spring restoring force (force constant \( k \)) to a massless shell (charge \( Y \), mass 0). Hence,
spring restoring force (force constant $k$) to a massless shell (charge $Y$, mass 0). Hence, the ion consists of two separate particles. The formal ionic charge is given by $Q = X + Y$ and the (free) electronic polarisability by

$$\alpha = \frac{Y^2}{k} \quad (1.46.)$$

The total charge of the ion is split between the core and the shell, and the separation all short-range ion-ion potentials are defined as acting between different ion shells. As a consequence, the true electronic polarisability of the ions becomes crystal dependent, which is an important physical effect (especially for anions) that is simply and economically described by the shell model. Conceptually, shell-model calculations are based on an ionic crystal model assuming formal ionic charges and dominating pairwise interionic potentials. They are given as long-range Coulomb interactions and short-range potentials resulting from the Pauli exclusion principle and interionic correlation effects. Short-range terms are conveniently described using Buckingham potentials:

$$V(r) = Ae^{-\rho r} - C/r^6 \quad (1.47.)$$

The van der Walls potential $-C/r^6$ is designed to model the interionic correlations. The potential parameters $A$, $\rho$, and $C$ depend on the interacting ion species and in most cases to some extent on the crystalline environment.

### 1.8. Outline of this Thesis

This thesis, which can be divided in three main parts, has been organized as follows:

- Chapter 2. describes the different experimental techniques used to prepare, to characterize the structure of the materials; and to explore the electronic and superficial properties of semiconducting oxides used for the development of gas-sensitive resistors.

- Chapter 3., 4. and 5. relate to the gas sensing properties of SnO$_2$ and (Sn-Sb)O$_2$ materials prepared by co-precipitation method. More precisely, Chapter 3., discusses the effect of firing temperature on Sb surface segregation checked by X-ray Photoelectron Spectroscopy and its effects on water adsorption and sensitivity.
The catalytic properties of these materials were also looked into. Chapter 4. refers to the effects of microstructure, and especially the particle size, on the behavior (sensitivity and selectivity) of these semiconducting oxide gas-sensitive resistors to carbon monoxide and methane. In Chapter 5. theoretical calculations methods were used to study the surface properties of (Sn-Sb)O₂ with regard to understanding the defect chemistry of antimony dopant using a new computer code (MARVIN). The effects of this transition metal dopant and point defect segregation at the surface were also investigated and compared with experimental results.

- Chapters 6., 7. and 8. concern different families of completely new materials or materials which have not been routinely used for gas-sensing applications before in the general literature. Furthermore, they all offer opportunities to manipulate the stoichiometry in order to attempt to tailor their gas-sensing properties. The properties of solid solution series and systematic cation substitution in these solid-solution materials as a way of understanding the gas response mechanism linked to the surface chemistry has been looked into in (CrNbO₄ₓ(Sn₁₋ₓSb₂O₂)₁₋ₓ (Chapter 6.), Ti-(Sn-Sb)O₂ (Chapter 7.) and (MWO₄ₓ([Sn-Ti]O₂)₁₋ₓ [with M: Mn, Fe, Co, Ni, Cu, Zn] (Chapter 8.) and the effects of stoichiometry, microstructure, combustion gradient and surface segregation on gas (H₂O, CO, CH₄, C₃H₈, NH₃) sensitivity have been observed. Hence, the results have been assessed against the simple model for composition dependence of gas-sensitivity developed by Williams and Moseley [16]. This model, overall, adequately described the behaviour of the materials.
References


Chapter 2: Experimental

This chapter gives general experimental conditions in procedures common to the work. Particular details are given in the chapter to which they specifically refer.

2.1. Materials Preparation

Powder mixing, fusion, and precipitation from solution are all conventional techniques for synthesis of traditional and advanced ceramics on both the laboratory and industrial scale. Solid ceramic bodies are generally produced by using the process of powder compaction followed by firing at high temperature. Sintering or densification occurs during this heat treatment and is associated with joining together of particles, volume reduction, decrease in porosity and increase in grain size. The phase distribution or microstructure within the ceramic is developed during sintering and different fabrication techniques are used for shaping ceramics. The aim of these techniques is to produce microstructures suitable for particular applications. It is evident that the electrical properties of a pressed powder cannot be expected to be closely reproducible. Intergranular contacts will vary in area and favoured high conductance paths for the current will be present and vary from sensor to sensor. Practically, such variations lead to the need to calibrate each sensor individually if accuracy is required.

2.1.1. Powder Mixing

All the compounds in all series in this work were prepared by powder mixing of multi-component oxides with the right relevant stoichiometries. Metal oxides and carbonates were used (as will be indicated along this thesis), after which the mixture were milled with zirconia ceramic beads in a ball mill containing acetone. The solvent was then evaporated, and the comminuted powders were calcined for at least 12 hours. The firing sequence was in some cases repeated several times with intermediate grinding stages. The solid produced was then pressed (1.5-2 tons) into 13
mm diameter pellets of approximately 1.5-2 mm thickness and then refired at the same temperature overnight.

2.1.2. Co-precipitation

For the Sn$_{1-y}$ Sb$_y$O$_2$ compounds the co-precipitation method (which will be described in chapter 3) was used in order to control the microstructure of the materials, especially the grain size.

2.1.3. Ink Preparation and Screen-Printing

The ink was prepared by mixing roughly the powder with a commercial printing vehicle (400-Vehicle, ESL Europe) and triton X-100 (Fluka) and consequently passed through a triple roll mill for several hours to ensure homogeneous dispersion of powder in the vehicle. Roughly, the percentage in weight was respectively 55% for the powder, 45% for the vehicle and 5% for the surfactant.

![Diagram of electrode configuration](image)

**Fig 2.1.** Electrode configuration of the sensors. Resistance measurements were taken between the large [L] and common [C] electrodes, with 200 µm gap, and between the small [S] and common electrodes, with 20 µm gap. The overall device dimensions 3 mm x 3 mm.
The ink was printed on an alumina substrate tile (3x3 mm²) with an interdigitated gold electrode pattern printed on one side and with a platinum heater track on the other side acting as a resistance thermometer. The alumina tiles were covered with seven layers (15 μm per layer) of ink using a DEK 1202 printing machine. The devices were fired at around 1073 K for a couple of hours to strengthen the powder attachment to the gold, raising the temperature slowly (1°C/min) to remove the vehicle. Contacts to the device were formed by spot welding 100 μm diameter platinum wire to the pads. The multiple electrode devices, consisting of a small, medium and large gap in respect to a common electrode are described in Fig 2.1., and have the advantage of detecting concentration gradients through the solid [1].

2.2. Material Characterisation

2.2.1. X-ray Powder Diffraction

X-ray powder diffraction is an analytical method widely used qualitatively to identify chemical compounds, the purity of materials or different phases. Atoms or ions located in regular array in a crystalline solid can diffract an X-ray beam and the resulting pattern can be analysed. Diffracted beams from atoms in successive planes can cancel each other unless they are in phase, which requires that they obey Bragg’s law:

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (2.1)

where \( n \) is an integer, \( d \) is the distance between planes, \( \lambda \) is the wavelength of the X-rays, and \( \theta \), the Bragg angle, is the angle of diffraction of the X-ray beam. Since the \( \theta \) values can be measured directly, the values of \( d \) can be calculated given the wavelength of the X-ray used. Measurement of intensities of the diffracted beam in each direction can give a complete structure determination.

Each material has its own characteristic X-ray diffraction pattern and the intensity of the peaks varies depending on the instrumental conditions and the method of sample preparation. Sample identification is achieved by comparing the diffractrogram with a standard pattern in the data base. Quantitative analysis can be performed by XRD
by adding a well-crystallised standard to the sample and comparing the different intensities. The Miller indices and consequently the lattice parameters of a material can also determined from the Bragg angles and the wavelength of the X-rays.

X-Ray powder diffractometry was performed using a Siemens D5000 with monochromated Cu-Kα radiation. All the samples were examined in transmission geometry, spread onto adhesive tape and placed in the middle of a rotating circular sample holder.

2.2.2. Scanning-Electron Microscopy

In obtaining an electron microscopic image the surface of the solid sample is swept with a finely focused beam of electrons. A secondary electron signal is produced from the surface when it is scanned with a energetic beam of electrons. The signals of interest are the backscattered and secondary electrons since they vary according to differences in their topography. High resolution in the order of 2 to 5 nm can be achieved as secondary emission occurs around the beam impact area. The electron optics give a large depth of field to the image.

The materials morphologies were characterised by scanning electron microscopy using a Hitachi s-570 SEM equipped with a LINK energy dispersive X-ray analyser. All the samples were gold coated in order to get rid of the surface sample charging which disrupts the surface potential and alters the quality of the SEM image. The instrument was operated at 20 kV and 60-80 μA (with a beam diameter of a few microns dependent on the aperture size). All the SEM photographs were taken with an Ilford HP5 black and white film. The developing and printing equipment including paper, developer, stopper and fixer were supplied by Ilford.

2.2.3. X-ray Photoelectron Spectroscopy

By definition, the ability of a solid state gas sensor to sense the presence of a gas depends on the nature of the interaction (chemical or electronic) between the gas
molecules and the surface of the sensing material. As the reactivity of a surface is critically dependent on the condition of the surface such as its elemental composition (including alloying, doping, segregating effects or impurity constituents) and its electronic and defect structure, surface analysis techniques such as X-ray Photoelectron Spectroscopy (XPS) are usefully applied to the study of the surfaces of sensor materials.

Hence, the surface of the material to be analysed is irradiated with photons, and the kinetic energies of the resultant photoelectrons are analysed. It is known from the Einstein principle that a photon must give all its energy when interacting with an electron. The kinetic energy of the ejected photoelectron can be expressed as such:

\[ E_e = h\nu - E_b \]  

(2.2)

where \( h\nu \) is the energy of the incoming photon and \( E_b \) represents the binding energy of the atomic level and \( E_e \) is the kinetic energy of the resulting photoelectrons. Electrons with sufficient kinetic energy to overcome the work function of the sample can escape from the surface. This process is known as the photoelectric effect (Fig 2.2.).

![Schematic of the XPS Photoelectron Emission.](image)

**Fig 2.2. Schematic of the XPS Photoelectron Emission.**
The photoelectrons emitted are collected and their energies measured. The number of photoelectrons collected is plotted against energy to produce an energy spectrum. The kinetic energy of the photoelectrons is determined by the energy they possess while still bound to their respective nuclei. Furthermore, as the measurement of $E_e$ involves passage of the electron through an energy analyser, which has an effective work function, a constant work function term has to be added to the previous equation. As the energy levels are quantised, the photoelectrons have a kinetic energy distribution consisting of a series of discrete bands that reflect the 'shells' from the electronic structure.

The samples were irradiated with monochromatised soft X-rays AlK$_\alpha$ (1486.6 eV) radiation using a VG ESCALAB 220i-XL spectrometer. The energy of the exciting X-ray is high enough that electrons from several shallow core levels can be ejected, and since two elements do not have the same set of core level binding energies, the ejected photoelectron spectrum gives an elemental analysis. Furthermore, any shifts in $E_B$ due to electron transfer as a result of a chemical reaction are showed directly in changes in $E_e$, giving information on the chemical state of the elements at the surface. Photoelectron spectra are recorded in the form of photoelectron current as a function either of binding energy or kinetic energy. The spectra can be in the form either of survey scan covering most of the range of available binding energies (typically from 0 to 1200 eV), and of detailed scans of the binding energy region around the peak of chosen elements. The latter are generally recorded at smaller incremental energy steps and higher energy resolution to enable chemical information to be obtained. Fig 2.3. represents the 'wide' scan in terms of binding energy from the surface of SnO$_2$ powder, using AlK$_\alpha$ radiation.

The peaks observed in Fig 2.3. can be grouped into three basic types; peaks due to photoemission from core levels and valence levels and peaks due to X-ray excited Auger emission.
Core levels

Features arising from Sn and from O, and also from a small contaminant C, can be observed. In the Sn photoelectron spectrum there are peaks corresponding to the ejection of electrons from the 4d, 4p, 4s, 3p, 3s atomic core levels and the spin-orbit splitting of 3d into 3d_3/2 and 3d_5/2, and of 3p into 3p_3/2 and 3p_1/2. The relative intensities of the doublet peaks are given by the ratio of their respective degeneracies (2j+1). The area ratios and designation of spin-orbit doublets are given in Table 2.1.

![Survey XPS scan from the surface of SnO₂ powder. The photoelectron features visible are the Sn 3s, 3p, 3d, 4s, 4p and 4d peaks, the O 1s peak, and a small C 1s peak from the surface contamination. Also seen in the spectrum are the Sn MNN and the O KLL Auger peaks.](image-url)
Table 2.1. Spin-orbit splitting parameters

<table>
<thead>
<tr>
<th>Subshell</th>
<th>j values</th>
<th>Area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>1/2,3/2</td>
<td>1:2</td>
</tr>
<tr>
<td>d</td>
<td>3/2,5/2</td>
<td>2:3</td>
</tr>
<tr>
<td>f</td>
<td>5/2,7/2</td>
<td>3:4</td>
</tr>
</tbody>
</table>

The basic parameter that governs the relative intensities of core level peaks in the atomic photoemission is the cross-section $\alpha$. Values of $\alpha$ have been directly calculated [2]. The transmission characteristics of the electron analyser, being a function of electron energy, apply an important modulation. The peak width, defined as the full width at half-maximum (FWHM) $\Delta E$, is a convolution of several contributions:

$$\Delta E = (\Delta E_A^2 + \Delta E_S^2 + \Delta E_N^2)^{1/2}$$  \hspace{1cm} (2.3)

where $\Delta E_A$ is the broadening contribution from the analyser, $\Delta E_S$ is the broadening contribution from the x-ray source and $\Delta E_N$ is the natural line width transition/peak assuming that all the components have a Gaussian line shape.

As mentioned previously the purpose of a narrow scan is to obtain accurate peak positions and detailed line shapes in order to determine chemical state information and to allow quantification of minor surface components. The width of the scan, therefore, should be wide enough to include the background on either side of the region.
Valence levels

Valence levels are those occupied by electrons of low binding energy (e.g. 0-20 eV) which are involved in de-localised or bonding orbitals. The spectrum in this region consists of many closely spaced levels giving rise to a band structure. In Fig 2.3, the peak labelled 4d is in fact the conduction band spectrum, which is dominated by 4d states. The complete spectrum at high resolution (Fig 2.5.) shows the band structure and the sharp cut-off in electron density at $E_F$. 

Fig 2.4. Detailed XPS scan of the Sn 3d$_{5/2}$ from the surface of SnO$_2$ powder.
The pressure inside the chamber has to be less than $5 \times 10^{-10}$ mbar to avoid surface contamination. The binding energies were referenced to the hydrocarbon C 1s peak at 284.5 eV and the sample charging was controlled with a flood gun. The data processing was carried out with a computer and quantification of the peaks was performed using a Shirley (in which the background intensity at a point is determined, by iterative analysis, to be proportional to the intensity of the total peak area above the background and to higher energy) or a straight background and sensitivity factors were extracted from Wagner et al [3, Appendix 2.1].
Table 2.2. Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Start</th>
<th>Centre</th>
<th>Height</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>533.2</td>
<td>530.6</td>
<td>17292.4</td>
<td>1.25</td>
</tr>
<tr>
<td>Sn 3d_5/2</td>
<td>489.7</td>
<td>486.7</td>
<td>50190.7</td>
<td>1.19</td>
</tr>
<tr>
<td>C 1s</td>
<td>286.2</td>
<td>284.6</td>
<td>607.4</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 2.3. Quantification Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Sensitivity Factor</th>
<th>Normalized Area [Atomic]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>0.66</td>
<td>0.05017 67.55</td>
</tr>
<tr>
<td>Sn 3d5</td>
<td>4.30</td>
<td>0.02038 27.44</td>
</tr>
<tr>
<td>C 1s</td>
<td>0.25</td>
<td>0.00372 5.001</td>
</tr>
</tbody>
</table>

Since XPS involves the emission of electrons from the sample it is inevitable that in the case of an insulating sample surfaces will be left charged positively. The surface charging leads to two general problems:

- general instability leading to spectral noise making analysis impossible
- shifting of the spectrum on the energy scale leading to difficulties interpreting chemical states. In this case differential charging in different regions of the surface may cause a given peak to broaden or to split into more than one peak.

2.2.4. Determination of Particle Size and Surface Area

2.2.4.1. X-ray line broadening

Additional broadening of a diffracted X-ray beam takes place when the average crystal size in a powder is below roughly 200 nm in diameter. From the measurement of this broadening an average particle size can be calculated. Generally in the absence of extra broadening due to small particle size, powder diffraction lines have a finite breadth because the focusing geometry is not always perfect, the radiation is not
Fig 2.6. Power X-ray Diffraction patterns of a mixture of $\text{Sn}_{0.095}\text{Sb}_{0.005}\text{O}_2$ (small particle size) and KCL (internal standard) calcined at different temperatures

$$D = \frac{0.9\lambda}{B\cos\theta_B} \tag{2.4}$$

where $D$ is the thickness of the crystal in $\AA$, $\lambda$ the X-ray wavelength and $\theta_B$ the Bragg angle. The actual line broadening, $B$, is calculated using the extra peak width at half peak from the Warren formula:

$$B^2 = B_M^2 - B_S^2 \tag{2.5}$$
where $B_M$ is the measured peak width in radians at half peak height and $B_s$ is the corresponding width of a peak of the internal standard material (KCI) mixed with the sample. Fig 2.6. shows a typical XRD spectrum of Sn$_{0.95}$Sb$_{0.05}$O$_2$ materials calcined at different temperatures.

The standard material should have a diffraction peak close to the relevant peak of the sample and a particle size considerably greater than 2000 Å. Usually for thickness $50 < D < 500$ Å the broadening is very easy to calculate and detect. The lower limit of detection takes place when the peaks are so broad that they disappear into the background. For small particle size, low angle peaks are used because the broadening increases with angle for a given crystal thickness.

### 2.2.4.2. Gas Adsorption

Physical adsorption investigations have been widely used for the measurements of surface areas and to obtain information about the pore geometry of solids.

**The Langmuir model**

This model considers that all adsorption sites are equivalent and can each adsorb one molecule. Further more, the probability of adsorption is considered not dependent on the occupancy of the nearby sites. At equilibrium the rate at which a molecule adsors on to a site of the adsorbent surface is equal to the rate at which they desorb from the occupied sites,

$$A + s \xleftrightarrow{\frac{k_1}{k_2}} A^{ads}$$  \hspace{1cm} (2.6)

where $k_1$ and $k_2$ represents respectively the adsorption and desorption rates constants. For a given pressure $p$ if $N$ is the total number of sites and $\theta$ is the fraction of occupied sites, then the rate of adsorption $d\theta/dt$ can be expressed as :

$$d\theta/dt = k_1 p N (1-\theta)$$  \hspace{1cm} (2.7)

As the rate of desorption is proportional to the number $N\theta$ of adsorbed molecules :

$$d\theta/dt = k_2 N \theta$$  \hspace{1cm} (2.8)
At equilibrium the rate of desorption is equal to the rate of adsorption. The Langmuir adsorption isotherm is then given by:

\[ \theta = \frac{n_t}{n_m} = \frac{bP}{1+bp} \]  \hspace{1cm} (2.9)

where \( b = k_f/k_2 \), \( n_m \) is the amount of species adsorbed per monolayer and \( n_t \) is the amount of species adsorbed at \( p \). As this is a monolayer adsorption model the isotherm saturates at \( n_m \) at high pressure.

The BET model

Brunauer, Emmet and Teller have extended the Langmuir treatment for use in surface area determinations by considering gas adsorption at pressures up to those at which the surface is covered by more than a single layer of adsorbed molecules. The equation derived, often known as the B.E.T. equation, is usually written in the form:

\[ n^* = \frac{n_m^* C}{(P_o - P)[1 + \frac{(C - 1)P}{P_o}]} \]  \hspace{1cm} (2.10)

where \( C \) is a constant which includes a term giving the difference between the heat of gas adsorption in the layer immediately adjacent to the solid surface and that for molecules in positions non-adjacent to the surface, and \( P_o \) is the saturation vapour pressure of the adsorbate at the adsorption temperature. At this stage an assumption is made that the heat of adsorption for supra-monolayers equals the heat of condensation of the adsorbate. \( C \) determines the shape of the isotherm as it is related to the heat of condensation of the adsorbate and to the heat of adsorption.

It is convenient to rewrite the BET equation as:

\[ \frac{P}{n^*(P_o - P)} = \frac{(C - 1)}{n_m^* C} \cdot \frac{P}{P_o} + \frac{1}{n_m^* C} \]  \hspace{1cm} (2.11)

to obtain the value of \( n_m^* \) from the slope \( \frac{(C - 1)}{n_m^* C} \) and the intercept \( \frac{1}{n_m^* C} \), \( n_m^* = \frac{1}{b + m} \).

The application of this model is rather limited. It can be applied only for \( 0.05 < P/P_o < 0.35 \) as for high pressure the effect of narrow porosity limits the thickness of the film and for low pressure any non-uniformity of the surface causes a variation of the heat of adsorption across the surface.
Surface area measurement

A convenient way to measure experimentally the area of solids with surfaces area > 5 m$^2$.g$^{-1}$ is to determine the volumes of nitrogen adsorbed at its boiling point (-195°C) for different values of gas equilibrium pressure in the range $0.05 < p/p_o < 0.3$. For small surface area < 5 m.g$^{-1}$ Krypton was used preferentially to N$_2$ because the saturation vapour pressure is much lower than that of N$_2$ since errors accumulate as the pressure increase.

The determination of the total surface area relies on the calculation from the adsorption isotherm of the monolayer uptake, i.e., the amount of adsorbate in a monolayer. The measurement requires non-specific physical adsorption, which can be achieved with non-polar molecules such as nitrogen or rare gases. If low surface area measurements are required adsorbates with low saturation vapour pressure can be advantageously used due to neglectable thermomolecular flow corrections. The calculation of the monolayer capacity can be achieved by fitting the data to a model for the adsorption process, such as the BET model to obtain an estimated monolayer coverage, $n_m^s$. The total surface area $S$ can then be expressed by:

$$S = N_A n_m^s a_m / m$$

(2.12)

where $N_A$ is the Avogadro constant, $a_m$ is the effective area per molecule in the monolayer assuming the cross-sectional area of adsorbed nitrogen to be 16.2 Å$^2$ and $m$ is the sample weight value. From the surface area, the average particle size, $D$, can be estimated by using the following equation:

$$D = 3/\rho S$$

(2.13)

where $\rho$ is the density of the material. This equation assumes spherical particles.

The dead space was determined using Helium (99.999%, BOC) at RT as He is not supposed to adsorb on the samples at this temperature. A pressure gauge (Vacuum General CMO) connected to a Keithley 179DMM autoranging voltmeter was used to measure the pressure. The samples consisted typically of roughly 0.2 g (exact weight accurately measured) of metal oxides in the form of broken pellets and was
introduced in $V_2$. The instrument used to calculate the surface area of the materials is shown in Fig 2.7.

It is necessary to ensure that the system has been allowed to reach equilibrium before each measurement is recorded. The solid sample was first thoroughly evacuated (outgassing) down to $10^{-3}$ Torr, then a small amount of Helium was introduced into $V_1$ up to $6.0 \times 10^{-2}$ Torr. The pressure $p_1$ in $V_1$ was recorded before opening the valve between $V_1$ and $V_2$. The resulting pressure $p_2$ was measured before opening the valve between $V_2$ and $V_3$ in order to measure $p_3$. As $V_3$ is a known quantity the unknown volumes ($V_2$ and $V_1$) can be traced back using the ideal gas law:

$$V_i = \frac{p_i V}{P_1 - P_2}$$

$$V_2 = \frac{(P_1 - P_2) p_3 V_3}{P_1 (P_2 - P_3)}$$

$$V_3 = 24.688cm^3$$  \hspace{1cm} (2.14)

($V_3$ was separately calibrated by weighing empty and filled with water).

---

**Fig 2.7.** Diagram of the surface area measurement apparatus.

---
The sample was cooled at liquid nitrogen temperature, then nitrogen applied with a succession of at least ten doses to obtain \( p_1 \) and \( p_2 \). The apparatus used for the surface area measurements (Fig 2.7.) is not at constant temperature. \( V_1 \) is at room temperature while \( V_2 \) is at liquid nitrogen. A correction has to be introduced as thermomolecular flow between the two regions of different temperature will establish a steady-state pressure difference. The ratio \( \frac{p_2}{p_{2,\text{corr}}} \), where \( p_2 \) corresponds to \( T_1 \) and \( p_{2,\text{corr}} \) corresponds to \( T_2 \) can be calculated. An example isotherm is shown in Fig 2.8.

![Graph showing multi-point BET surface area measurement](https://via.placeholder.com/150)

**Fig 2.8.** Multi-point BET surface area measurement for 0.21 g of SnO\(_2\) powder (prepared by co-precipitation) fired at 800°C. Nitrogen was used as the adsorbate.

As \( n^g_m = 1 \div (\text{Slope} + \text{Intercept}) \) and \( S = N_A n^g_m a_m / m = 5.99 \text{ m}^2 \cdot \text{g}^{-1} \)

\( N_A = 6.02E23 \) molecules.g\(^{-1}\) and \( a_m = 16.2E-20 \text{ m}^2 \)
2.3. Experimental Methods

2.3.1. Gas-Response Measurements

All the samples were tested in an automatic 4-pellet computer-controlled test rig, described in Fig 2.9. The rig consists of a ceramic sample holder inside which the pellets are sandwiched between gold electrodes separated by alumina spacers. The sample holder is mounted in a long quartz glass tube containing a thermocouple. The tube is fitted inside a tubular furnace (Carbolite, MTF 12/38A). The resistance and the thermocouple voltage are monitored by a Keithley 175A autoranging multimeter connected to a computer which records the data separately for each of the sample. As well as the temperature of the furnace, the computer controls the amount of gas flowing through the glass tube via mass flow controllers and solenoid valves. The resistance measurements were 2-terminal DC measurements without explicit control of the potential difference across the specimen. Therefore results had to be examined carefully to check for possible effects of polarisation at the electrodes.

Fig 2.9. Overall diagram of the pellet test rig
The gases were switched on and off by solenoid valves and their flow regulated using Tylan FC-260 mass flow controllers (MFCs) as can be seen on Fig 2.10. Each mass flow controller was connected to a gas-control box (RO-28-RS Tylan) which was run from the computer via a digital-analogue converter (DAC). The MFCs had a maximum flowrate of 500 cm$^3$.min$^{-1}$ and a minimum rate of 6 cm$^3$.min$^{-1}$, maintained with an accuracy of 4% for all gases.

![Flow diagram of the multiple pellet rig.](image)

The rig used with the devices is similar to the one described previously except that as the devices are mounted on a heater track the use of a furnace and a ceramic sample holder is not necessary. Instead, the gas sensor is directly attached to a glass tube by an SQ28 fitting and the computer records the data separately for each pair of electrode (small, medium, large).
The gases (1% in air, BOC) were mixed using mass flow controllers (Tylan). The sensitivity ($S_{gas}$) was defined as:

$$S_{gas} = \frac{R_{air} - R_{gas}}{R_{gas}} = \Delta \sigma R$$  \hspace{1cm} (2.15)

where $R_{air}$ refers to the resistance in air, $R_{gas}$ the resistance in the gas, and $\sigma$ the conductivity. Fig 11. and 12. illustrate the experimental routine used to explore the behaviour of a large number of oxides.

![Graph showing response of SnO2 pellet to 10 minutes pulses of 1% CH4 in air while ramping up and down the temperature.](image-url)

**Fig 2.11.** Response of an SnO2 pellet to 10 minutes pulses of 1% CH4 in air while ramping up and down the temperature.
Fig 2.12. Typical gas response trace showing the variation in resistance with CH$_4$ concentration with a SnO$_2$ pellet.

If response is plotted against CH$_4$ concentration (obtained from Fig 2.12.) the straight line in Fig 2.13. shows that the response is related by a power law to [CH$_4$]. In this case, the following relationship applies:

$$ S = \beta \log([CH_4]) + B \quad (2.16) $$

where $\beta = \frac{1}{2}$ represents the gradient coefficient and is referred to as the response exponent, and B is the intercept.
2.3.2. Gas Combustion Measurements

Gas combustion measurements were performed with a quartz reactor tube and quartz frit upon which 1g of the powder were placed. The reacting gases were supplied to the reactor tube (at 50ml.min$^{-1}$) mounted vertically in a tube furnace through mass-flow controllers (Tylan). The temperature was ramped from 25°C to 600°C at 10°C.min$^{-1}$. A Micromass PC Quadrupole Mass Spectrometer was used to measure the concentration of methane and carbon monoxide in the gas stream after passage through the reaction tube. For CO oxidation the synthetic air mixtures (1000 ppm in O$_2$ and Ar) contained Ar instead of air to remove the mass 28 interference by dinitrogen. The apparent rate constants for the surface catalysed combustion of the
different gases determined in the packed-bed flow through reactor by applications of equations given in Appendix 2.2.
References


Appendix 2.1. Photoelectron Energies and Sensitivity Factors for XPS

### Photoelectron Energies.

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<tr>
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### Empirically Derived Atomic Sensitivity Factors.

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Appendix 2.2. Derivation of rate laws from measurements of conversion in a packed-bed, flow-through reactor.

In the experiment, a gas (concentration \( c \) with initial value \( c_o \)) flows, at a volume flow rate \( v \), through a packed bed, depth \( h \) and cross-sectional area \( A \), of a catalyst, solid phase density \( \rho \) and mass \( m \) and is decomposed. The variables are the bed depth and the volume flow rate. The concentration of the gas at the exit of the bed, \( c_f \) is measured. The objective is to deduce the rate law for the conversion.

The residence time of gas in the bed is

\[
\tau = \frac{hA \varepsilon}{v}
\]  

(2.1)

and the combustion rate law is expressed as a pseudo-first-order process in which the rate constant to deduce is some function \( k(c, T) \) of the reactant gas concentration and the temperature:

\[
\frac{dc_f}{d\tau} = -k(c_f, T)c_f
\]  

(2.2)

Here, \( \varepsilon \) refers to the volume fraction of gas in the bed:

\[
\varepsilon = 1 - \frac{m}{Ah \rho}
\]  

(2.3)

From the previous equations and with \( \Delta c = c_o - c_f \)

\[
\frac{d(\Delta c)}{d(h/v)} = -k(c_f, T)c_f A \varepsilon
\]  

(2.4)

The required variation of rate constant with concentration could be obtained from the slope of graphs of \( \Delta c \) against \( v \) at constant \( h \), or of \( \Delta c \) against \( h \) at constant \( v \):

\[
\frac{d(\Delta c)}{dh} = -k(c_f, T)c_f \left( \frac{Ah}{v} \right)
\]

\[
\frac{d(\Delta c)}{dv} = \left( \frac{h}{v^2} \right) k(c_f, T)c_f A \varepsilon
\]  

(2.5)

If the reaction is truly first order, the equation are readily integrated, and the result, expressed in terms of the conversion, \( \gamma = (1 - \frac{c_f}{c_o}) \) is:

\[
\ln(1 - \gamma) = -\left( \frac{Ah}{v} \right) k(T)
\]  

(2.6)
In the limit of low conversion, $\ln(1 - \gamma) \approx \gamma$ and:

$$k(c_o, T) = \left( \frac{\gamma v}{A e h} \right)$$

(2.7)
Chapter 3. Sb(III) as a Surface Site for Water Adsorption on Sn(Sb)O₂, and its Effect on Catalytic Activity and Sensor Behaviour

Vincent Dusastre and David E. Williams

This chapter has been published in essentially the same form in:


Abstract

Surface segregation of Sb in polycrystalline Sn(Sb)O₂ is known to affect the rate of surface-catalysed combustion of hydrocarbons and carbon monoxide over this material. This combustion rate is also known to be affected by the presence of water vapour. We show that Sb segregation to the surface as Sb(III) in Sn₁₋ₓSbxO₂ (x = 0.005, 0.05), controllable by thermal treatment, strongly alters the effect of water vapour both upon the surface-catalysed combustion rate of carbon monoxide and upon the elevated-temperature electrical conductivity. We suggest that the surface defect states which mediate both the electrical behaviour and the surface-catalysed combustion are best formulated as an association complex of an oxygen vacancy with Sn(II) or Sb(III) and are then able to propose a simple model which unifies the interpretation of the behaviour of SnO₂ as both a gas sensor and a combustion catalyst. We postulate: that a correct formulation of the ‘adsorbed oxygen’ (O²⁻) surface species mediating the electrical response is an oxygen molecule trapped in or on a surface oxygen vacancy; that the combustion reaction proceeds partly through these species and partly through lattice oxygen at the surface; that water competes with oxygen for the surface vacancies, blocking this route; and that the binding energy of water to the [SbSn/V₂⁺.SbSn/V₂⁺] surface defect complex is less than that to the [Sn₇/Sn/V₂⁺] complex.
3.1. Introduction

Antimony-tin oxide catalysts are well-known to be active and selective for olefin oxidation, oxidative dehydrogenation and ammoxidation of alkenes notably propylene to acrolein and acrylonitrile [1-3], and have previously been developed for the selective oxidation of hydrocarbons (methane [4]). The behaviour contrasts with that of pure SnO₂, which favors deep oxidation [5,6]. Optimal catalytic activity is obtained with fairly large antimony concentrations (~ 30% Sb cations [1]). Although Sb substitution appears to occur without strong modification of the SnO₂ lattice, the reported solubility limit of antimony cations in the rutile phase of SnO₂, from structural studies, varies from 3% [7] to 40% [8]. The catalytic performance of these compounds depends critically upon the conditions of preparation and particularly upon the calcination temperature adopted. These conditions have been reported [9,10] to have an effect on the properties of the materials, such as the surface area, the particle size, and the surface composition. The surface composition of these oxides varies from the bulk composition. There is, especially, surface enrichment in antimony which takes place to an extent dependent upon bulk composition and calcination temperature. Pronounced enrichment by antimony at the surface was observed by X-ray Photoelectron Spectroscopy (XPS) with a heat of segregation varying from roughly 10 (40 atom% Sb) to 40 (0.5 atom% Sb) kJ/mol [11]. Comparison of the influence of calcination temperature upon surface composition (by XPS) with the effect upon bulk phase composition (X-ray Diffraction study) has shown [9,12] a region which contains a Sb₂O₄ surface phase which appears at high temperature and which exhibits decreasing surface antimony composition with increasing temperature as a consequence of vaporisation of Sb₂O₄.

Cross and Pyke [11] studied Sb segregation upon calcination of oxides prepared by a co-precipitation method. As water was lost from the hydrous oxide, the onset of antimony surface enrichment at 400°C corresponded exactly to a change in colour from white to deep blue, which the authors interpreted as due to antimony lattice diffusion and reconstruction. At 600°C, by analogy with (NH₄)₂SbBr₆ [13], the colour change is possibly due to charge transfer between Sb³⁺ and Sb⁵⁺ within a random array.
of disordered SnO$_6$ and SbO$_6$ octahedra [7]. The results are therefore consistent with
the prediction that catalyst preparation forces antimony into an environment in which
it is not particularly stable, so that at high temperatures segregation to surfaces takes
place where antimony could occupy an energetically more favorable situation,
probably as Sb$^{3+}$ [14,15].

SnO$_2$ is a semiconductor with a direct band gap of 3.6 eV between the full oxygen 2p
valence band and the tin 5s states at the bottom of the conduction band (see Fig 3.1.).

Fig 3.1. Schematic energy level diagram of SnO$_2$ band structure.

The electronic conduction of stannic oxide has been attributed to oxygen vacancy
donor levels and can be enhanced by reduction [16]. Introducing carriers in SnO$_2$ by
antimony doping results in a dramatic increase in the electrical conductivity due to
substitution of Sb(V) into the SnO$_2$ lattice [17,18]. Model calculations compared with
infrared reflectance measurements for various Sb doping levels suggested, however,
that for doping levels > 1 at.% the sample might be covered with a reduced carrier
concentration surface layer, consistent with Sb segregation to the surface as Sb(III) [19]. The presence of bulk Sb(V) ions in an octahedral environment with Sb(III) ions at the surface has been observed [4].

Catalytic reaction between reducing species and surface-adsorbed oxygen at elevated temperatures releases carriers in the tin dioxide conduction band. Changes in conductivity of tin dioxide associated with the interaction with reducing gases provide the basis for application of these systems as gas sensors [20]. The electrical conductivity is, in fact, a very sensitive probe of the surface state of the oxide. Semiconductor gas detectors are sensitive to water vapour and their response to combustible gases is affected by the ambient humidity [21,22]. Thus, it has been observed that water adsorbs in greater quantities than oxygen on the surface of tin dioxide [23]. Water is strongly bound to an SnO$_2$ surface, possibly as surface Sn-OH groups. On heating, minor water loss is observed at 373 K, the major loss taking place in the range 520-720 K. The effect of moisture on gas sensitivity has been discussed [21,22] in terms of the displacement of chemisorbed oxygen by H$_2$O and OH. On SnO$_2$ the chemisorption of water seems to introduce a surface electronic state such as a surface hydroxyl species [24]. Recently, the presence of dissociatively adsorbed water on SnO$_2$ (110) has been observed using a combination of UPS and TDS [25]. In these studies, H$_2$O acts as an electron donor, bending the bands down at the surface and increasing the surface carrier concentration. The increase in surface conductivity caused by H$_2$O is greater on slightly reduced surfaces than on heavily reduced, disordered ones [26].

The behaviour of Sb-doped tin dioxide as a gas sensor material has been extensively reported. However, there has been little or no investigation of the effect of antimony enrichment at the surface as Sb(III) on either adsorption or catalysis or gas sensor behaviour, despite the speculation by Egdell et al [27] that there should be an interaction of Sb(III) surface species with molecules which can act as electron donors. In the present chapter, we show that the surface segregation of Sb in Sb-doped SnO$_2$ can be controlled by an appropriate preparation regime. We confirm earlier XPS observation implying the presence of Sb(III) at the surface and correlate this with the
measurements of surface segregation. By measurements of the electrical behaviour in response to exposure to water vapour in air at elevated temperature we then deduce the existence of an electrically active surface state associated with preferential water adsorption on Sb(III), thereby supporting earlier speculation concerning the significance of this state [27,28]. Finally, we demonstrate an effect of Sb(III) segregation on oxidation catalysis. The effect is found only in the presence of water vapour. We propose a connection between the electrical properties and the catalytic activity which rationalises the results.

3.2. Experimental

The oxides Sn_{1-y}Sb_yO_2 (y = 0, 0.005, 0.05) were prepared by coprecipitation [7] using the following procedure. Weighed amounts of antimony (Ventron, purity > 99.999%) and tin (Fluka, purity > 99.999%) were dissolved in aqua regia. An excess of NH_3 was added to the solution to make it alkaline. After boiling for a few hours, the resulting precipitate was washed and collected. After overnight drying at 120°C, the powdered materials were fired for 12 hours at different temperatures (600, 800, 1000, and 1200°C) in air in recrystallised alumina crucibles. The co-precipitated materials were white in colour after drying at 120°C, and became blue on heating to 600°C. The blue colour darkened with increasing firing temperature. The materials were then ground, pressed at 1 ton into 13 mm diameter 1.5 mm thick pellets and fired at the same temperature as the initial firing for 12 hours.

The electrical behaviour of the pellets under controlled humidity and temperature conditions was monitored in a computer controlled rig (described in [29]). Two-terminal DC resistance measurements were employed, the accuracy of these measurements having been independently cross-checked against AC measurements. Water vapour pressure was controlled by mixing dry gas with gas that had been saturated with water vapour by passing through a bubbler.

X-ray powder diffractrometry (Siemens D5000, transmission mode with incident beam monochromator and Cu-Kα radiation) showed the presence of a single well
crystallised rutile phase, whose lattice parameters were the same as undoped SnO₂. The average crystallite size, determined from the diffraction line width and cross-checked by scanning electron microscopy and surface area measurement, increased smoothly with calcination temperature from roughly 25 nm (600°C; consistent with [7]) to 150 nm (1200°C) for 0.5% Sb-doped materials. X-ray Photoelectron (XPS) spectra were recorded with a VG ESCALAB 220i XL using focused (300 μm spot size) monochromatised Al-Kα radiation. The scans were acquired with a step size of 100 meV and the spectrometer pass energy was 20 meV. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV and the sample charging was controlled with a 3 eV flood gun. Spectrum quantification and curve fitting was performed using a Shirley background and sensitivity factors were obtained from Wagner et al [30].

Gas combustion measurements were performed with a quartz reactor tube (15 mm in diameter) and quartz frit upon which 1g of the powder was placed. The reacting gases (1000 ppm in 21% O₂, 79% N₂ or Ar) were supplied at 50 cm³.min⁻¹ through mass-flow controllers (Tylan) to the reactor tube mounted vertically in a tube furnace. The temperature was ramped from 25°C to 600°C at 10°C.min⁻¹. A quadrupole mass spectrometer was used to measure the concentrations in the gas stream after passage through the reaction tube. For CO oxidation the gas mixtures contained Ar instead of N₂ to remove the mass 28 interference. Carbon dioxide was the only product detected. The mass spectrometer signal was linear in concentration of CO, CH₄ and CO₂. The pseudo-first order rate constant for the surface catalysed combustion was calculated as previously described [32]. Specific surface area was determined by krypton adsorption at 77K using a volumetric procedure. Values very similar to those noted by Brown and Patterson [4] were obtained. For comparison of materials, the rate constant was normalised by the surface area of the sample.
3.3. Results

3.3.1. Sb surface segregation

The variation of electrical conductivity with calcination temperature is shown in Fig 3.2. The material calcined at 600°C had properties essentially the same as those of the undoped SnO₂ calcined at the same temperature, and it must be concluded that this material was unreacted. Such a material has been described as an unordered assembly of Sb- and Sn-centred octahedra [4,7]. The variation of conductivity with reaction temperature could, in absence of other information, be taken simply to illustrate the variation in degree of reaction with calcination temperature.

![Graph showing electrical resistance of Snₓ₋₀.₀₀₅Sbₓ₀.₀₀₅O₂ as a function of temperature](image)

**Fig 3.2.** Electrical resistance of Snₓ₋₀.₀₀₅Sbₓ₀.₀₀₅O₂ exposed to dry air at 400°C as a function of temperature

80
However, XPS demonstrates that the effect is related to the temperature dependent surface segregation of Sb. Al K$_\alpha$ excited photoelectron spectra in the region O1s and Sb3d are shown in Fig 3.3. The Sb 3d$_{5/2}$ peak overlaps with the O1s peak but from the intensity and assuming the Sb3d$_{3/2}$ / Sb3d$_{5/2}$ intensity ratio the atomic % of Sb segregation could be calculated.

![Photoelectron spectra of the O 1s and Sb 3d region for Sn$_{0.095}$Sb$_{0.005}$O$_2$ calcined at different temperature.](image)

**Fig 3.3.** Photoelectron spectra of the O 1s and Sb 3d region for Sn$_{0.095}$Sb$_{0.005}$O$_2$ calcined at different temperature.

Variation of the calcination temperature produced systematic changes in surface composition determined from XPS data (Fig 3.4.). The surface enrichment factor was observed to vary dramatically with bulk composition (by a factor of ten between 0.5
and 5% Sb-doped compounds at 800°C) at constant calcination temperature. Both series of doped materials (0.5 and 5% Sb) exhibited a firing temperature of maximum Sb enrichment, the maximum shifting to higher temperature (1000°C instead of 800°C) at higher antimony concentration. If the effect were simply due to a variation in degree of reaction, then a monotonic variation of Sb signal with calcination temperature would be expected, rather than the observed maximum.

![Graph showing variation in surface composition with calcination temperature.](image)

**Fig 3.4.** Variation in surface composition with calcination temperature at constant bulk composition and constant calcination period (12h)

XPS and UPS study of conduction electrons in Sb-implanted SnO₂ showed [33] that not all the implanted Sb ions on the surface acted as donor centres but that some behaved as trapping centres. The mechanism for carrier trapping was explained by consideration of photoemission structure in the bandgap region between the VB and
the CB [34]. The significant structure was a small shoulder at the valence band edge of the pure SnO₂, which was removed by Sb implantation. Photoemission difference spectra (Sb-implanted - pure SnO₂) were used to display this effect clearly. Our XPS measurements in the valence band region confirmed this effect and showed its correlation with Sb segregation (see Fig 3.5.). Materials fired at 800°C which correspond to the highest Sb segregation showed a strong difference peak at 3 eV binding energy. This difference peak did not appear for materials calcined at 600°C, confirming the interpretation that this was unreacted. For materials calcined at higher temperature the difference peak intensity correlated with the surface segregation, being greatest for largest surface Sb concentration.

**Fig 3.5.** Photoemission difference spectrum between undoped and doped SnO₂ sintered at different temperatures. The spectra were normalised to the intensity of the valence band maximum.
3.3.2. Elevated-temperature electrical response to changing water vapour pressure

The sensitivity of the electrical resistivity to variations of water vapour pressure ($S_{\text{H}_2\text{O}}$) is defined as $S_{\text{H}_2\text{O}} = (R_{\text{dry}} - R_{\text{wet}}) / R_{\text{wet}}$. The sensitivity to water as a function of partial pressure of the gas at 25°C, determined at 400°C for pure SnO$_2$ materials fired at different temperatures, is shown in Fig 3.6.

![Graph showing sensitivity to water vapour pressure at different temperatures.](image)

**Fig 3.6.** Sensitivity of SnO$_2$ to humidity at 400°C as a function of saturated vapour pressure (Pa)

The sensitivity increased roughly linearly with the partial pressure. Whereas for undoped materials the sensitivity, expressed as the slope of the line relating response to water vapour pressure correlated with the change in crystallite size, the Sb-doped
materials behaved differently. The effect was particularly noticeable for the smaller Sb-doping (as for the 5% Sb-doped materials the resistivity was much too small) which exhibited an enhanced sensitivity (by a factor of 2) to water at a calcination temperature of 800°C. Comparing $S_{\text{H}_2\text{O}}$ (50% RH at 20°C = 1244Pa ) at 400°C (Fig 3.7.) for undoped and 0.5% Sb-doped materials shows the clear correlation of $S_{\text{H}_2\text{O}}$ with surface antimony segregation.

**Fig 3.7.** Sensitivity to moisture (1244 saturated vapour pressure = 50% RH) of $\text{Sn}_{1.3}\text{Sb}_0.7\text{O}_2$ pellets at 400°C as a function of calcination temperature
3.3.3. Catalysed combustion

The reaction product of both methane and carbon monoxide (dry and wet) over Sn$_1$.ySb$_2$O$_2$ was carbon dioxide. The reaction of these gas was monitored by looking at the mass 44 intensity as a function of temperature. Fig 3.8. shows the onset temperature of methane combustion at around 420°C for SnO$_2$. The onset temperature was found to be around 450°C for the antimony-doped samples, while carbon monoxide oxidation occurred at around 300°C for all our materials. On Fig 3.8. at 400°C the mass spectrometry data indicated that 60% of the carbon monoxide and virtually none of the methane had reacted upon passage through the packed bed of the solid.

![Fig 3.8. Catalytic oxidation of CO and CH$_4$ in a packed-bed, flow-through reactor: mass 44 (CO$_2^+$) intensity against reactor temperature for oxidation of 1000 ppm CO and 10000 ppm CH$_4$ in 21%O$_2$+79%Ar over SnO$_2$ calcined at 800°C](image)
The first-order rate constant for methane combustion, calculated from these data, was approximately 100 times greater than that given by Brown and Patterson [4], consistent with the 100-times increase in oxygen partial pressure.

Fig 3.9. represents the variation of the pseudo-first-order rate constant with temperature for surface catalysed combustion of dry and wet CO for materials fired at different temperature. The variation with temperature follows an Arrhenius form. The consistency of results for the undoped SnO₂ indicates a relative error of no more than ±10% in the rate constant normalised to the surface area. On the undoped SnO₂, the effect of introduction of water vapour was to decrease the rate but leave the activation energy unchanged. In dry gas, the rate constant for the Sb-doped materials was identical within experimental error to that of the undoped SnO₂. However, in wet gas, the activation energy for combustion catalysed on the Sb-doped materials was increased, to a degree dependent on the calcination temperature.

![Figure 3.9](image_url)

**Fig 3.9.** First-order rate constant, $k_1$, for catalysed oxidation of CO, against temperature, $1/T$. The labels (20%, 50%, 80%) refer to the degree of conversion of CO to CO$_2$ on passage through the reactor bed.
The activation energy for combustion over all the materials with dry and wet CO is plotted against calcination temperature in Fig 3.10. A clear maximum, correlating with the temperature-dependent surface segregation of Sb, is shown. The effect of Sb segregation is perhaps better described as causing, over the temperature range of observation, an increase in rate of combustion in wet gas from that characteristic of wet gas on undoped SnO\textsubscript{2} to that characteristic of dry gas on SnO\textsubscript{2}.

**Fig 3.10.** Activation energy for CO oxidation in both wet (2500 Pa \(\approx\) 100% relative humidity at room temperature) and dry gas against calcination temperature of the Sn\textsubscript{1.3}Sb\textsubscript{0.7}O\textsubscript{2} catalyst.
3.4. Discussion

We have demonstrated that Sb(III) segregated to the surface of SnO₂ forms an electrically active surface state which interacts with water. We have demonstrated an effect of this surface interaction upon the rate of the surface catalysed combustion of carbon monoxide.

Dramatic antimony segregation in SnO₂ has previously been demonstrated by XPS [11] and it has been suggested [33] that, as not all the implanted Sb ions on the surface act as donor centres, Sb can also act as a trapping centre. The mechanism for carrier trapping was supported by consideration of photoemission structure in the band gap region between valence and conduction bands. SnO₂ thin films have shown [34] pronounced photoemission intensity above the main valence band structure responsible for a shoulder that tails into the band gap region. Experiments performed on SnO₂ (110) [35] confirmed earlier suggestions [28] that this structure is to be associated with Sn ions at surface sites that trap a pair of electrons to become Sn(II) rather than Sn(IV). After implantation, the Sn(II) bandgap structure was significantly attenuated (compare with Fig 3.4.). The evident changes in difference spectra suggest that antimony ions substitute for surface Sn ions and electrons are then trapped into Sb⁺⁺⁻⁻ like surface states which lie at higher BE than the Sn²⁺ states and overlap the main O 2p valence band intensity. Hence, the energy of the Sn(II) surface state is represented by a peak at 3 eV in the difference spectrum but it is not possible to observe the Sb(III) surface state energy directly in difference spectra.

A maximum Sb segregation was obtained at 800°C for the 0.05% Sb-doped compounds (see Fig 3.3). At 600°C the decrease in apparent segregation, which was roughly the same for 0.5 and 0.05% Sb-doped materials, was probably due to incomplete reaction, because the valence band structure observed by XPS was almost indistinguishable from that of pure SnO₂, and because the electrical conductivity of this material was almost identical to that of pure SnO₂ calcined at the same temperature. At higher calcination temperatures (1000 and 1200°C) a decrease in Sb(III) concentration was observed, from the maximum obtained at 800°C, which
could be due to the diffusion of Sb$^{3+}$ into the bulk of the material. Our results on Sb surface segregation agree quantitatively with those of Cross and Pyke [11], who showed that for calcination temperatures greater than 400°C the surfaces became increasingly enriched in antimony, reaching a maximum for calcination temperature close to 1000°C, with a surface enrichment factor of 7 with 4% atom of Sb and of 35 for 0.5% atom of Sb.

In the presence of gaseous oxygen, the elevated-temperature electrical conductivity of SnO$_2$ is determined by chemisorbed oxygen, trapping conduction electron in surface states formulated as O$_2^*$, O$^-$ and O$^{2-}$. Gas sensitivity of the electrical conductivity arises from changes in the surface concentration of these states [24]. Previous discussions have particularly identified changes in the surface concentration of the O$^{2-}$ state as being responsible for the gas effects. Given this background, previous discussions[24] of the effect of water have postulated a transformation such as

$$O^{2-}_{ads} + H_2O \rightarrow 2OH^-_{ads} \quad (3.1)$$

The trap state represented by $OH^-_{ads}$ is supposed to lie higher in the band gap than that represented by O$^{2-}$, to account for the transformation causing an increase in conductivity. The expected effect of substitution of an electron donor into the lattice, giving an increase in conductivity, is to cause a decrease in the sensitivity to gases. Thus, the expected trend in the sensitivity to H$_2$O, taking into account that the material calcined at 600°C was essentially unreacted, is shown by the dashed line in Fig 3.6. Clearly, for a calcination temperature of 800°C there was a significant enhancement of the electrical response to H$_2$O, correlating with the segregation of Sb and the formation of the Sb(III) surface species. On these materials, the response to CO and CH$_4$, dry, showed only effects attributable to the variation in particle size with calcination temperature as will be observed in Chapter 4. Therefore, we have unequivocally demonstrated that the sensitivity to one chemical species (water) is specifically enhanced as a consequence of surface segregation changing the surface composition.

Sb(III) is a surface trap state state for electrons [28]. Water therefore acts as an electron donor into this state, causing an increase in conductivity, confirming the
speculation of Egdell [27]. This is a molecular adsorption of H$_2$O, rather than the dissociative adsorption postulated by equation (3.1). Sn(II)$_{surf}$ is also a surface trap for electrons, and the effect of water on undoped SnO$_2$ could, therefore, also be due to molecular adsorption onto the Sn(II) state.

Water vapour had a very strong effect on the surface catalysed oxidation of CO over doped and undoped SnO$_2$. At a given temperature (e.g. 400°C) the rate of combustion normalised to the surface area of all the materials for CO was greater under dry conditions than wet. However, the effect of Sb segregation was to cause a transition, over the temperature range of observation, from behaviour characteristic of ‘wet’ SnO$_2$ to that characteristic of ‘dry’ SnO$_2$. We can develop an interpretation which unifies the treatment of the electrical and the catalytic behaviour by following the arguments advanced by Brown and Patterson [4]. These authors showed that the exchange of oxygen between the lattice and gaseous carbon dioxide or water was very rapid, even at room temperature, and that, in the oxidation of methane, the carbon dioxide formed incorporated equally oxygen derived from the lattice and oxygen adsorbed onto the surface from the gas. They showed that oxygen exchange between gas and lattice required much higher temperature, and that the reversible dissociative adsorption of oxygen contributed negligibly to this exchange. They postulated that surface oxygen vacancies mediated the oxygen exchange and that the catalytically active surface species was molecular oxygen adsorbed at reduced Sn sites. These ideas contrast with those put forward for the electrical behaviour, which emphasise the importance of dissociative ionosorption of oxygen. Thus, in the case of an n-type semiconducting oxide, such as SnO$_2$, the chemistry taking place at the surface can be modelled by two main reactions. In the first reaction, atmospheric oxygen becomes chemisorbed to the surface consuming electrons

$$\frac{1}{2} O_2(g) + e^{-} \xleftrightarrow[k_4]{k_{-4}} O^-(ads)$$

(3.2)

Reducing gases such as CO, present in the ambient air, produce a counter reaction

$$CO + O^-(ads) \xrightarrow{k_5} CO_2 + e^{-}$$

(3.3)

where $e^{-}$ is a conductance electron. The reducing gas removes the chemisorbed oxygen, frees up an electronic carrier, $e^{-}$, and raises the conductivity of the sensor.
Analysis of the conductance variation with gas concentration implies that the active oxygen species is best formulated as $O^{2-}$. As noted before, the effects of water vapour have been discussed [21,22] in terms of the displacement of chemisorbed oxygen by $H_2O$ and $OH^-$, producing, on $SnO_2$, a surface electronic state such as a surface hydroxyl species [24], which lies higher in energy than the oxygen species which is displaced.

First, we postulate that a correct formulation of ‘adsorbed oxygen’ is an oxygen molecule trapped in or on a surface oxygen vacancy. Following Brown and Patterson, we propose that the combustion reaction proceeds partly through these species and partly through lattice oxygen at the surface. Then we propose that water competes with oxygen for the surface vacancies, blocking this route. This accounts for the diminution in the rate of the surface catalysed reaction in the presence of water. To account for the effect of antimony segregation on the reaction, we presume that the surface vacancy is correctly formulated as an association of Sn(II) with the vacancy in the absence of antimony, and of Sb(III) with the vacancy in the presence of surface segregated antimony. Then we propose that the binding energy of water to the Sb(III).$V_O$ surface defect complex is less than that to the Sn(II).$V_O$ complex. The temperature variation of combustion rate would then correspond simply to the desorption of water from the defect complex. The apparent activation energy for combustion on the Sb-segregated sample would measure the heat of adsorption of water onto the surface defect.

Now we can make a connection between this interpretation and the electrical behaviour. First, an elementary reaction between oxygen and a surface defect complex can be written:

$$2e'$$

$$[Sn_{Sn}^{n'/2}.V_{O}^{**}] + O_2 \rightarrow [Sn_{Sn}.O_O]-O \rightarrow [Sn_{Sn}.O_O]-O^{2-} \quad (3.4.)$$

The overall stoichiometry of this reaction can be represented as

$$4n' + V_O^{**} + O_2 \rightarrow O_O^{x} + O^{2-}_{ads}$$
in which two electrons are trapped for each surface oxygen atom, as the interpretation of the electrical behaviour requires. Interestingly, the mechanism as formulated here does not require dissociation of molecular oxygen.

A dissociative adsorption of water onto the surface defect complex is proposed:

\[
[S\text{ns}_{\text{Sn}}.\text{Vo}^{**} ] + \text{O}_\text{O} + \text{HOH} \rightarrow [\text{OH}_{\text{O}}^{*}.\text{Sn}_{\text{Sn}}^{**}.\text{OH}_{\text{O}}^{*} ] \tag{3.5.}
\]

In comparison with (3.4.), the surface electron trap in (3.5.) may lie at higher energy in the band gap, so replacement with water of oxygen adsorbed at the defect results in an increase of conductivity. Where Sb is surface segregated, the surface defect complex could be written \([S\text{bs}_{\text{Sn}}.\text{Vo}^{**}.\text{Sb}_{\text{Sn}}']\). A similar formulation for the surface reactions can then be made. If the energy difference between OH state and oxygen state is bigger on this site, then the effect of water vapour on the conductivity would be larger. Such a statement is consistent with water being less strongly bound at this state than at the tin defect state represented in (3.5), and is thus consistent with the interpretation of the effect on combustion kinetics advanced above.

3.5. Conclusion

In summary, the study of the effect on electrical response and on combustion kinetics of Sb segregation in SnO₂ has identified consequences linked to the adsorption of water. Discussion of these has suggested formulations for the surface defect states which mediate the electrical behaviour.


Chapter 4. Particle Size Effect on the Gas Response of Sn(Sb)O₂ Gas-sensitive Resistors, when Debye Length and Particle Radius are Comparable.

Abstract

Metal oxide additives such as Sb in polycrystalline tin oxides are known to stabilise SnO₂ particles grain growth. The granular state of Sn(Sb)O₂ investigated by SEM and XRD is also expected to have profound effects on its gas sensing properties. The space charge layer thickness, $L$, depends on the surface charge, which also depends on temperature, gas concentration and gas type. For undoped SnO₂ there is no threshold in base line resistance, yet there is a threshold in gas response. An interpretation based on the variation in surface potential, $\phi$, has been proposed. For Sb-doped SnO₂ the variation in conductance was due to a spatial change in donor density (i.e. Sb⁴⁺) in the bulk. Upon Sb doping the particle-size threshold in gas response has moved to lower particle size, which correspond to a grain control regime ($D < 2L$) since the Debye length ($L_D$) depends upon donor density. Effects of water vapour on gas response are due to the effect of water adsorption upon $L$ since H₂O is electrically active and adsorbed independently on different sites than the reactive ionosorbed O species as demonstrated in Chapter 3.
4.1. Introduction

As indicated in Chapter 1.6.1. profound effects of microstructure on the behaviour of semiconducting oxide gas-sensitive resistors are to be expected. Quite generally, for these devices, adsorption or reaction at the gas-solid interface changes the surface concentration of an electrically active surface state, and this change is signalled by a change in the measured electrical conductivity. For the case where the only mobile charge carriers are electrons or holes, the presence of surface states implies a depletion or accumulation layer at the interface, and the measured effect is then, in principle, simply related to the dimension of this space-charge layer in relation to the dimensions of the bulk conduction path. In this present study, we show that some dramatic and previously unsuspected effects, whose interpretation is very subtle, can arise in the case where the device is fabricated in the form of a porous solid with average particle radius comparable to the space charge layer thickness (Debye length). The subsequent discussion clarifies some aspects of the interpretation of interaction effects between different gases when more than one gaseous species is present: a technologically particularly important effect like this is that of the variation in water vapour pressure upon the elevated-temperature response of a semiconducting oxide to a reactive gas such as methane or carbon monoxide present at low concentration in air.

A number of authors have discussed microstructure effects on semiconducting oxides gas-sensitive resistors fabricated in the form of porous layers [1,2,3]. Two limiting cases have been identified. The first is the surface trap limited case, where the Debye length substantially exceeds the particle dimensions. In this case, the conductivity is related directly to the surface trap concentration [4]. The second is the Schottky barrier limit, where the conductance is determined by the overlap of depletion layers at interparticle contacts, creating a circumstance equivalent to a potential barrier between the crystallites, with conductivity controlled by the barrier height [5,6]. Intermediate cases, focusing on the dimension relative to the depletion layer thickness of the ‘necks’ between particles in a sintered microstructure have been discussed on previous occasions [1,6,7] and in Chapter 1.
Overall, there have been rather few systematic experimental studies of the effect of microstructure on response. Some authors [8,9,10,11] have attempted to explain the role played by the microstructure on the sensitivity insisting on the importance of controlling accurately the neck size and the coordination number of the materials. Others [1,7,12,13], have shown how both baseline resistance and response rise markedly as crystallite size decreases, postulating that the effect occurs when crystallite dimension and Debye length become comparable.

The effect of microstructure on response, where the microstructure is altered as a consequence of the addition of dopants can be confused with the electrical effects of the dopants. For example, increasing donor density by doping SnO$_2$ with Sb(V) obviously causes a decrease in depletion layer thickness with a consequent decrease in gas sensitivity. However, V-valent dopants in SnO$_2$ inhibit grain growth on sintering, [12], so another effect of Sb addition is to give smaller particle size in the final device; an effect, which according to the accepted interpretation advanced above, would tend to act to increase gas sensitivity. Such dopants can also be surface-segregated [14], giving effects either directly on the surface chemistry (as indicated in Chapter 3.) or indirectly through the electrical consequences of an inhomogeneous donor distribution.

A secondary but significant effect of microstructure on response arises when a concentration gradient of the gas being detected can be developed within the porous sensor structure as a consequence of the surface-catalysed decomposition of the gas. The concentration gradient induces a conductivity gradient, which translates into an effect on the measured conductance dependent on the device geometry. This effect is dependent on the gas decomposition rate, which is in turn dependent on the internal surface area of the sensor and upon the gas diffusivity within the porous solid [15]. Thus, the microstructure can have a profound effect upon gas response, which is not related to the details of the space charge layer thickness in relation to the particle size and other factors concerning fundamentals of the electrical behaviour. To isolate
such effects it is necessary to eliminate or compensate for the secondary effect of reaction-diffusion within the porous structure of the device.

In the present work, by systematically studying the effect of calcination temperature on the gas-sensing behaviour of Sb-doped SnO$_2$ prepared in fine-particle form, supported by measurements of surface area, particle size and surface composition, we show how the interplay of all these subtle effects can have quite dramatic consequences.

4.2. Experimental

The oxides Sn$_{1-y}$Sb$_y$O$_2$ ($y = 0, 0.005, 0.05$) were prepared by co-precipitation [7] using the same method described in Chapter 3.2. The experimental methods used were identical to those given in 3.2 and 2.2.

The electrical behaviour under controlled humidity and temperature conditions was monitored in a computer-controlled rig (described in Chapter 2 and [17]) upon exposure to ppm quantities in air of methane, carbon monoxide, and water. The gas flow was controlled using mass-flow controllers.

X-ray powder diffractrometry (Siemens 5000 with Cu-K$_\alpha$ radiation) showed the presence of a single well-crystalised rutile phase, whose lattice parameters were the same as undoped SnO$_2$. The average size of the crystallites could be estimated from the broadening of the XRD diffraction line (101) and deduced from the Scherrer equation [18]. The microstructure was examined using a Hitachi S-570 model Scanning Electron Microscope (SEM). All the samples were gold coated. The instrument was operated at 20 kV and 60-80 mA (with a beam diameter of a few microns dependent on the aperture size). The measurement of the tin-antimony dioxide surface area was carried out straightforwardly using the BET isotherm in which an inert gas (Krypton or Nitrogen) at low temperature (77 K) is physisorbed in layers onto the surface.
XPS spectra were acquired using focused (300 μm spot size) monochromatised Al-K radiation (VG ESCALAB 220i XL). The scans were acquired with a step size of 100 meV and the spectrometer pass energy was 20 eV. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV and the sample charging was controlled with a 3 eV flood gun.

4.3. Results

4.3.1. Materials characterisation

The grain size of Sn$_{1-x}$Sb$_x$O$_2$ depended mainly on the calcination or sintering temperature as well as the amount of antimony. Fig 4.1. shows the particle size, $D$, as well as the specific surface area of SnO$_2$ and Sn(Sb)O$_2$ powder as a function of calcination temperature (calcination time 12 h).

All the doped samples retained larger specific surface areas (SA) over the whole calcination temperature range. Increasing the amount of additives from 0.5 to 5% had the effect of increasing SA and decreasing $D$, thus stabilising the undoped material confirming previous studies by Xu et al [12]. Tin-antimony oxides undergo crystal growth (typically from 20 to 200 nm) with a rise in calcination temperature.
Fig 4.1. Variation of particle size (Scherrer equation XRD) and the surface area (BET) with calcination temperature for Sn$_{1-y}$Sb$_y$O$_2$

The granular state of the Sn$_{0.95}$Sb$_{0.05}$O$_2$ materials is shown on SEM photographs (Fig 4.2.) for different firing temperature. The estimated increasing grain sizes with calcination temperature obtained from these photographs were found to coincide with those based on XRD analysis. Corresponding changes were also observed in the surface areas of these materials.
The specific surface areas ($S_a$), obtained from BET isotherm data of $N_2$ and $Kr$ adsorption at $-196^\circ C$, increased with antimony concentration at a given firing temperature, and decreased with increasing calcination temperature. These results were in agreement with similar work [18]. Relevant properties of the materials are given in Table 4.1. Necks form between particles when coagulation of $SnO_2$ particles occurs. The grain size ($D$) of the particles can be correlated with the neck size and specific surface area can be related to particle size and shape [19]. In the simplest
case of spherical particles which will be considered in this study there is no difficulty in defining the particle size.

Table 4.1. Surface area \( (m^2.g^{-1}) \) of antimony-tin oxide compounds.

<table>
<thead>
<tr>
<th>Calcination temperature ( (°C) )</th>
<th>bulk Sb (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5 4.8</td>
</tr>
<tr>
<td>600</td>
<td>10.1 19.2 24.9</td>
</tr>
<tr>
<td>800</td>
<td>6.0 11.0 16.3</td>
</tr>
<tr>
<td>1000</td>
<td>3.8 7.3 11.7</td>
</tr>
<tr>
<td>1200</td>
<td>2.1 4.6 8.1</td>
</tr>
</tbody>
</table>

Thus, the volume, \( V \), and the surface area, \( SA \), of \( n \) equal size particles of constant shapes can be expressed as

\[
\begin{align*}
SA &= \alpha_s nD^2 \\
V &= \alpha_v nD^3
\end{align*}
\]  

where \( \alpha_s \) is the surface coefficient or the surface shape factor and \( \alpha_v \) is the volume coefficient or the volume shape factor. The numerical values of these coefficients depend on the particle shape and on the definition of \( D \). The coordination number \( (N) \) of particles in the coagulated state which represent the number of neighbours a particle is bonded with can be estimated using the correlation between specific surface area \( (SA) \) and grain size \( (D) \) as shown in Fig 4.3. If \( K = \alpha_s / \alpha_v \) and when all particles are free \((N=0, \text{ assemblage of spherical particles with the same diameter})\), the specific surface area by weight can be written as:

\[
SA = K/\rho D
\]  

where \( K \) is known as the specific surface coefficient or simply the shape factor and \( \rho \) is the density of particles \((7.0 \text{ g.cm}^{-3} \text{ for SnO}_2)\). In this study, the increase in calcination temperature resulted in a steep increase of crystallite size, while porous nature was barely affected. Surface area data gave an indication on the geometry of the crystallites. The surface area for SnO\(_2\) fired at 1200, 1000, and 800°C, for example, amounted to only 41, 58 and 66% of those expected for the assemblies of free spheres of diameter \( D \). The difference can be explained by a loss of free surface of each particle due to coordination with its neighbours. The theoretical relation for
free spherical particles ($K = 6$) deviate from the experimental data and is plotted in Fig 4.3.

SnO$_2$ is known to be resistive to sintering into dense blocks. Heat treatment below 1200°C has been observed [20] to cause grain growth of SnO$_2$ particles without shrinkage or increase in apparent density of the sintered body. Hence, it would seem that the grain growth involves no bulk diffusion and occurs by a mechanism other than volume diffusion. In fact surface diffusion mechanism and evaporation-condensation mechanism could have an effect in the sintering of SnO$_2$ depending on the sintering temperature. It also appears that antimony added suppresses the surface diffusion, leading to the stabilisation of SnO$_2$ particle against grain growth.
4.3.2. Surface analysis

As indicated in Chapter 3, the Sb 3d$_{5/2}$ peak overlap with the O1s peak but from the Sb3d$_{5/2}$ intensity ratio the exact atomic % of Sb segregation could be calculated. The XPS data of the materials are given in Table 4.2. Both series of doped materials (0.5 and 5% Sb) exhibited a firing temperature of maximum Sb enrichment, the maximum shifting to higher temperature (1000°C instead of 800°C) at higher antimony concentration.

Table 4.2. XPS binding energies and Sn:Sb ratios for Sn$_{1.2}$Sb$_x$O$_2$

<table>
<thead>
<tr>
<th>Calcination temperature /°C</th>
<th>Sn 3d$_{5/2}$</th>
<th>Sb 3d$_{5/2}$</th>
<th>Sn:Sb</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{0.95}$Sb$</em>{0.05}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>486.7</td>
<td>540.0</td>
<td>32.4</td>
<td>530.6</td>
</tr>
<tr>
<td>800</td>
<td>486.9</td>
<td>540.2</td>
<td>4.3</td>
<td>530.8</td>
</tr>
<tr>
<td>1000</td>
<td>486.9</td>
<td>540.3</td>
<td>8.3</td>
<td>531.1</td>
</tr>
<tr>
<td>1200</td>
<td>487.1</td>
<td>540.7</td>
<td>8.4</td>
<td>531.1</td>
</tr>
<tr>
<td>Sn$<em>{0.95}$Sb$</em>{0.05}$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>486.9</td>
<td>540.4</td>
<td>9.8</td>
<td>530.9</td>
</tr>
<tr>
<td>800</td>
<td>486.9</td>
<td>540.4</td>
<td>7.1</td>
<td>530.9</td>
</tr>
<tr>
<td>1000</td>
<td>486.7</td>
<td>540.3</td>
<td>3.2</td>
<td>530.9</td>
</tr>
<tr>
<td>1200</td>
<td>487.0</td>
<td>540.6</td>
<td>5.9</td>
<td>531.1</td>
</tr>
</tbody>
</table>

4.3.3. Electrical Resistance and Gas Response

The electrical resistivity at 400°C and activation energy for conduction in dry air, measured for over the temperature range 450-550°C is given in Table 4.3. These data in part repeat those given in Chapter 3, but are presented again in order to aid the subsequent discussion. As expected for a given calcination temperature, the resistivity decreased upon addition of Sb$^{5+}$. Fig 4.4. shows the electrical resistance measured at 400°C in air for 0.5% Sb-doped tin oxide system as well as pure SnO$_2$ systems, as a function of their respective crystallite size, $D$. 
The resistivity of the 5% Sb-doped materials was too low for any gas sensing applications. Whereas the resistivity of the undoped materials increased slightly with increasing grain size, the doped compounds behaved inversely. The activation energies followed the resistivity pattern. The drop in activation energy correlates with the diffusion of Sb throughout the material.

The sensitivity to 1% carbon monoxide and methane in dry air at 400°C for SnO₂ and Sn₀.₉₉₅Sb₀.₀₀₅O₂ is shown as a function of crystallite size in Fig 4.5 and 4.6.
Table 4.3. Resistivity at 400°C and activation energies for the Sn$_{1-y}$Sb$_y$O$_2$ compounds sintered at different temperature

<table>
<thead>
<tr>
<th>Calcination temperature / °C</th>
<th>Resistivity / Ωcm</th>
<th>$E_a$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk Sb (atom %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>600</td>
<td>1200</td>
<td>450</td>
</tr>
<tr>
<td>800</td>
<td>1950</td>
<td>22.5</td>
</tr>
<tr>
<td>1000</td>
<td>3000</td>
<td>1.05</td>
</tr>
<tr>
<td>1200</td>
<td>3900</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fig 4.5. Sensitivity of Sn$_{1-y}$Sb$_y$O$_2$ materials to 1% CH$_4$ in dry air at 400°C as a function of crystallite size.
A few points can be observed. Firstly, all the materials showed, as expected, a n-type conductivity. Secondly, the grain size had a similar effect on the sensitivity of the semiconducting oxides to CO and CH₄. All materials exhibited a critical crystallite size threshold towards their sensitivity to CO and CH₄, although this threshold appeared at a lower grain size for antimony-doped materials (typically switching from around 60 nm for 0.5% Sb to 100 nm for SnO₂). Thirdly, the 0.5% antimony doped compounds exhibited similar sensitivities to the undoped compounds. Fourthly, all the materials exhibited a temperature of maximum sensitivity at around 400°C for both CO and CH₄.

The sensitivity of the materials to methane and carbon monoxide under dry and wet conditions was proportional to the square root of the gas concentrations ($S_{gas} = \sqrt{C_{gas}}$).
$A^*/[\text{gas}]^{1/2}$). Fig 4.7. and 4.8. shows $A_{\text{dry gas}} / A_{\text{wet gas}}$ as a function of calcination temperature at 400°C for the response to carbon monoxide and methane. It is clear that, firstly the Sb-doped materials for both gases showed a correlation of the ratio $A_{\text{dry}} / A_{\text{wet}}$ with surface antimony segregation ($A_{\text{dry}} / A_{\text{wet}}$ is maximum at a calcination temperature of 800°C which corresponds to a surface enrichment factor in antimony of 38). Secondly, all the materials showed $A_{\text{dry}} / A_{\text{wet}}$ close or less than unity for CO and greater than 1 for CH₄. That is, the effect of the presence of water vapour was to increase the sensitivity to methane but to decrease the sensitivity to CO.

![Figure 4.7](image)

**Fig 4.7.** $A_{\text{dry}} / A_{\text{wet}}$ as a function of crystallite size with $A = S_{\text{gas}} / [\text{CO}]^{1/2}$
Fig 4.8. $A_{\text{dry}} / A_{\text{wet}}$ as a function of crystallite size

with $A = S_{\text{gas}} / [\text{CH}_4]^{1/2}$

4.4. Discussion

Yamazoe et al [1] have observed a characteristic change in behaviour of electrical resistance which seems to occur at a critical crystallite size ($D = 6$ nm) which is understood as being associated with the formation of an electron depleted space charge layer (thickness, $L$) on the constituent particles. Xu et al. [21] have also looked into the correlation between crystallite size and the gas sensing characteristics of SnO$_2$-based sensors, where SnO$_2$ grain size was controlled by the addition of several dopants. It was found that the gas sensitivity increased with decreasing crystallite size (around 5-10 nm). In the case of the sensor doped with rare-earth or
alkaline-earth metals or with Ni and Zn (more or less stable valency), the crystallite size was about 5 nm, and in these cases the gas sensitivity was found to be exceptionally high.

Theoretically, in the semi-infinite case, the thickness of the space charge layer or screening length \( (L) \) at the semiconductor interface is related to the surface charge, \( q_s \), and to the density of positive charge in the space charge layer, \( N_D \), by

\[
L = \frac{q_s}{eN_D}
\]  

(4.3)

Theoretically the Debye length \( (L_D) \) is been defined as:

\[
L_D = \left[ \frac{\varepsilon \varepsilon_0 kT}{e^2 N_D} \right]^{1/2}
\]  

(4.4)

Equation (3) and (4) relate \( L \) to \( L_D \) via the thermal energy, \( kT \), and the surface potential, \( e\phi_s \)

\[
\frac{L}{L_D} = \sqrt{\frac{2e\phi_s}{kT}}
\]  

(4.5)

As \( L_D \) is an intrinsic value for each material, the surface potential, \( \phi_s \), depends upon the charge trapped in the surface states. In a constant gaseous environment, \( \phi_s \) is therefore constant. Yamazoe et al. [1] proposed, given that the thickness, \( L \), of the space charge region is kept essentially constant, that the proportion of space charge region in each particle decreases relatively with increasing \( D \). This critical crystallite size is assumed to correspond to a point where \( D \) becomes equal to twice the charge layer \( (D = 2L) \). A similar proposal with WO_3-based NO_x sensor was made by Miura and Yamazoe [13] suggesting that \( L \) could also depend on the amount of adsorbed NO_2 on the WO_3 surface.

Thus, there are particle size effects on response which are more-or-less well known. A threshold at a particular crystallite size (see Fig 4.5.) could reasonably be taken as a Debye length effect. The present work, however, shows more subtlety than the previous works. The particle-size thresholds in response depend on the gas that is present. There is no threshold in baseline resistance for the undoped SnO_2, yet, there
is a threshold in gas response. We will develop in the following an interpretation based on the variation in surface potential, $\phi_S$.

### 4.4.1. Behaviour of undoped SnO$_2$

The particle size effect for SnO$_2$ has been interpreted [1] to be due to a change in Debye length, $L_D$. When the surface trap state density is changed, as a consequence of exposure to gas, $L_D$ should change which predicts a threshold dependent on gas concentration. $D$ has also has an influence on gas sensitivity for SnO$_2$-based devices. For these devices, SnO$_2$ particles have been observed [1] to be mostly connected to neighbours by necks. Sometimes, these contacts are made by grain boundaries, which are believed to be the main origin of the $D$-dependence on the gas sensitivity.

For pure tin dioxide a slight increase (from $1.2 \times 10^3$ to $3.9 \times 10^3 \ \Omega$), only, of resistivity at 400°C in air was observed for particle size increasing from 35 to 175 nm (Fig 4.4.) as expected from previous studies [1]. Nevertheless, a threshold effect on sensitivity for varying crystallite size ($D$) varying in the same range was clearly observed (Fig 4.5), the value of $D$ at the threshold being dependent on the type of gas once effects of surface segregation had been allowed for H$_2$O (no effect) $<$ CO $<$ CH$_4$. This observation has not previously been reported. The threshold value of $D$ correlated with the sensitivity, which also went in the order H$_2$O $<$ CO $<$ CH$_4$ for the gas concentration and temperature studied.

For SnO$_2$ (undoped) at 400°C the sensitivity threshold to 1% CH$_4$ in air, roughly 120 nm, has moved to a slightly lower particle size with 1% CO in air, roughly 100 nm. This could be interpreted as a gas effect on $D$ because the sensitivity to carbon monoxide is overall smaller than methane.

The observations appear different to those previously reported, which showed effects at the same particle radius on both the baseline and sensitivity, as particle radius decreased. Hence, the interpretation of these results relies on the answer to this legitimate question: why should a particle size effect be observed on the gas response.
and not on the baseline resistance, if the answer to this question is that the increase of response is when $D \approx 2L$?

The sensitivity thresholds observed are not an effect of surface catalysed combustion either because CH$_4$ does not burn at this temperature. Combustion effects on CO response could lead to a decrease of signal for CO, greatest at smallest particle size, thus tending to damp the apparent threshold. Water does not burn and does not show a threshold either. Therefore the threshold can not be related to reaction-diffusion effects.

One interpretation of the slight resistivity increase of our SnO$_2$ materials with grain size could be explained by the fact that the space charge region is thinner than the radius of the necks between crystallites ($D>2L$) resulting in a good channel for electrical conduction through the necks and that the effect on response does not have this interpretation as its origin.

Eq. (4.3) shows that the space charge layer thickness, $L$, depends on the surface charge which depends on temperature, gas concentration and gas type. $L$ should be affected by gas concentration and type of gas. Hence, there should be a range of particle size where the variation of $L$ with gas concentration and type could be a very important effect. If in the absence of gas $L < D$ over the experimental range there would be little or no variation of baseline resistance with particle size. However, if the gas altered $\phi_0$ such that $L > D$ at some value within the experimental range, a particle size threshold in response would be evident. The theoretical development of these ideas is taken up later. We also note that the concentration dependence on sensitivity was found to be linear in $[\text{gas}]^{1/2}$ for all concentrations and particle size over the range studied. Hence, there were no threshold effects in the concentration dependence.
4.4.2. Behaviour of Sb-doped SnO$_2$

Sb$^{5+}$ doping causes the reduction of Sn$^{4+}$ species to Sn$^{2+}$ to compensate the charge giving a decrease in the resistivity. This implies that introduction of impurity cations inside the SnO$_2$ lattice should result in changes in $L$ and $L_D$, consequently attenuate or promote gas sensitivity at a given grain size. In a previous study [1], doping with 1% Sb resulted in a total loss of sensitivity which was interpreted as a decrease in $L_D$ with Sb$^{5+}$.

The resistivity of these materials exhibits a drastic baseline resistance change with change in calcination temperature. For Sn(Sb)$_2$O$_2$ the variation in conductance was due to a change in donor density (i.e. Sb(V)) in the bulk. For a calcination temperature of 600°C Sb evidently had not completely reacted because the resistivity and all the other behaviour was comparable to that of SnO$_2$ fired at the same temperature. At 800°C there was evidence of Sb surface segregation as Sb$^{3+}$ surface states. Electrons might be trapped on Sb(III) at the surface but there was also some bulk Sb(V) present giving a decrease in resistivity. For higher calcination temperatures (1000 and 1200°C) the resistivity dropped significantly indicating the dominant presence of bulk Sb$^{5+}$. At sufficiently high firing temperature Sb was uniformly distributed through the bulk of the material and was electrically active. These observations would indicate that the conductance is governed in part by the spatial variation of donor density.

As mentioned previously, for undoped materials, the threshold could come from variation of $\phi_S$ in gas as stated by Eq. (4.3). Upon addition of Sb, $L_D$ is decreased as $L_D$ depends upon donor density via Eq. (4.4). Antimony segregation, for the sample fired at 800°C, and lack of reaction, for the sample fired at 600°C, mean that we cannot develop an interpretation for the variation of baseline resistance with particle size which simply ascribes the variation to an increase in the $L/D$ ratio. However, Fig 4.5. and 4.6. shows that the Sb-doped materials display a particle-size threshold in gas response, and shows clearly that the threshold has moved to lower particle size than that for the undoped SnO$_2$. The result is consistent with the interpretation that the
threshold represents $L < 2D$ since $L_D$ in Eq. (4.3) depends upon donor density (the Sb(V) concentration) through Eq. (4.4). That $N_D$ might be spatially variable depending on the firing temperature is a complication, but does not change the interpretation.

The fact that the threshold in methane response is not as pronounced as for carbon monoxide could be explained as before as such: the Debye length change is due to a variation in surface acceptor state density, for which the change is bigger for CH$_4$ than for CO.

### 4.4.3. Effects of water vapour on baseline and response.

For the Sb-doped materials specific effects of surface segregation show up clearly in the influence of water vapour on the baseline resistance and on the response to other gases. The effects on the baseline have been discussed in Chapter 3. For SnO$_2$, the particle size dependence effect of H$_2$O on gas sensitivity mirrors the threshold effect of dry gas. The effect of H$_2$O on sensitivity was largest when response was smallest. There was no apparent effect of particle size on the response of H$_2$O alone.

From 250°C the adsorption of H$_2$O on SnO$_2$ generates surface hydroxyl groups OH$_{ads}^-$ which slowly desorb up to 500°C [22].

$$H_2O + O_{lat}^{2-} \rightarrow OH_{lat}^- + OH_{surf}^-$$

Thus, the effects of water vapour on gas sensitivity have in the past been interpreted [23,24] in terms of the displacement of chemisorbed oxygen by H$_2$O and OH$^-$. This competing surface reaction can be expressed as:

$$O_{ads}^- + H_2O \leftrightarrow 2OH_{ads}^-$$

The effect of moisture on the response to a gas (R) could be due to the reaction of this gas with both $O_{ads}^-$ and OH$_{ads}^-$ on the surface, formally written as:

$$R + 2OH_{ads}^- \rightarrow RO_2 + H_2O + 2e^-$$

The surface reaction rate of OH$_{ads}^-$ with gas is different from that with $O_{ads}^-$. 

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However, this explanation is not consistent with the particle size effects and surface segregation effects observed here. A simple explanation consistent with our results is that:

- \( \text{H}_2\text{O} \) is independently adsorbed on different sites than the reactive ionosorbed O species.
- \( \text{H}_2\text{O} \) is electrically active; that is, it traps charges at the interface, thus changing the surface charge, and hence \( L \).

The effect on the gas response is thus due to the effect of water adsorption upon \( L \). A full theoretical description requires a relation between surface charge, \( q_s \) and a surface potential, \( \phi_s \), which is independent of Eq. 4.3. and 4.5. A satisfactory formulation has not yet been given and is beyond the scope of this work.

### 4.5. Conclusion

By using a co-precipitation method starting from pure metals (Sn and Sb), the crystallite size \( (D) \) of \( \text{Sn(Sb)}\text{O}_2 \) could be controlled in the range 16 to 180 nm. For undoped \( \text{SnO}_2 \) the electrical conductivity in air and in CO or \( \text{CH}_4 \) containing air do not exhibit the same characteristics with a change in \( D \). An interpretation based on the variation in surface potential, \( \phi_s \) has been proposed. For Sb-doped \( \text{SnO}_2 \) the variation in conductance in air and in gas show a particle-size threshold dependence, which can be well understood by assuming a classical grain boundary contact model. Effects of water vapour on gas response are due to the effect of water adsorption upon the space charge layer thickness, \( L \), since \( \text{H}_2\text{O} \) is electrically active and adsorbed independently on different sites than the reactive ionosorbed O species.
References


Chapter 5. Study of Surface Segregation of Antimony on SnO$_2$ by Computer-simulation Techniques.

Abstract

In chapter 3. Sb segregation to the surface of SnO$_2$ powder was demonstrated and a correlation with sensitivity to water vapour was observed. Antimony segregation as Sb$^{3+}$ was deduced. The importance of Sn$^{2+}$ states at the surface was also indicated. In this Chapter computational methods have been applied to study the surface segregation of Sb$^{3+}$ and Sb$^{5+}$. The simulations clearly demonstrate that Sb$^{3+}$ segregates to the surface which correlates with the XPS experimental data presented in Chapter 3.
5.1. Introduction

Theoretical and computational studies have been mainly confined to the bulk properties of tin dioxide, which have predicted [1] that anion vacancies are the dominant type of defect in non-stoichiometric SnO$_{2-x}$, that a good proportion of dopants are in interstitial sites and that doping with pentavalent species such as Sb$_2$O$_5$ results in good n-type conductivity.

Thus, in this work we have examined the surface properties of stoichiometric SnO$_2$ with special emphasis on the surface defect chemistry of antimony dopants. In particular the effects of segregation of both the dopant and point defects to the surface have been investigated. It has been observed [2] that both the oxygen and tin species remain fully ionic at the surfaces in their formal valence states of -2 and +4 respectively.

The computer code (MARVIN) [3] developed at the Royal Institution and described in Chapter 1.7. has been used firstly to study the stability of a number of surfaces of the oxide assuming such an ionic model and secondly to calculate the segregation energies of neutral defects (Sb$^{5+}$/Sb$^{3+}$) and defect clusters. The program considers a known number of layers of the structure suitably oriented to terminate with the required free surface. The surface structure can be relaxed fully by moving the ions of the 2D cell to minimise the energy of the system. This energy is then compared with the bulk energy per unit cell to give the surface energy, which will provide indications on the stability of the possible crystallographic surfaces. The repeating layers of the initial cell are chosen to have no dipole moment and must be electrically neutral for the calculation to converge.

5.2. Computer Modelling

All calculations were undertaken using the energy minimisation facilities of the surface simulation program MARVIN on a Silicon Graphics work station, performing an energy minimisation calculation at 0 K which allows us to predict equilibrium
surface structures, crystal morphologies, and to dock molecules onto surfaces. The main feature of MARVIN that separates it from other modelling programs is that it calculates the long range electrostatic potential using a 2-D (two dimensional) Ewald sum [4]. We have used the shell model in which an ion is modelled by a core connected by a harmonic spring to a massless shell is used in order to take into account the electronic polarisation. Several potential types have been implemented to describe the long range van der Waals attraction and the short-range repulsion between atoms. Presently, the physical and chemical properties that MARVIN calculates are the surface energy, the attachment energy and the coordinates of the atoms (shells and cores). The surface energy is the difference between the cut crystal and the surface. The program computes this value during its calculation of the total energy:

$$E_{\text{surface}} = 16.4(E_{\text{total}} - E_{\text{boundary}} - n_{\text{units}}E_{\text{bulk}}) / \text{Area} \quad (5.1)$$

The final set of potential parameters used for SnO$_2$ were those developed by Freeman and Catlow [2]. Since Sb is a dilute impurity in this study potential parameters for Sn were simply rescaled based on the ionic radii of Sn$^{2+}$, Sb$^{3+}$ and Sb$^{5+}$, and are presented in Table 5.1.

**Table 5.1. Potential parameters**

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A / eV</th>
<th>(\rho / \text{Å} )</th>
<th>C / eVÅ$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^2-$ - Sn$^{4+}$</td>
<td>1056.8</td>
<td>0.3683</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^2-$ - O$^{2-}$</td>
<td>15123.6</td>
<td>0.2230</td>
<td>28.43</td>
</tr>
<tr>
<td>O$^2-$ - Sb$^{5+}$</td>
<td>1349.3</td>
<td>0.3683</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^2-$ - Sb$^{3+}$</td>
<td>922.6</td>
<td>0.3683</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^2-$ - Sn$^{2+}$</td>
<td>1920.5</td>
<td>0.3683</td>
<td>0.0</td>
</tr>
</tbody>
</table>

These Sb$^{3+}$ and Sb$^{5+}$ potentials are not definitive. However, since the electrostatic contribution dominates the total energy, the repulsion parameters are of secondary importance, and the results should show the correct qualitative behaviour. Secondly, the antimony is only an impurity, which diminishes the importance of these parameters.
potentials. In this study the total energy and structure were the computed properties of most interest. Appendix 5.1. represents a sample input file for tin dioxide which needs to be created and then MARVIN’S Program is run specifying the input and output files (see Appendix 5.2.). In the present work the number of unit cells for the SnO₂ structure is increased from a 2x2x2 supercell for calculations on the stability of clean surfaces to a 3x3x3 supercell for calculations involving defects. The simulation box consisted of 96 independent atoms (32 Sn ions and 64 oxygen ions) in the first case and 430 independent atoms (144 Sn ions and 288 oxygen ions) in the second case.

5.3. Results

The results of the clean surface calculations for a number of different surfaces are given in Table 5.2. in order of relative energy. The data are in very good correlation with the values calculated by Mulheran and Harding[5] who used different interionic potentials. The interplanar space (dhkl) is given since this is the simplest guide to morphological importance, with planes with a larger spacing dominating. The faces (100) and (001) have a plane of symmetry bisecting the crystal cell, which reduces dhkl for those planes by a factor of 2 [6].

Clearly we could not study every surface and so we have chosen to work through a set of Miller indices. The two surfaces that we have chosen to investigate are the (110) because it is the most stable and the (001) since the tin cations are evenly spaced along the surface normal.

The structural lattice parameters were a = 4.70990 Å and c = 3.30846 Å. These are taken from a bulk constant pressure calculation with GULP [7] using the same potential parameters. This is important because residual strain in the unit cell can distort the surface. Fig 5.1. gives a representation of the tetragonal unit cell of the SnO₂ (001) face calculated with MARVIN using 430 ions with 288 O²⁻ ions represented by red sphere and 144 Sn⁴⁺ions represented by grey spheres.
Table 5.2. Unrelaxed and relaxed surface energies of SnO$_2$ surfaces listed in order of thermodynamic stability.

<table>
<thead>
<tr>
<th>face</th>
<th>$d_{hkl}$</th>
<th>unrelaxed</th>
<th>relaxed</th>
<th>relaxed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>3.35</td>
<td>3.263</td>
<td>1.349</td>
<td>1.380</td>
</tr>
<tr>
<td>(210)</td>
<td>2.12</td>
<td></td>
<td>1.452</td>
<td>1.487</td>
</tr>
<tr>
<td>(101)</td>
<td>2.64</td>
<td>3.096</td>
<td>1.558</td>
<td>1.554</td>
</tr>
<tr>
<td>(100)</td>
<td>4.74 (2.37)</td>
<td>3.671</td>
<td>1.641</td>
<td>1.664</td>
</tr>
<tr>
<td>(310)</td>
<td>1.50</td>
<td></td>
<td>1.656</td>
<td>1.679</td>
</tr>
<tr>
<td>(321)</td>
<td>1.21</td>
<td>4.531</td>
<td>1.731</td>
<td>1.758</td>
</tr>
<tr>
<td>(211)</td>
<td>1.76</td>
<td>4.572</td>
<td>1.799</td>
<td>1.821</td>
</tr>
<tr>
<td>(301)</td>
<td>1.41</td>
<td>5.172</td>
<td>1.842</td>
<td>1.860</td>
</tr>
<tr>
<td>(311)</td>
<td>1.35</td>
<td></td>
<td>1.874</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>2.31</td>
<td>7.386</td>
<td>2.217</td>
<td>2.217</td>
</tr>
<tr>
<td>(001)</td>
<td>3.19 (1.59)</td>
<td>4.738</td>
<td>2.345</td>
<td>2.366</td>
</tr>
<tr>
<td>(212)</td>
<td>1.27</td>
<td></td>
<td>3.013</td>
<td></td>
</tr>
<tr>
<td>(221)</td>
<td>1.48</td>
<td></td>
<td>3.638</td>
<td></td>
</tr>
<tr>
<td>(112)</td>
<td>1.44</td>
<td></td>
<td>4.531</td>
<td></td>
</tr>
</tbody>
</table>

*calculated by Mulheran and Harding [5]

There is no simple correspondence between $d_{hkl}$ (unit cell depth normal to the surface) and the relative energies of the surfaces. Note that the values vary by less than a factor of two from the lowest to the highest. The (110) surface is the most stable and the (001) is relatively unstable. This type of behaviour has been observed before in other rutile structures [2]. Some of the higher-indexed surfaces also display considerable stability.

The segregation energies of neutral defects with substitutional Sb$^{5+}$/Sb$^{3+}$ ions, Sn$^{2+}$/O$^{2-}$ vacancy and 2Sb$^{3+}$/O$^{2-}$ vacancy were calculated for the basal plane (001) and substitutional Sb$^{5+}$/Sb$^{3+}$ ions for the thermodynamically favoured (110) face. Defects pairs were studied in order to keep the whole unit cell neutral. For each pair the procedure was to fix one of the defects either at the surface or at the base of the cell, then move away from it, either towards the surface or towards the base. The segregation energy was expressed as the difference between the ideal total energy of one face and the substituted total energy of the same face moving the defects down, away from the surface. The effect of moving apart the two elements of the defect pairs are shown graphically in Fig 5.2. As an example, Fig 5.2. represents the SnO$_2$
(110) face with Sb$^{3+}$ at the surface and Sb$^{5+}$ five layers down. Table 5.3., 5.4. and Fig 5.3., 5.4. and 5.5. show the effects of segregation for the different defect species.

Fig 5.1. Tetragonal unit cell of the SnO$_2$ (001) face calculated by MARVIN with 288 O$^{2-}$ ions represented by red sphere and 144 Sn$^{4+}$ ions represented by grey spheres.
Fig 5.2. Tetragonal unit cell of the SnO₂ (110) face calculated with MARVIN with 288 O²⁻ ions represented by red spheres, 144 Sn⁴⁺ ions represented by grey spheres, 1 Sb⁵⁺ (at the surface) and 1 Sb³⁺ (5th atomic layer) ions represented by blue spheres.
Fig 5.3. Energy difference, $\Delta E = (\text{defect crystal} - \text{ideal crystal})$ vs. defect position (numbers of layers) for 1 O$^{2-}$ vacancy and 1 Sn$^{2+}$ substitutional configurations for SnO$_2$ (001).

Table 5.3. Total energies calculated by MARVIN with SnO$_2$ (001) for different substitutional Sb$^{3+}$ and Sb$^{5+}$ ions. Index $j = 1$ means the defect is at the surface.

<table>
<thead>
<tr>
<th></th>
<th>$E_T$ (eV)</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal surface</td>
<td>-7999.296</td>
<td></td>
</tr>
<tr>
<td>Sb$^{5+}$ fixed at base of cell</td>
<td>-8005.094</td>
<td>1</td>
</tr>
<tr>
<td>Sb$^{5+}$ in layer j</td>
<td>-8004.576</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>-8004.455</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>-8004.188</td>
<td>4</td>
</tr>
<tr>
<td>Sb$^{3+}$ fixed at base of cell</td>
<td>-8002.555</td>
<td>1</td>
</tr>
<tr>
<td>Sb$^{5+}$ in layer j</td>
<td>-8003.848</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>-8004.413</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>-8004.188</td>
<td>4</td>
</tr>
<tr>
<td>Sb$^{3+}$ and Sb$^{5+}$ moving together (both ions in layer j)</td>
<td>-8004.141</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>-8004.398</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>-8004.275</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>-8004.153</td>
<td>4</td>
</tr>
</tbody>
</table>
Fig 5.4. *Energy difference, $\Delta E = (\text{defect crystal} - \text{ideal crystal})$ vs. defect position (numbers of layers) for substitutional Sb$^{3+}$ and Sb$^{5+}$ configurations with SnO$_2$ (001).*

Fig 5.5. *Energy difference, $\Delta E = (\text{defect crystal} - \text{ideal crystal})$ vs. defect position (numbers of layers) for 1 O$^{2-}$ vacancy and 2 Sb$^{3+}$ substitutional configurations for SnO$_2$ (001).*
Table 5.4. Segregation energies calculated by MARVIN with SnO\(_2\) (110) for different substitutional Sb\(^{3+}\) and Sb\(^{5+}\) ions with A representing the surface layer and I the layer at the base of the calculation cell furthest from the interface.

<table>
<thead>
<tr>
<th>Sb(^{3+}) Site</th>
<th>Sb(^{5+}) Site</th>
<th>(E_{\text{tot}} - E_{\text{perfect}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>-3.71</td>
</tr>
<tr>
<td>B</td>
<td>I</td>
<td>-5.96</td>
</tr>
<tr>
<td>C</td>
<td>I</td>
<td>-4.46</td>
</tr>
<tr>
<td>D</td>
<td>I</td>
<td>-4.97</td>
</tr>
<tr>
<td>E</td>
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5.4. Discussion

Direct comparison between these theoretical results and experimental data are obviously not straightforward. One of the most relevant evidence refers to thin SnO\(_2\) films where the interface (substrate-oxide) of the free and doped-surface have an effect on the surface properties. However, there are some features in the experimental observations that agree with the trends founds in this study.

Using chemical vapour deposition to grow Sb-doped tin dioxide films, Belanger et al [8] demonstrated that thin films favoured (110) orientations and that thicker ones contained a variety of other orientations such as (200), (301) and (211) which seems to indicate that a low-index surface grows initially whilst other thermodynamically stable surfaces emerge in the anneal. Rastomjee et al [9] have also observed that several low-index configurations were present in SnO\(_2\) deposited films including (110), (101), (211) and (002). After annealing the (110) and (211) faces remained
whilst the (301) and (321) faces emerged which can be interpreted in terms of the thermodynamic stability of these surfaces. The behaviour of the (001) face supports the fact that whilst low-index surfaces may have low excess energies per unit cell, the thermodynamic stability of a surface depends upon its precise structure and the amount it can relax to minimise the energy. These stepped surfaces could also play a role in the sensor behaviour of the material since they provide likely sites for gas molecule adsorption.

Fig 5.3. shows the behaviour of undoped (001) SnO₂ with 1 O²⁻ vacancy and 1 Sn²⁺ in a substitutional configuration. From the segregation energy calculated Sn(II) species segregate at the surface which confirms the suggestion [10] that the SnO₂ (110) structure is to be associated with Sn ions at surface sites that trap a pair of electron to become Sn(II) rather than Sn(IV). Furthermore, the most stable configuration appears to be the surface defect complex [Sn_sn⁻.Vo⁺⁺] when the ionic species are in the same layer which would confirm (speculations made in Chapter 3.) the presence of a [Sn_sn⁻.Vo⁺⁺] surface defect complex.

The calculations displayed in Fig 5.4. clearly demonstrate that Sb³⁺ segregates preferentially to Sb⁵⁺ on the surface of the (001) SnO₂ face which correlates with the XPS experimental results discussed in Chapter 3. The behaviour of the most stable face (110) is less clear, but would seem to indicate that Sb could be surface segregated as a surface defect complex [Sb³⁺-Sb⁵⁺].

In Fig 5.5. Sb³⁺ and O²⁻ associated at the surface form the most stable energetic configuration, which would confirm formulations speculated in Chapter 3. that the surface defect can be thought to be a surface defect complex expressed as [Sb_Sb⁻.Vo⁺⁺.Sb_Sn⁺].

5.5. Conclusion

In conclusion, we have examined by computer simulation methods the surface properties of stoichiometric SnO₂ rutile with special emphasis on the surface defect
chemistry of antimony dopants. In particular, the effects of segregation of both the dopant (Sb) and point defects (\(V_0^{**}\)) to the surface have been investigated. Discussion of these have suggested formulations of the surface defect states which seem to be in agreement with our experimental results and could confirm our interpretation concerning the effect on electrical response and on combustion kinetics described in Chapter 3.

References


Appendix 5.1. Marvin Program Input file

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0.0000000000 0.0000000000 3.3084639916
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buckingham
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buckingham
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Appendix 5.2. Marvin Program Output file

************************************************
MARVIN'S Program
Version 1.65
Compiled on Dec 5 1994 at 13:43:15

Minimization And Relaxation of Vacancies
and Interstitials Near Surfaces Program
David Gay and Andrew Rohl
The Royal Institution of Great Britain
1991 - 1992
************************************************

MARVIN reading file a100.mvn
Reading keyword...
source title surface latvec basis bulk-energy buckingham buckingham spring
spring element accuracy title miller region shift
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Type (Angstroms)

Universal potentials
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O shell O shell Buckingham 15123.6000 0.2230 28.4300 0.00 7.10

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Maximum Interaction 9.55865

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No Ion Type Coordinates Molecule

132
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Gnorm = 16.02232133

ENERGY BREAKDOWN

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Four-Body Energy = 0.00000000 eV
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Attachment Energy = -7.10925086 eV/mol
Slice Energy = -214.27286400 eV/mol
Surface Energy = 3.6707 (0.0000) J/m²

BEGIN BFGS MINIMIZATION

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Cycle 2: Energy = -887.4985864  Gnorm = 0.64496  Cpu = 4.89
Cycle 3: Energy = -887.5011853  Gnorm = 0.33341  Cpu = 6.75
Cycle 4: Energy = -887.5019952  Gnorm = 0.11728  Cpu = 8.25
Cycle 5: Energy = -887.5020296  Gnorm = 0.08934  Cpu = 9.75
Cycle 6: Energy = -887.5020435  Gnorm = 0.07747  Cpu = 11.25
Cycle 7: Energy = -887.5020466  Gnorm = 0.07455  Cpu = 12.75
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BLOCK A REGION 1 (REGION 1A)

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Gnorm = 0.07454638

ENERGY BREAKDOWN

Repulsive Energy = 183.28651487 eV
Polarization Energy = 0.54155701 eV
Electrostatic Energy = -1067.76009910 eV
Real = -1072.85215114 eV
Reciprocal = 5.09205204 eV
Three-Body Energy = 0.00000000 eV
Four-Body Energy = 0.00000000 eV
Boundary Interaction = -3.57001940 eV
Total Energy = -887.50204662 eV

Attachment Energy = -7.02905899 eV/mol
Slice Energy = -216.29024726 eV/mol

Surface Energy = 1.6414 (0.0001) J/m^2

*** MARVIN HAS FINISHED***
Chapter 6. Properties of the Solid Solution Series

\((\text{CrNbO}_4)_x(\text{Sn}_{1-y}\text{Sb}_y\text{O}_2)_{1-x},\)

\((0 < x < 1, y = 0, 0.01, 0.05).\)

Vincent Dusastre, Geoff. S. Henshaw and David Williams

This chapter has been published in essentially the same form in:

*J. Mater. Chem.*, 1996, 6(8), 1351.

Abstract

The response of gas-sensitive resistors fabricated from solid solutions compounds of the form \((\text{CrNbO}_4)_x(\text{Sn}_{1-y}\text{Sb}_y\text{O}_2)_{1-x}\) where \(0 < x < 1\) and \(y = 0, 0.01, 0.05\) to carbon monoxide, propane and water have been studied. An n-p transition occurred at a CrNbO\(_4\) stoichiometry that increased with the level of Sb\(^{5+}\) doping. XPS demonstrated the surface enrichment of Nb\(^{5+}\) in the CrNbO\(_4\) substituted compounds and a Fermi level shift of 0.6 eV between the n-type and p-type materials. The n-type compounds exhibited higher sensitivity to CO and C\(_3\)H\(_8\) than the p-type compounds which was rationalised using a compensated semiconductor conduction model in which both the energy of the surface acceptor state relative to the conduction band, and the surface acceptor state density determined the sensitivity. Both the n-type and p-type compounds exhibited a resistance decrease upon exposure to water and this was explained in terms of the relative energies of the trap states \(O_{\text{ads}}^-\) and \(OH_{\text{ads}}^-\). \(OH_{\text{ads}}^-\) lies higher in energy than \(O_{\text{ads}}^-\) in the n-type but lower in the p-type compounds.
6.1. Introduction

Despite the existence of models for semiconducting oxide gas sensors the level of understanding required to predict the gas sensing behaviour of an oxide from its electrical and structural properties has not been reached, therefore an empirical approach is usually taken to determine which properties might be important. Systematic cation substitution in solid solution compounds has been previously studied in $\text{Cr}_2\text{yTi}_x\text{O}_{2+x}$ [1,2] and $\text{Ba}_x\text{Fe}_y\text{Nb}_{10-x}\text{O}_{30}$ [3], and the effects of surface segregation, stoichiometry, microstructure, and combustion gradients have been noted on gas response.

A model which rationalises the effects of bulk donor doping has been developed[4] which predicts a conductance minimum and switch from n- to p-type response at some value of the bulk donor density. It is possible that for materials with doping levels such that they are close to the minimum in conductance the magnitude of the response to certain gases may be sufficiently different that a degree of selectivity could be achieved.

As noted in Chapter 1, oxide materials which form solid solutions provide an opportunity to study separately the effect of cation substitution and changes in the donor state density on the gas response. Both are expected to be important in defining the gas sensing behaviour of an oxide, the latter for reasons described in Chapter 1. and the former because transition metal oxides display systematic differences in their surface reactivity.

$\text{CrNbO}_4$ and $\text{SnO}_2$ both exhibit a rutile structure[5] and solid solution $(\text{CrNbO}_4)_x(\text{SnO}_2)_{1-x}$ can be prepared. $\text{CrNbO}_4$ is a p-type oxide[6] while $\text{SnO}_2$ is n-type, therefore a n-p transition is expected for some value of $x$. In principle, in this system the donor density could be controlled by substitution of $\text{Sb}^V$ for $\text{Sn}^{IV}$.

In this study the effects of changing cation composition by the incorporation of $\text{CrNbO}_4$ and donor doping by substitution by $\text{Sb}^{5+}$ have been explored on the gas sensing behaviour to water, carbon monoxide and propane of the solid solution series $(\text{CrNbO}_4)_x(\text{Sn}_{1-y}\text{Sb}_y\text{O}_2)_{1-x}$ with $0<x<1$ and $y=0$, 0.01 and 0.05.
6.2. Experimental

The procedure followed those described in Chapter 2.1. The series of compounds was prepared by ball milling in acetone for 24 hours stoichiometric amounts of Nb$_2$O$_5$ (Johnson Matthey Grade 1), Cr$_2$O$_3$ (Fluka, >99% pure), SnO$_2$ and Sb$_2$O$_5$ (Fluka, >99% pure). The acetone was then evaporated and the resultant powders were fired in a furnace at 1300 °C for 12 hours.

X-ray powder diffractometry of the samples was performed using a Siemens 5000 with CuK$_\alpha$ radiation which demonstrated a phase pure tetragonal rutile structure across the whole series (0 ≤ x ≤ 1) had been achieved. Rietveld refinement method demonstrated that the lattice parameters decreased slightly with increasing CrNbO$_4$ mole fraction as can be observed on Table 1.

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XPS spectra of the pellets were recorded on a VG ESCALAB 220i XL using focused (300 µm spot size) monochromatised Al-K$_\alpha$ radiation. The spectrometer pass energy was 20 eV and scans were acquired with a step size of 100 meV. A 4 eV flood gun was used to control the sample charging and binding energies were referenced to the "adventitious" hydrocarbon C 1s peak at 284.80 eV. Spectrum quantification and curve fitting was
performed with a straight line background and sensitivity factors obtained from Wagner[7].

6.3. Results

The elemental surface concentrations for \( (\text{CrNbO}_4)_x(\text{Sn}_{0.99}\text{Sb}_{0.01}\text{O}_2)_{1-x} \) compounds, determined by XPS, are given in Table 6.2. The Nb and to a lesser extent Sb (determined using the Sb 3d\text{3/2} peak since the 3d\text{5/2} peak overlapped with the O 1s) concentrations were higher than expected from stoichiometric argument and therefore surface enriched. The Nb 3d\text{5/2} binding energy varied from 206.65 to 207.30 eV (due to Fermi level shifts; see discussion below) which falls in the range for Nb\text{5+} species (c.f Nb\text{2O}_5, BE(Nb3d\text{5/2})=207.6 eV and K\text{NbO}_3 BE(Nb3d\text{5/2})=206.5 eV)[7]). The Cr2p\text{3/2} peak was broad with a Fermi level dependent binding energy of about 576.7 eV, indicative of Cr\text{3+}[7]. The oxygen:Smetal ratio increased from 1.9 for Sn_{0.99}Sb_{0.01}O_2 to around 2.5 for the CrNbO_4 substituted materials which suggested, in conjunction with the Nb surface enrichment noted above, that a surface phase of stoichiometry approaching Nb_2O_5 was formed.

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<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Nb/Cr</td>
<td>-</td>
<td>4.0</td>
<td>1.5</td>
<td>1.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The electrical resistivity at 500 °C and activation energy for conduction in dry air, measured over the temperature range 450 - 550 °C, is given in figure 1 for pellets with 5% Sb substitution for Sn. The resistivity of Sn_{0.99}Sb_{0.05}O_2 rose by 5 orders of magnitude upon addition of 10 % mol fraction of CrNbO_4; further CrNbO_4 substitution decreased the resistivity.

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Fig 6.1. Resistivity at 500°C and activation energy for conduction, determined over the temperature range 450-550°C, vs. CrNbO$_4$ mole fraction in (CrNbO$_4$)$_x$(SnO$_2$)$_{1-x}$ solid solution compounds.

The (CrNbO$_4$)$_x$(SnO$_2$)$_{1-x}$ (0.1 ≤ x ≤ 0.9) pellets, which contained no Sb doping, all showed a resistance increase upon exposure to ppm concentrations of the reducing gases CO and C$_3$H$_8$ which classify these materials as p-type semiconductors, as can be observed in Table 6.3. For the other, Sb doped, compounds a transition from n-type to p-type response occurred at x>0.1 for 1% Sb substitution for Sn and at x>0.2 for 5% Sb substitution. The electrical response to water, on the other hand, did not follow this pattern since all the materials, both n and p-type, exhibited a decrease in resistance on
switching from dry to wet air. This demonstrated that the mechanism of response to water was different to that of carbon monoxide and propane.

Table 6.3. Sign of resistance changes of \((\text{CrNbO}_4)_{x}(\text{Sn}_{1-y}\text{Sb}_y\text{O}_2)_{1-x}\) upon exposure to wet air, 1% carbon monoxide in air, and 1% propane in air, where + = resistance increase, - = resistance decrease and sensitivity to water, \((S_{\text{H}_2\text{O}}) = (R_{\text{wet}} - R_{\text{dry}})/R_{\text{dry}}\) at 370 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(H_2O)</th>
<th>(C_2H_8)</th>
<th>CO</th>
<th>type</th>
<th>(S_{\text{H}_2\text{O}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SnO}_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>n</td>
<td>1.4</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.1}(\text{SnO}<em>2)</em>{0.9})</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>p</td>
<td>0.2</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.1}(\text{Sn}<em>{0.99}\text{Sb}</em>{0.01}\text{O}<em>2)</em>{0.9})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>n</td>
<td>0.1</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.1}(\text{Sn}<em>{0.99}\text{Sb}</em>{0.05}\text{O}<em>2)</em>{0.9})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>n</td>
<td>0.2</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.2}(\text{Sn}<em>{0.99}\text{Sb}</em>{0.01}\text{O}<em>2)</em>{0.8})</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>p</td>
<td>0.7</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.2}(\text{Sn}<em>{0.99}\text{Sb}</em>{0.05}\text{O}<em>2)</em>{0.8})</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>n</td>
<td>0.1</td>
</tr>
<tr>
<td>((\text{CrNbO}<em>4)</em>{0.6}(\text{Sn}<em>{0.99}\text{Sb}</em>{0.01}\text{O}<em>2)</em>{0.4})</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>p</td>
<td>0.5</td>
</tr>
<tr>
<td>(\text{CrNbO}_4)</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>p</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The sensitivity of the compounds to 1% carbon monoxide and propane in dry air as a function of composition is given in figure 2. Several points are worth noting about the effect of composition on sensitivity. Firstly, the n-type compounds exhibited much higher sensitivity to the two gases than the p-type materials; secondly, Sb doping generally increased the sensitivity of the n-type materials but had little effect on the p-type; thirdly, a small amount of \(\text{CrNbO}_4\) substitution (10 % mole fraction) also appeared to increase sensitivity of the Sb-doped materials; fourthly, the sensitivity of the p-type materials was largely invariant with composition. Clearly the balance between donor and acceptor state densities dominated the sensitivity of the solid solution compounds to carbon monoxide and propane.

The sensitivity of the solid solution compounds to carbon monoxide and propane in wet and dry air was proportional to the square root of the gas concentrations. The responses of \(\text{SnO}_2\) and \((\text{CrNbO}_4)_{0.1}(\text{Sn}_{0.99}\text{Sb}_{0.05}\text{O}_2)_{0.9}\) (n-type) are compared in Fig. 6.3. and it is apparent that, firstly, \(\text{SnO}_2\) displayed greater sensitivity to CO in wet air (100% relative humidity) than dry air while the \(\text{CrNbO}_4\) substituted material displayed lower sensitivity to CO under wet air conditions; secondly, the magnitude of the difference in sensitivity under dry and wet conditions was greater for \(\text{SnO}_2\).
Fig 6.2. Sensitivity at 500°C to 1% carbon monoxide and 1% propane in air as a function of CrNbO$_4$ mole fraction in (CrNbO$_4$)$_x$(Sn$_{1-x}$Sb$_x$O$_3$)$_{1-x}$ compounds.
Fig 6.3. Sensitivity vs. the square root of the carbon monoxide concentration in dry and wet (100% RH) air at 415°C.
The O1s binding energies are plotted versus that for Sn 3d$_{5/2}$ for several compounds in Fig 6.4. The points were least squares fitted to a straight line with slope = 1.04. The Nb3d$_{5/2}$ and Cr2p$_{3/2}$ binding energies also exhibited a similar correlation with the O1s. These binding energy shifts are due to a change in the Fermi level to valence band separation ($E_F - E_V$) of about 0.6 eV caused by either a shift in the Fermi level[8,9] or band bending[10] or both. Two distinct groupings were observed which correlated to n-type (high binding energy) and p-type (low binding energy).

**Fig 6.4.** Graph of O 1s vs. Sn 3d$_{5/2}$ binding energies for (CrNbO$_4$)$_x$(SnO$_2$)$_{1-x}$ solid solution compounds.
6.4. Discussion

The large increase in resistivity upon addition 10% mole fraction CrNbO$_4$ to the Sb doped SnO$_2$ can be explained by the formation of a surface Nb rich phase (XPS Nb/Cr ratio = 4) which leaves Cr$^{3+}$ as a bulk dopant. SnO$_2$ is a oxygen deficient oxide in which the excess positive charge is balanced by Sn$^{2+}$ which acts as a bulk donor. Cr$^{3+}$ doping would reduce the Sn$^{2+}$ concentration and increase the resistivity (see In$^{3+}$ in SnO$_2$ [11]). The eventual switch to p-type conduction upon further substitution of CrNbO$_4$ would then be a consequence of the loss of bulk donors and the introduction of acceptor states. This would imply that the reduction of $\Delta (E_F - E_d)$ observed in the p-type materials was due to a drop in the Fermi level rather than an increase in band bending. The conduction model for the solid solution compounds is a compensated semiconductor (Fig 6.5.).

![Diagram](image)

**Fig 6.5.** Surface-trap limited, compensated semiconductor model for the solid solution compounds, showing two surface acceptor states, $E_{s1}$ and $E_{s2}$, which refer to the OH and O' trap states, respectively. In the case of the n-type materials, the OH trap lies above O' (as shown) but the order is reversed for the p-type materials. In the limit when the Debye length is greater than the grain radius, the surface potential barrier $\Delta \phi_s$ adds to the surface trap depth.
The activation energy decreased from a value of about 0.65 eV at 0.1 mole fraction CrNbO₄ (Fig 6.1.) which was probably close to the full compensation and $E_a \approx \frac{1}{2}E_g$, to 0.3 eV at 0.9 mole fraction CrNbO₄ where $E_a \approx (E_A-E_V)$. The near plateau in the activation energy between 0.2 - 0.6 mole fraction CrNbO₄ can be explained by the reduction in Nb surface segregation thereby reducing the number of bulk acceptor states produced per unit increase in CrNbO₄ content.

The effect of surface acceptor state density on the conductivity of n-type porous metal oxides in the limit of low bulk donor density (surface-trap limited conduction) has been formulated previously [4]. This can be extended to calculate the carrier concentrations for a surface-trap limited, compensated semiconducting oxide by consideration of the following equilibria:

1. thermal excitation of carriers,

   \[ X \leftrightarrow h^+ + e^-; \]

   \[ K_1 = N_c \exp(-\Delta E_g/2kT) = pn \tag{6.1} \]

   ($\Delta E_g$ is the band gap, $N_c$ is the density of states at the conduction band edge, $p$ and $n$ are the concentrations of holes and electrons, respectively);

2. ionisation of donors,

   \[ D \leftrightarrow D^+ + e^-; \]

   \[ K_2 = N_c \exp(-\Delta E_D/kT) = n_fD/(1-f_D) \tag{6.2} \]

   ($\Delta E_D$ is the donor ionisation energy, $f_D$ is the fraction of donors ionised);

3. ionisation of surface acceptors,

   \[ S \leftrightarrow S + e^-; \]

   \[ K_3 = N_s \exp(-\Delta E_S/kT) = n(1-f_S)/f_S \tag{6.3} \]

   ($\Delta E_S$ is the surface acceptor ionisation energy, $f_S$ is the fraction of surface acceptors with trapped electrons);

4. equilibrium of valence-band holes with surface oxygen,

   \[ S \leftrightarrow S^* + h^+; \]

   \[ K_4 = N_v \exp(-\Delta E_g-\Delta E_S/kT) = p_fS/(1-f_S) \tag{6.4} \]

   where $N_v$ is the density of states at the valence band edge;
(5) ionisation of bulk acceptors,
\[ A^+ \leftrightarrow A + h^+; \]
\[ K_3 = N_a \exp(-\Delta E_A/kT) = p(1-f_A)/f_A \quad (6.5) \]
(\(\Delta E_A\) is the bulk acceptor ionisation energy and \(f_A\) is the fraction of acceptors ionised);

(6) charge balance,
\[ p + f_A N_A + f_D N_D = n + f_D N_S \quad (6.6) \]

where \(N_A\) and \(N_D\) are the bulk acceptor and donor state densities, respectively, and \(N_S\) is the surface acceptor state density.

Assuming \(N_S \gg N_D, N_A\) for surface-trap limited conduction [4] so \(n\) is small and \(K_1 \approx K_3, K_2, K_5\), i.e. the bulk donor state lies just below the conduction band, the bulk acceptor state just above the valence band, and the surface acceptor state lies somewhere in between (see figure 5), then manipulation of eqn. (1) - (6) yields after simplification,

\[ nK_1K_3K_5N_A + nK_1K_2K_3N_D - n^2K_1K_2N_S + n^2K_2K_3K_5N_D \approx 0 \quad (6.7) \]

therefore,
\[ n \approx K_3(N_A + N_D)/N_S \quad (6.8) \]

and
\[ p \approx K_4N_S(N_A + N_D) \quad (6.9) \]

since \(K_1 \approx K_4K_3\)

The conductivity can be expressed in terms of the surface acceptor state density,
\[ \frac{\sigma}{e} = \mu_e K_3 \frac{(N_A + N_D)}{N_S} + \mu_p K_4 \frac{N_S}{(N_A + N_D)} \quad (6.10) \]

If the majority charge carriers are electrons then the first term dominates and if holes then the second. Differentiating equation (10) with respect to \(N_S\) gives the dependence of the conductivity on the surface trap concentration i.e. the sensitivity \(S_{\text{sat}}\),

\[ \frac{d(\sigma/e)}{dN_S} = -\mu_e K_3 \frac{(N_A + N_D)}{N_S^2} + \frac{\mu_p K_4}{(N_A + N_D)} \quad (6.11) \]

The sensitivity of a compensated, surface trap limited n-type oxide will be determined by the first term and will show a strong dependence on \(N_S\), whereas the sensitivity of a p-
type material will be independent of the surface acceptor state density. Therefore, in a solid solution series which exhibits a switch from n-type to p-type conduction at some stoichiometry the sensitivity of the n-type compounds, assuming no changes in microstructure, will be higher than the p-type if \( N_S \) is small and \( K_3 \gg K_4 \). The magnitude of \( K_3 \) and \( K_4 \) is determined by the surface acceptor state energy \( E_S \). The condition above is met if the energy of the surface acceptor state (formulated as \( O_{ads} \)) is close to the conduction band. Since the values of \( K_3 \) and \( K_4 \) vary exponentially with \( \Delta E_S \), small changes in the surface acceptor state energy could have a large effect on the sensitivity.

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The sign of the resistance change associated with adsorption of water by the oxides can also be rationalised in terms of the surface hydroxide trap energy; in particular its position relative to the \( O_{ads} \) trap state. The n-type oxides exhibit a resistance decrease upon exposure to water which means, assuming dissociative adsorption, the \( OH_{ads} \) trap state lies higher in energy than the \( O_{ads} \) state. Conversely, for the p-type materials the observed resistance decrease means the \( OH_{ads} \) state lies lower in energy than \( O_{ads} \). This might arise by either there being more than one hydroxide surface trap and the addition of \( CrNbO_4 \) causing the loss of the one lying to higher energy, or simply \( CrNbO_4 \) produces a surface in which the energy of \( OH_{ads} \) has shifted below \( O_{ads} \).

The sensitivity to water (\( S_{H_2O} \)) of the compounds would depend exponentially on the energy difference between the two states. Since the compounds that contain \( CrNbO_4 \) exhibit small \( S_{H_2O} \) values the energies of their acceptor states \( O_{ads} \) and \( OH_{ads} \) must be closer together than for \( SnO_2 \).

6.5. Conclusion

The response of gas-sensitive resistors fabricated from solid solutions compounds of the form \( (CrNbO_4)_x(Sn_{1-y}Sb_yO_2)_{1-x} \) where \( 0<x<1 \) and \( y=0, 0.01, 0.05 \) to carbon monoxide, propane and water has been studied. An n-p transition occurred at a \( CrNbO_4 \) stoichiometry that increased with the level of \( Sb^{5+} \) doping: at \( x=0.1 \) for \( y=0 \) up to \( x=0.2 \) for \( y=0.05 \). The n-type compounds exhibited higher sensitivity to CO and \( C_3H_8 \) than the p-type compounds which was rationalised by a model in which both the energy of the
surface acceptor state (formulated as $O_{ads}^{-}$) relative to the conduction band and the 
surface acceptor state density determined the sensitivity. The response of the compounds 
to water (resistance decrease for both n-type and p-type materials) was similarly 
described in terms of the relative energies of the trap states $O_{ads}^{-}$ and $OH_{ads}$ - $OH_{ads}$ lies 
higher in energy than $O_{ads}^{-}$ in the n-type but lower in the p-type compounds. The 
sensitivity to water would then be determined by the energy difference between the two 
trap states. The compound $(CrNbO_4)_{0.1}(Sn_{0.95}Sb_{0.5}O_2)_{0.9}$ exhibited sensitivity to carbon 
monoxide and propane comparable to $SnO_2$ but much reduced sensitivity to water, a 
result of potential practical importance.
References

Chapter 7. Properties of the Solid Solution Series
$\text{Ti}_x(\text{Sn}_{1-y}\text{Sb}_y)_{1-x}\text{O}_2 \ (0 < x < 1, y=0, 0.01, 0.05)$

Vincent Dusastre and David E. Williams
Accepted for publication in $\textit{J. Mater. Chem.}$

Abstract

The response of gas-sensitive resistors fabricated from solid solutions compounds of the form $\text{Ti}_x(\text{Sn}_{1-y}\text{Sb}_y)_{1-x}\text{O}_2$ where $0<x<1$ and $y=0, 0.01, 0.05$ to carbon monoxide, methane and water have been studied. For the single phase materials the variation of both conductance and conductance activation energy with composition has been explained using a model described in Chapter 6. This model is either a surface trap limited conductance for undoped materials or a Schottky barrier controlled conductance for Sb-doped materials. The effect of dopant density and surface composition on the gas response was explained using the same compensated semiconductor conduction model. The different sensitivity to water vapour compared to other gases, especially in the range $0.8 < x < 1$, was thought to be due to different value of the surface state energy equilibrium constant with respect to the conduction band edge, $K_s$, for states associated with water, $K_{s,\text{H}_2\text{O}}$. The resistivity and gas sensitivity of spinodally decomposed materials could be interpreted in terms of the phase diagram which indicated no noticeable differences from the single-phase materials.
7.1. Introduction

Recently, metal oxide solid solutions such as ZnO-SnO$_2$ [1] and SnO$_2$-TiO$_2$ [2,3] system have been investigated for their improved sensitivity, selectivity and long term stability to hydrocarbon gases. TiO$_2$ and SnO$_2$ gas sensor materials have been widely used for combustible and toxic gas detection: CO, hydrocarbons, alcohols and NO$_x$ [4]. It has also been reported that the (Ti-Sn)O$_2$ system can be used as a stable humidity sensor [5,6] which is believed to be due to the conductivity increase induced by excess proton conduction in a physisorbed multilayer. Tin and titanium dioxides show the same rutile structure and form a complete solid solution at 1430°C [7,8] as shown in the phase diagram in Fig 7.1.

![Phase diagram of the TiO$_2$-SnO$_2$ system determined by Park et al [8].](image)

At the same time, both oxides are n-type semiconductors induced by oxygen-deficient defect structures, in which donor levels are formed by electrons trapped on cations.
associated with oxygen vacancies. The electrical conductivity is enhanced by appropriate doping (Nb for TiO2 and Sb for SnO2). It has been observed that the complete ionisation of donor levels introduced by these dopants take place at lower temperature in SnO2 than in TiO2, which explains why the electrical resistivity of Sb-doped SnO2 is several orders of magnitude lower than Nb-doped TiO2 [9].

SnO2 and TiO2 also exhibit rather different surface properties. On the surface of oxide catalysts and into zeolites, Ti cation act as Lewis acid sites [10]. Lewis acidity strength is expected to depend on the ion charge, the degree of coordinative unsaturation and the availability of empty orbitals (i.e., the bandgap). Whereas removal of oxygens from SnO2 leading to the formation of surface Sn^{2+} (with a pair of electrons occupying the Sn 5s orbitals) is expected to inhibit the acid/base interaction, strong Lewis acidity is expected with Ti^{4+} surface species [11]. Therefore, if there were some effect of the acid/base character of the oxide surface upon the processes which give rise to electrical conductivity changes, it could show up in the behaviour of the (Ti-Sn)O2 solid solution. A previous description of SnO2-TiO2 thick film gas sensors showed a maximum in sensitivity to CH4 with composition upon introducing 5% mol TiO2 [2,3]. These authors interpreted these effects as a variation of the Schottky barrier height, which becomes higher upon doping with TiO2.

The tetragonal TiO2-SnO2 solid solution system contains a subsolidus immiscibility gap [8] with a critical temperature, Tc, of around 1400°C (varying according to different sources [7,8,12]), inside which phase separation is characterised by coherent spinodal decomposition corresponding to [001] modulations [8,13,14]. A study of decomposition rates outside the spinodal suggested that the ionic mobility of diffusing tin was much slower than that of titanium in the alloy system [15]. Furthermore, aliovalent dopants are expected to affect the kinetics of phase separation either by nucleation and growth mechanism or by a cellular mechanism [16]. Doping with pentavalent species is expected to decrease the cation interstitial concentration and thereby decrease the kinetics [17,18]. Doping with antimony (V) atoms has been shown to strongly suppress the phase separation both inside and outside the spinodal [15]. Therefore, this solid solution system also offers the opportunity to study the
consequences if any of spinodal decomposition upon the electrical response to gas reaction on the surface.

In this chapter we report a systematic study of the series of compounds \((\text{Sn}_{1-y}\text{Sb}_y)_1 \cdot x\text{Ti}_x\text{O}_2 (0 \leq x \leq 1, y = 0, 0.01, 0.05)\) and their response to humidity, carbon monoxide, methane and propane have been examined. The effects of preparation methods, composition, Sb-doping and changes in surface composition on electrical properties and gas sensing characteristics were also looked into. As in Chapter 6, the results have been assessed against the simple model for composition dependence of gas-sensitivity developed by Williams and Moseley [19]. This model adequately described the behaviour of our materials.

### 7.2. Experimental

The series of compounds \(\text{Ti}_x(\text{Sn}_{1-y}\text{Sb}_y)_{1-x}\text{O}_2 (0< x < 1, y = 0, 0.01, 0.05)\) was prepared by milling in acetone for 24 hours stoichiometric amounts of \(\text{SnO}_2\), \(\text{TiO}_2\), and \(\text{Sb}_2\text{O}_3\) (all Fluka, >99% pure). The acetone was then evaporated and the resultant powders were subjected to an annealing treatment at 1400°C for 2 hours and allowed to cool quickly in order to obtain single-phase solid solutions, as confirmed by XRD. The samples were subsequently fired in a furnace at 1000°C for 12 hours. The compounds were ground, pressed to 1 ton into about 1.5 mm thick pellets (13 mm in diameter) and sintered at 900°C for 12 hours. A new series of materials \(\text{Ti}_x\text{Sn}_{1-x}\text{O}_2\), and \(\text{Ti}_x(\text{Sn}_{0.95}\text{Sb}_{0.05})_{1-x}\text{O}_2 \ (x<0.3)\) was prepared by mixing the powders in water with a high shear mixer using control of pH and a non-ionic surfactant to promote dispersion. The water was removed under reduced pressure in a rotary evaporator with the flask immersed in an ultrasonic bath, so that the dispersion and mixing of the powders was maintained throughout the evaporation. These powders were subsequently fired at 800, 1000, and 1200°C to study the effect of the microstructure and spinodal decomposition on the sensitivity to different gases.
X-ray powder diffractometry (Siemens 5000, CuKα radiation) demonstrated a phase pure rutile structure (solid solution) across the whole series for materials annealed at 1400°C.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using an Escalab 220i-XL. Monochromated Al-Kα X-rays (E = 1486.6 eV) were used with a 300 μm spot size. The spectra were acquired with a step size of 50 meV and with an analyser pass energy of 20eV. Sample charging was controlled using a 3 eV electron flood gun. The binding energies were referenced to the adventitious hydrocarbon C 1s peak at 284.8 eV, quantifications were performed using a Shirley background and sensitivity factors were obtained from Wagner et al. The sample pressure was less than 5x10⁻¹⁰ mbar.

7.3. Results

7.3.1 Characterisation of the materials

XRD patterns confirmed that solid solution with rutile structure was achieved for the complete range, 0 ≤ x ≤ 1 for materials prepared by the ball-milling method. Fig 7.2. shows the a and c parameters of Ti(Sn-Sb)O₂ solid solutions as a function TiO₂ mole ratio, including the pure end components.

Both lattice parameters (a, c) values decreased with TiO₂ mole ratio following Vegard’s law quite well, which was undoubtfully due to the smaller ionic radius of Ti⁴⁺ (0.61 Å) vs. Sn⁴⁺ (0.69 Å). Further more, the change in the lattice parameters due to antimony content suggests that the Sb component of the solid solution must mostly comprise Sb⁵⁺, which are small enough to contract the (TiSn)O₂ lattice (see Fig 7.2.), since its ionic radii is 0.60 Å compared to 0.76 Å for Sb³⁺.
As expected, the comparison between two identical materials prepared by a different method showed (comparing XRD data on Fig 7.3.), firstly, the appearance of the "spinodal decomposition" for materials fired at lower temperature, and secondly, that powders with a lower particle size (calculated with the Scherrer equation) could be prepared by using the homogenisation method (see Table 7.1.).

**Fig 7.2.** Lattice parameter (a, c) as a function of composition x in Ti_x(Sn_{1-y}Sb_y)O_2_{1-x}

**Table 7.1.** Comparison of particle sizes for materials sintered at different temperatures and prepared by different methods.

<table>
<thead>
<tr>
<th>Sintering T (°C)</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Ti_{0.1}Sn_{0.9}O_2</td>
<td>Ti_{0.1}Sn_{0.9}O_2</td>
<td>x=0.1, y=0.05 Ti_{0.1}Sn_{0.9}O_2</td>
</tr>
<tr>
<td>Preparation</td>
<td>homogenisation</td>
<td>homogenisation</td>
<td>Particle size (nm)</td>
</tr>
<tr>
<td></td>
<td>89.4</td>
<td>94.6</td>
<td>80.2</td>
</tr>
<tr>
<td></td>
<td>108.2</td>
<td>114.4</td>
<td>102.0</td>
</tr>
</tbody>
</table>
As expected the particle size increased with increasing sintering temperature. The specific surface areas, obtained from BET isotherm data of Kr adsorption at -196°C, slightly decreased from 1.7 to 1.0 m² g⁻¹ for materials respectively sintered at 800°C.
and 1200°C. Doping with 5% Sb had the effect of decreasing the particle size confirming the previous observation from Chapter 4.

Sb surface analysis determined by XPS using the Sb 3d$_{3/2}$ peak since the 3d$_{5/2}$ peak overlapped with O 1s confirmed that Sb was surface enriched in the Ti(SnSb)O$_2$ series as can be seen on Fig 3., the segregation being possibly driven by Sb$^{3+}$ formation. The oxygen:metal ratio increased steadily across the series. Table 7.2. shows electron binding energies for tin, titanium, and antimony for the 5% Sb-doped materials. The Ti 2p$_{3/2}$ binding energies for the mixed metal oxides were slightly higher than for TiO$_2$. No evidence of lower oxidation surface states for Ti were observed.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Ti 2p$_{3/2}$</th>
<th>Sn 3d$_{5/2}$</th>
<th>Sb 3d$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>459.25</td>
<td>487.31</td>
<td>540.91</td>
</tr>
<tr>
<td>0.25</td>
<td>459.31</td>
<td>487.25</td>
<td>540.66</td>
</tr>
<tr>
<td>0.5</td>
<td>459.38</td>
<td>487.19</td>
<td>540.66</td>
</tr>
<tr>
<td>0.75</td>
<td>459.50</td>
<td>487.38</td>
<td>541.00</td>
</tr>
<tr>
<td>0.9</td>
<td>459.38</td>
<td>487.63</td>
<td>541.41</td>
</tr>
<tr>
<td>1</td>
<td>458.70</td>
<td>-</td>
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7.3.2. Electrical properties and Gas-sensing characteristics

The base line resistances at the operating temperature (400°C) are shown in Fig 7.5. The undoped SnO₂-TiO₂ mixtures exhibit a higher resistivity than the Sb-doped oxides in the overall range of compositions. For both substituted materials the resistivity rose by 2 orders of magnitude upon addition of 10% mole fraction of TiO₂; further TiO₂ substitution increased the resistivity up to x=0.75 with a clear plateau observed between for 0.1 < x < 0.5.
The specific resistivities of several sintered bodies of doped and dopant free materials were measured in the process of heating from room temperature (RT) to 700°C and back to RT. The resistivity of the materials prepared by homogenisation method (spinodally decomposed materials) and sintered at 1000°C exhibited a lower resistivity than those prepared by ball-milling whereas the ones sintered at 1200°C exhibited similar behaviour to the single phase materials.
The activation energies ($E_a$) for electric conduction as a function of composition, $x$, were calculated from the linear part of the temperature dependence curve in the range 400-500°C and are shown in Fig. 7.6.

The Ti$_x$(Sn$_y$Sb$_{1-y}$)$_{1-x}$ pellets all showed resistance decrease upon exposure to ppm concentrations of reducing gases CH$_4$, C$_2$H$_6$, and CO as well as H$_2$O which classifies these materials as n-type semiconductors. The sensitivity of the compounds to 1% methane and carbon monoxide in dry air at different temperatures (400, 500 and 600°C) as a function of composition is given in Fig. 7.7.

The sensitivity of the single phase Ti$_x$(Sn$_{0.99}$Sb$_{0.01}$)$_{1-x}$O$_2$ decreased across the series from $x=0.1$ to $x=0.75$ upon exposure to CH$_4$ and to $x=0.5$ upon exposure to CO, and subsequently increased from this $x$ value to pure TiO$_2$. This pattern of behaviour was maintained for all the operating temperature studied. Overall the sensitivity of all the materials followed $S_{C_3H_8} > S_{CO} > S_{CH_4}$. The 1% Sb-doped materials were overall more sensitive to CO and CH$_4$ than the 5% doped ones.
The spinodally decomposed materials \((0 < x < 0.25)\) showed sensitivity to all gases similar to that of single-phase materials. Nevertheless, whereas the sensitivity of single-phase materials rose upon introduction of \(10\%\) mol fraction of TiO\(_2\) and consequently decreased at higher composition, the sensitivity of the spinodally decomposed materials increased monotonically with composition over the range studied.
Fig 7.7. Sensitivity vs. composition for Ti_{x}(Sn_{0.95}Sb_{0.05})_{1-x}O_2 to CO and CH_4, determined at different operating temperatures for materials prepared at different firing temperature.
The single phase materials also clearly showed a carbon monoxide-methane selectivity ($S_{CO}/S_{CH_4}$) as a function of temperature and composition as can be observed in Fig 7.8.

\[ S_{CO}/S_{CH_4} \]

This suggests that the reaction kinetics of carbon monoxide oxidation and methane combustion may be different on these materials as has been observed in previous work [20]. A maximum in selectivity was achieved at 400°C for $(Sn_{0.99}Sb_{0.01})_{0.1}TiO_2$.

A plot of sensitivity to water ($S_{H_2O}$ at 100% RH) vs composition is given in Fig 7.9. A maximum in sensitivity was observed at 10% TiO$_2$ mole ratio.
This maximum was at the same composition as the maximum in sensitivity to other gases, but the behaviour on further increase of Ti content was clearly different to that observed for other gases, there being no minimum followed by a second maximum.

7.4. Discussion

It has been known for a long time that the semiconducting behaviour of TiO$_2$ and SnO$_2$ is due to metal excess defect or oxygen-deficient structures, in which donor levels are formed by the emission of electrons trapped at oxygen vacancies or by the ionisation of interstitial cations. In TiO$_2$, alicovalent doping with charge compensation
by reduction of Ti(IV) to Ti(III) results in an n-type material which is highly conductive. Similarly, for SnO₂, bulk doping with Sb(V) causes reduction of Sn(IV) to Sn(II) with a consequent increase in conductivity.

7.4.1. Behaviour of single-phase materials

Variation of baseline in air with composition of the material

The variation of both conductance (Fig 7.5.) and conductance activation energy (Fig 7.6.) with composition taken together with the variation of surface composition (Fig 7.4.) show that there is some subtle interplay of different effects which it is necessary to interpret before interpreting the gas behaviour. The behaviour of pure SnO₂ has been interpreted as that of an extrinsic semiconductor in which the trap states controlling the conductivity are oxygen species at the surface of the crystallites. As outlined in the Introduction (Chapter 1.) and developed further in Chapter 6. The model, at the two extremes, is either a surface trap limited conductance or a Schottky barrier controlled conductance. The activation energy for conduction is then either the energy gap between surface state and conduction band edge ($\Delta E_S$ in Fig 6.5.) or the surface barrier height whilst the charge carrier concentration is controlled by the concentration of bulk donor states. Given that the band gap of SnO₂ and TiO₂ are respectively 3.6 [21] and 3.0 eV [22] and that the bulk donor states Sn⁺⁺Sn and Ti⁺⁺Ti are respectively $\approx 0.15$ and 0.8 eV below the conduction band edge in the pure oxides SnO₂ and TiO₂ (110) ([23]; and $\Delta E_D$ in Fig 6.5.), this interpretation is reasonable.

So, for the undoped materials, the activation energy for conduction decreases linearly with increase of TiO₂ mole fraction (Fig 7.6.), from 1 eV for pure SnO₂ to 0.4 eV for pure TiO₂. This is consistent with a surface trap limited conductivity with the position of the surface trap level with respect to the valence band edge (oxygen p-states) remaining approximately constant with change of composition. Hence, as the band gap decreases from SnO₂ to TiO₂, $\Delta E_S$ decreases also.
The effect of Sb addition was markedly to decrease the activation energy for (Sn-Sb)O₂. The interpretation is straightforward: as noted in Chapter 4., increase of Sb concentration increases the donor concentration which decreases both the Debye length (so that a surface trap-limited model becomes inappropriate) and the surface barrier height. In this case, the conduction activation energy is taken to be the surface barrier height.

For the undoped materials, the decrease in conductivity with addition of TiO₂ to SnO₂ implies a decrease in bulk donor density; to a minimum when X_TiO₂ ≈ 0.8. Trace impurities in the oxides (e.g. trivalent elements such as Fe and Al), at different concentration in the two oxides, might cause this effect. More spectacular is the effect of addition of TiO₂ to the Sb-doped SnO₂, where the addition of small amount of Ti caused a decrease in conductivity by 2-3 orders of magnitude. Since the Sb/Sn is maintained constant, addition of Ti would dilute the Sb and hence decrease the charge carrier concentration. The effect is not, however, linear in TiO₂ mole fraction. It seems that Ti substitution enhances the surface segregation of Sb (Fig 7.4.) and thus decreases the bulk donor density more that expected by the simple effect of dilution. The surface might even be saturated in Sb. The sharp decrease in activation energy also caused by Ti substitution into the doped material might be interpreted as an effect of the surface segregation upon the surface barrier height, perhaps because there would be consequentially a non-uniform spatial distribution of bulk donor states. For the Sb-doped materials, therefore, for compositions where (Sn-Sb) O₂ is the major constituent, the behaviour should be dominated by the distribution of Sb between bulk and surface. This effect would explain the plateau in conductivity for x_TiO₂ = 0.1-0.5. When TiO₂ becomes the major constituent, the behaviour of the undoped and doped materials becomes similar.

Effects of composition variation upon gas sensitivity

Surface enrichment demonstrated that the gas response of these compounds was mediated at a surface with a quite different composition to the bulk. Thus, the effect of dopant density and surface composition are intimately linked. Hence, the cation
composition of the lattice had an effect on the dopant density by changing the
electron occupancy of non-bonding states localised on the metal, and altering the
do
dopant density by changing the Sb concentration changed the surface composition as
a result of surface segregation.

The effect of surface acceptor-state density on the conductivity of n-type porous metal
oxides in the limit of low bulk-donor density (surface-trap limited model) has been
formulated previously [19] and developed in Chapter 6. The conductivity can be
expressed in terms of surface acceptor-state density,

\[ \sigma / e = \mu_e K_3 (N_A + N_D) / N_S + \mu_p K_4 N_S / (N_A + N_D) \]  (7.1)

Here, equilibrium between surface acceptors (oxygen species) with the conduction
and the valence bands can be expressed as:

\[ S^- \leftrightarrow S + e^- \]

\[ K_3 = N_e \exp(-\Delta E_S / kT) \]

and

\[ S \leftrightarrow S^- + p^+ \]

\[ K_4 = N_v \exp[-(\Delta E_G - \Delta E_S) / kT] \]

where \( N_A \) and \( N_D \) denote the bulk concentrations of acceptor and donor states,
respectively. These are identified as empty and filled metal d-orbitals, so that
\( (N_A + N_D) \) is constant. Here, also, \( N_v \) and \( N_c \) are the densities of states at the valence
and conduction band edge, \( \Delta E_G \) represents the band gap, \( \Delta E_S \) is the surface state
energy with respect to the conduction band edge and \( N_s \) denotes the total surface
state density. If the majority of charge carriers are electrons then the first term of
equation (7.1.) dominates, and if holes then the second.

As in Chapter 6., the dependence of the conductivity on the surface trap
concentration, i.e. the sensitivity \( S_{bas} \) is obtained by differentiating equation (7.1.)
with respect to \( N_S \).

\[ d(\sigma / e) / dN_S = -\mu_e K_3 (N_A + N_D) / N_S^2 + \mu_p K_4 / (N_A + N_D) \]  (7.2)

For n-type semiconducting oxides such as Ti(SnSb)O\(_2\), the sensitivity according to
this compensated surface-trap limited model will be determined by the first term of
equation (7.2.) and will show a strong dependence on \( N_S \). The magnitude of \( K_3 \) is
controlled by the surface acceptor-state energy, $E^a$. Hence, since the value of $K_3$ varies exponentially with $E^a$, small changes in the surface acceptor-state energy could have a large effect on the sensitivity.

Equation 7.2 explains the broad features of the variation in response to methane and carbon monoxide with variation of composition, in the range $x_{\text{TiO}_2} = 0.1-1$. Taking the undoped materials first, Fig 7.5 was interpreted as showing a decrease in $N_D$ with composition, in the range $x_{\text{TiO}_2} = 0-0.8$, followed by an increase in $N_D$ with further increase in $x_{\text{TiO}_2}$. Fig 7.6 was interpreted as showing a linear decrease of $\Delta E^a$ with increase of $x_{\text{TiO}_2}$ over the whole range. A linear decrease of $\Delta E^a$ with increase of $x_{\text{TiO}_2}$ would cause an exponential decrease in $K_3$. Fig 7.7 shows a steady decrease in sensitivity to CO and CH$_4$ with increase of $x_{\text{TiO}_2}$ in the range 0.1 to 0.8; with minimum at $x_{\text{TiO}_2} = 0.8$ and then an increase with further increase of $x_{\text{TiO}_2}$. In this, the variation of sensitivity exactly parallels the variation of conductivity and the variation of $N_D$. According to equation 7.2 the range $x_{\text{TiO}_2} = 0.1-0.8$, the decrease in both $N_D$ and $K_3$ would act to decrease the sensitivity. Over the range $x_{\text{TiO}_2} = 0.8-1$, $N_D$ increases markedly but the change in $K_3$ is not great. Qualitatively, therefore the increase in sensitivity is explained.

What is not explained by equation 7.2 is the marked increase in sensitivity from $x_{\text{TiO}_2} = 0$ to $x_{\text{TiO}_2} = 0.1$. Furthermore, Sb doping of SnO$_2$ increases $N_D$ but markedly decreases sensitivity. Both facts draw attention to the assumption of a surface trap-limited conductivity in fully depleted crystallites, which underlies equation 7.2. The behaviour can be interpreted both by Schottky barrier-limited conductivity model and by the effects of charge in doing upon barrier height and Debye length as elucidated in Chapter 4. Increasing donor density decreases surface barrier height and Debye length. Both effect give a decrease in sensitivity. Decreasing donor density would then increase sensitivity. Fig 7.4 and 7.5 have been interpreted by a marked decrease in donor density caused by Ti addition to the doped materials. Therefore, the increase in sensitivity in the range $x_{\text{TiO}_2} = 0-0.1$ is interpreted as the effect of decreasing donor density causing an increase in Debye length and leading to a transition from a surface barrier to a surface limited regime.
Comparison of sensitivity to water vapour with that to other gases

The notable difference between the effects of water vapour and those of CO and CH₄ is that the increase in sensitivity for \( x_{TiO_2} = 0.8-1 \) was not observed. Equation 7.2 gives a framework for interpretation. The increase insensitivity to CH₄ and CO was interpreted above as an effect of variation of \( N_D \) dominating an effect of variation of \( K_3 \). However, if the binding site for water were different to the reaction site for other gases, that is if \( K_3 \) were different, then the result might be different. It was shown in both Chapter 3. and 6. that an assumption of a different value of \( K_3 \) for states associated with water, \( K_{3,H2O} \), would be plausible. It was further shown that an assumption of \( K_{3,H2O} \) which was sensitive to the surface composition would also be plausible. Therefore, the monotonic decrease of \( S_{H2O} \) with \( x_{TiO_2} \) is interpreted, within the framework of equation 7.2., as the result of a monotonic decrease in \( K_{3,H2O} \) which dominates over the effect of increasing \( N_D \) for \( x_{TiO_2} > 0.8 \).

7.4.2. Behaviour of materials decomposed by spinodal mechanism.

One objective of the present work was to assess whether there was special effect associated with the spinodal decomposition. Such effects could be caused for example by the segregation of the dopants to the spinodal boundaries resulting in the trapping of conduction electrons on these species. From Fig 7.5. the resistivity of the 5%Sb-doped material fired at 1000°C indeed exhibited a significant difference from the single phase material which can not be interpreted as a variation of particle size. The gas sensitivity of material fired at both 1000 and 1200°C also showed a somewhat different variation with composition to the of the single phase material.

However, whilst it is not certain that particular effects are absent, the results can be interpreted in terms of the phase diagram of Fig 7.1. if it is assumed that the resistivity and gas sensitivity are determined simply by the volume fraction of the two different phases. Thus, at low \( x_{TiO_2} \), the dominant phase is SnO₂ containing a rather small fraction of TiO₂ than that added. If the diagrams of gas sensitivity and resistivity are
plotted in terms of mole fraction of TiO$_2$ in solution in SnO$_2$, then, the behaviour of
the spinodally decomposed material seems, within experimental error and taking into
account possible problems due to only partial reaction, indistinguishable from that of
the single phase material. Hence, within the limitation of the present work, there do
not seem to be any special effects of the spinodal decomposition.

7.5. Conclusion

The variation of both conductance and conductance activation energy with composition
for the single phase materials has been explained using a model which is either a surface
trap limited conductance for undoped materials or a Schottky barrier controlled
conductance for Sb-doped materials. The effect of dopant density and surface
composition on the gas response was explained using the same compensated
semiconductor conduction model. The different sensitivity to water vapour compared to
other gases, especially in the range $0.8 < x < 1$, was thought to be due to different value of
the surface state energy equilibrium constant with respect to the conduction band edge,
$K_3$, for states associated with water, $K_{S,H_2O}$. The compounds $\text{Ti}_x(\text{Sn}_{0.99}\text{Sb}_{0.01})_{1-x}\text{O}_2$ in the
range $0.8 < x < 1$ exhibited high sensitivity and selectivity to carbon monoxide and
methane but a low sensitivity to water compared to pure SnO$_2$, a result of potential
practical and technological importance.
References


Chapter 8. Selectivity and Composition Dependence Response of Wolframites-based 
\[(\text{MWO}_4)_x(\text{[Sn-Ti]O}_2)_{1-x}, \text{ } 0<x<1 \text{ and M: Mn, Fe, Co, Ni, Cu, Zn}] \text{ Gas Sensitive Resistors.}

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Abstract

The response of gas-sensitive resistors fabricated from solid solutions compounds of Wolframites-based \[(\text{MWO}_4)_x(\text{[Sn-Ti]O}_2)_{1-x}, \text{ } 0<x<1 \text{ and M: Mn, Fe, Co, Ni, Cu, Zn}] \text{ to carbon monoxide, methane, ammonia and water have been studied. The conductance and the activation energy for conductance variation with composition associated with the energy and number density of 3d-transition metal states depend upon the nature of the transition metal ion and its concentration. The resistivity behaviours of all the compounds are believed to be due to e_g states acting as donors leading to the oxidation of cations. The activation energy for conduction gives an indication on where the localised d-states lie with respect to the conduction or valence band. Difficulties in interpreting the results can also arise upon surface segregation of one of the constituent. The surface trap-limited conductivity model can explain, at least partially, the switch from n- to p-type response to reducing gases if assumptions are made about the local state occupancy and the energy of these states with respect to the energy associated with O adsorbed on the surface. The sign of response to water was not always consistent with that expected with the other reactive gases which clearly represents a results of technological importance. The sign of resistance change associated with adsorption of water can be explained in terms of the surface OH trap energy relative to the \( \text{\text{O}}_{\text{ads}}^- \) trap state. This observation implies that there are surface binding sites for water vapour, which are specifically associated with particular transition metal ions.
8.1. Introduction

Semiconducting oxide gas sensors have been primarily used for the detection of combustible gases such as carbon monoxide and hydrocarbons. The response mechanism, described in details elsewhere (Chapter 1. and [1-2]), relies on the bulk resistance of porous solids mainly depending on ionosorbed oxygen species acting as electrons traps. Thus, the interaction of a gas with these surfaces species results in a coverage change affecting the solid resistance. Systematic cation substitution in solid-solution materials as a way of understanding the gas response mechanism linked to the surface chemistry has been previously studied for Cr$_{2-y}$Ti$_y$O$_{2+x}$ [3,4], Ba$_x$Fe$_{10-x}$O$_{30}$ [5], (CrNbO$_4$)$_{1-x}$(Sn$_{1-y}$Sb$_y$O$_2$)$_{1-x}$ [6], FeNbO$_4$-CrNbO$_4$-TiO$_2$ [7] and Ti-(Sn-Sb)O$_2$ [8], and the effects of stoichiometry, microstructure, gas concentration gradients, and surface segregation on gas sensitivity have been observed. A model which rationalises the effects of bulk donor doping has been developed [9] which predicts a switch from n- to p-type response and conductance minimum at some value of the bulk donor density.

The previous Chapters (6. and 7.) have considered solid solution series with transition metal ions in high oxidation states. The present work considers solid solution series with transition metal ions in low oxidation states. The divalent transition metal tungstates, AWO$_4$ (A = Mn, Fe, Co, Ni, Cu, and Zn), also referred to as NiWO$_4$-type tungstates, are members of a large family of structurally related compounds with small cations which crystallize with the wolframite structure [10]. The structure is monoclinic with Z = 2 and space group P2/c ($C_{2h}^{4}$). For pure FeWO$_4$ (feberite), $a = 4.730$ Å, $b = 5.703$ Å, $c = 4.952$ Å, and $\beta = 90^\circ 05'$ [11]. The structure consists of a hexagonal close-packed oxygen array in which one-half of the octahedral holes are occupied. The cation distribution in the octahedral interstices give rise to zigzag chains of skew-edge linked octahedra extending along the c-axis, and in any single chain there is only one type of cation. The zigzag chains are arranged in alternating layers, perpendicular to the a direction. Between layers, the chains are connected by corner-sharing octahedra so that no chain of one type of cation is linked to another of the same cation. The structural similarity between wolframite and rutile implied the
possibility of solid solution series of SnO₂ or TiO₂ with the transition metal tungstates, which would allow the systematic investigation of effects of d-electron population on gas sensitivity. Such a study would give a further test of the general model for gas response given earlier and, by comparison of the effects of different gases, might reveal particular effects attributable to some specific chemistry of the surface. The present chapter reports this study.

Tungstates have been investigated for other technological applications. Single crystals of zinc tungstate have, in particular, received much attention because of their potential technological significance in applications such as scintillation detectors, photoanodes and masers. Several studies have looked into a wide range of properties of these materials. Watterich et al [12] have looked into the properties of paramagnetic defects in ZnWO₄ single-crystals induced by electron-irradiation. Intrinsic paramagnetic defects in undoped zinc tungstate crystals have been observed by ESR after electron irradiation. The only hole-type defect was attributed to a hole trapped at an O²⁻ ion near a zinc vacancy. Two electron-excess centers were due to a single electron trapped at an oxygen vacancy where the defects differed in the oxygen vacancy position. Ti(III) centers in reduced ZnWO₄-Ti single crystals were also looked into [13] by ESR methods which resulted in the characterization of a new Ti³⁺ centre expressed as [Ti³⁺-H].

The d.c. electrical conductivity and thermoelectric power of CuWO₄ have been measured [14] in the temperature range 300 to 700 K on single crystals and on polycrystalline pellets. It has been found that CuWO₄ is an n-type semiconductor. The intrinsic nature of the compound is observed above 455 K with an activation energy of 1.06 eV for polycrystalline pellets. CuWO₄ can be considered as an intrinsic semiconductor with a band gap of 1.52 eV [15].

Measurement of a.c. and d.c. electrical conductivity in crystal of nickel tungstate have demonstrated [16] that NiWO₄ was a semiconductor with a band gap of 2.10 eV. Because of the electronic structure and band formation of this material it is believed that the conduction mechanism above 500 K (with high resistivity ≈ 10⁹ Ω.cm and Eₘ
= 1.5 eV) can be considered as an electron transfer from one Ni$^{2+}$ to an adjacent Ni$^{2+}$ ion. Such a transfer will lead to the formation of Ni$^{3+}$ ions (Ni$^{2+}$ + Ni$^{2+}$ → Ni$^{3+}$ + Ni$^{+}$) which requires high energy as both Ni$^{3+}$ and Ni$^{+}$ ions are less stable than Ni$^{2+}$.

Conductivity measurement in CoWO$_4$ single crystals have shown [17] that cobalt tungstate was a p-type semiconductor. The solid exhibit extrinsic behaviour up to 750K ($E_A = 0.64$ eV) and intrinsic behaviour above this temperature ($E_A = 1.4$ eV). The energy band gap of the solid has been found to be 2.80 eV.

Single crystals and polycrystalline samples of FeWO$_4$ were prepared and characterized by Sieber et al. [18]. From high temperature paramagnetic data, the presence of high spin state iron(II) 3d$^6$ was confirmed. Qualitative Seebeck measurements indicated p-type conductivity, and the room temperature resistivity of single crystals was $\approx 100\Omega - cm$ with an activation energy of 0.16 eV. The p-type conductivity is consistent with a small amount of iron(III) being present due to the formation of a small quantity of Fe$_2$WO$_6$, which is able to form a solid solution with FeWO$_4$. Another study by Bharati et al. [19] suggested that the solid exhibited extrinsic behaviour up to 900K ($E_A = 0.27$ eV) characteristic of conductivity governed by impurities or defects and intrinsic behaviour above this temperature ($E_A = 0.64$ eV).

Electrical conductivity of a single crystal of MnWO$_4$ are reported [20] in the temperature range 300-1200K. It was found that the dominant charge carriers are holes (p-type material) over the entire temperature range studied. A break in the Arrhenius plot ($\sigma$ vs 1/T) occurred around 600K. The activation energy below and above this break temperature has been estimated as 0.53 and 0.57 eV respectively.

The A(II)B(VI)O$_4$ tungstates are potential compounds for use as photoelectrodes for the photoassisted decomposition of water using sunlight, and as gas detectors because these materials have the possibility of being either p-type or n-type semiconductors. P-type behavior could be observed when a small amount of one of the transition metals is oxidized, e.g., the introduction of a small amount of iron(III) as Fe$_2$WO$_6$ in
iron(II) tungstate. In addition, n-type behavior might be produced when one of the metals in the structure is reduced to a lower oxidation state, e.g., the reduction of W(VI) to W(V). Thus, the ABO$_4$ tungstates have potential use as either photocathodes or photoanodes in the photoassisted decomposition of water [21, 22]. Some metal tungstates and their composites with carbonates have also been investigated for application to semiconductor-type sensors capable of detecting nitrogen oxides at elevated temperature [23].

The present study was concerned with the synthesis of some new wolframite-based oxides over the complete range of solid solution: (MWO$_4$)$_x$([Sn-Ti]O$_2$)$_{1-x}$, 0<x<1 and M: Mn, Fe, Co, Ni, Cu and Zn and the exploration of their use as gas sensitive resistors. The effect of changing the transition metal ion from the wolframite on the electrical properties and sensing behavior to carbon monoxide, ammonia and methane has been examined. As indicated previously wolframites can be n-type or p-type while SnO$_2$ and TiO$_2$ are n-types, therefore an n-p transition can be expected at some value of composition. The aim was to elucidate any systematic trends in behavior caused by systematic change of the composition of the oxide.

8.2. Experimental

The materials system investigated in this study was based on the wolframite structure, MWO$_4$ (with M: Mg, Mn, Fe, Co, Ni, Cu, and Zn). The first step was to establish a procedure for preparing the wolframites by precipitation from aqueous solution. Ammonium tungstate solution and metal nitrate solution gave a precipitate of metal tungstate. It was necessary to control the pH - not too alkaline - to avoid metal hydroxide precipitation – but not too acid, to ensure that the predominant solution species is tungstate. All the materials precipitated from the neutral, mixed solutions. The correct preparations were confirmed by X-ray powder diffractrometry using CuK$_\alpha$ radiation (Siemens D5000 in transmission, with incident beam monochromator). The electrical resistivity of these preparations was extremely high (R > 10$^9$ Ω.cm at elevated temperature > 500°C). The wolframites were miscible in the solid state with SnO$_2$ and TiO$_2$. The complete range of solid solutions
(MWO₄)ₓ([Sn-Ti]O₂)₁₋ₓ, 0<x<1 and M: Mg, Mn, Fe, Co, Ni, Cu and Zn, was successfully prepared by classical solid state synthesis with a range of calcination temperature 1000 < T < 1300°C and confirmed by X-ray powder diffraction. Overall, a small quantity (< 5%) of impurity phase content Fe₂WO₆ and Cu₂WO₄ were detected in the FeWO₄- and CuWO₄-substituted materials.

Gas sensitivity and selectivity measurement was made after the pellets had been stabilized in dry air at 400°C for 2 h. Carbon monoxide, ammonia and methane at low concentration in air were introduced into the rig and the pellet resistance measured at 400 and 500°C. Fig 8.1. illustrates the typical experimental routine used, which was additional to the routine experiments described in Chapter 2.

**Fig 8.1.** Resistance vs. time upon exposure to 1% CO and CH₄ in air with a (FeWO₄₀.₁(SnO₂)₀.₉ pellet at 420 and 520°C.
A VG ESCALAB 220i XL using focused (300 μm spot size) monochromatised Al-K radiation was used to record the XPS spectra of the pellets. The scans were acquired with a step size of 100 meV and the spectrometer pass energy was 20 meV. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV and the sample charging was controlled with a 3 eV flood gun.

8.3. Results

8.3.1. Electrical properties and gas sensing characteristics

The compounds studied covered the range from $d^5$ to $d^{10}$ with TiO$_2$ ($d^0$) and SnO$_2$ ($d^{10}$) as end members. Fig 8.2. shows electrical resistivity as a function of composition at 400°C.
Even small substitutions of Ti or Sn (x = 0.1) brought the resistivity into a measurable range ($5 \times 10^4 \leq R (\Omega \text{cm}) \leq 2 \times 10^6$). It is notable that small substitutions of FeWO$_4$ into either TiO$_2$ or SnO$_2$ greatly decreased the resistivity. The behaviour is in contrast to the effect of a direct substitution of Fe, which causes a marked resistivity increase. For small substitutions of NiWO$_4$ into TiO$_2$ and SnO$_2$, the resistivity increase by a factor of two and remained high upon further substitution. Substitutions of the other tungstates gave resistivities clustering in a fairly narrow band well separated from either of these two extremes. An estimation of the activation energies for ($E_A$) conduction were calculated (from the resistivities of the materials at 400 and 500°C) and plotted in Fig 8.3. Overall, the activation energies were higher for SnO$_2$-substituted materials than TiO$_2$ which is consistent considering the band gaps of pure TiO$_2$ and SnO$_2$ to be respectively, 3.0 eV and 3.6eV.

The NiWO$_4$-and FeWO$_4$-substituted materials respectively exhibited the highest and lowest activation energy values, which tend to agree with the literature results given in the introduction. All activation energies for the rest of the substituted materials were clustered between these values.

There was an obvious and quite general pattern of variation of $E_A$ with composition for all the compounds; a marked change in activation energy from small substitution of SnO$_2$ into MWO$_4$; and a monotonic but small variation with composition between these limits.
Fig 8.3. Activation energies of $(MWO_4)_{1-x}(M'O_2)x$ at 400-500°C with $M = Mn, Fe, Co, Ni, Cu, Zn$ and $M' = Sn, Ti$

Table 8.1. shows the sign of resistance changes of $(MWO_4)_{1-x}(M'O_2)x$ $(M = Mn, Fe, Co, Ni, Cu, Zn, and M' = Sn, Ti)$ upon exposure to wet air, 1% CO, 0.1% NH$_3$, and 1% CH$_4$ in air and the sensitivity to water. The reactive gases CO, CH$_4$ and NH$_3$ were consistent in their classification of the materials as n- or p-type. However, the sign of response to water vapour was not always consistent. The effect of even small substitutions of the tungstates were greatly to decrease the sensitivity of SnO$_2$ to water vapour shifting typically from 1.4 to less than 0.2 for all the tungstates substituted materials. The cases where the sign of the electrical response to water is different to that of the other gases demonstrate that the mechanism of response to water was different to that of the other gases and could certainly be of technological importance.
Fig 8.4, 8.5, and 8.6. show the variation in sensitivity to 1% carbon monoxide, to 1% methane and to 0.1% NH₃ in air across the two solid solution series at 400°C.

Fig 8.4. Sensitivity of (MnO₄)ₓ₋₁(MO₂)ₓ to 1% CO in air at 400°C with \( M = \text{Mn, Fe, Co, Ni, Cu, Zn and } M = \text{Sn, Ti} \).
Table 8.1. Sign of resistance changes of $(MWO)_x/(M'O_2)_{1-x}$ ($M = Mn, Fe, Co, Ni, Cu, Zn, and M' = Sn, Ti$) upon exposure to wet air, 1% CO, 0.1% NH$_3$, and 1% CH$_4$ in air, sensitivity to water and resistivity at 400°C.

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Several points are worth noting concerning the effect of composition on sensitivity. As expected, a notable feature is that, with change in composition along both series, the behaviour for some materials changes from 'n-type' (resistance decrease in the presence of the reducing gas) to 'p-type' (gas causes a resistance increase).

Only the Ni- and Cu-based materials remained n-type along both series (SnO$_2$ and TiO$_2$). These two sets of materials did show a minimum in sensitivity across the range. For the Ni series, the minimum was on the TiO$_2$ side, whereas for the Cu
series it was on the SnO$_2$ side. The n-type compounds exhibited much higher sensitivity to CO than the p-type materials but for CH$_4$, the differences between n- and p-type materials were not so marked. The Co series was notable in showing a rather strong p-type sensitivity to CH$_4$ on the SnO$_2$ branch, just before the n-p transition. The n-p transition was found over the same composition range for all the reactive gases. Considering the mole fraction of tungstate, $y$, at which the n-p transition takes place, the sequence along the TiO$_2$ branch is Zn < Mn, Co < Fe and along the SnO$_2$ branch is Co < Mn < Zn, Fe, so the zinc compound was notable in showing asymmetrical behaviour with respect to the two end members. There was a remarkable maximum in the sensitivity to CO at $y = 0.3-0.5$ along the SnO$_2$ branch, for the Fe, Ni, Cu and Zn series, but not for the Mn or Co series. Any such maximum along the TiO$_2$ branch was not nearly so marked. For sensitivity to methane, a similar maximum was observed, but only for the Ni series.

![Diagram showing sensitivity to CH$_4$ for different compositions of $x$.](image-url)
The carbon monoxide-methane selectivity of all the compounds determined at 400°C is given in Fig 8.7. as well as the carbon monoxide-ammonia selectivity with the Mn, Fe and Zn compounds in Fig 8.8. In Fig 8.7. the Mn, Co, Ni and Cu compounds showed a very stable selectivity along both branches varying from 1 for Mn to 5 for Cu. For Fe and Zn the selectivity remained stable along the TiO₂ branch, but then went through a strong maximum along the SnO₂ branch, increasing by a factor up to 10. In Fig 8.8. the Mn and Fe compounds showed as well a stable selectivity (0 < S_{CO} / S_{NH₃} < 1) along both series. The Zn compounds however exhibited a different behavior with a high selectivity (up to 7) along the TiO₂ branch.
Fig 8.7. Selectivity ($S_{CO} / S_{CH4}$) of $(MWO_4)_{1-x}(M'O_2)_x$ at 400°C with $M = Mn, Fe, Co, Ni, Cu, Zn$ and $M' = Sn, Ti$.

Fig 8.8. Selectivity ($S_{CO} / S_{NH3}$) of $(MWO_4)_{1-x}(M'O_2)_x$ at 400°C with $M = Mn, Fe, Zn$ and $M' = Sn, Ti$. 

[Diagram showing selectivity plots for various metal combinations and oxygen ratios.]
8.3.2. Surface analysis by XPS

Fig 8.9. and 8.10. give the surface concentration (atom%) vs. TiO₂ and SnO₂ mole ratio obtained by XPS surface analysis for the Fe- and Co-based materials. It is quite clear from these diagrams that the switch from n-type to p-type gas sensitivity appeared to occur when the surface concentration of Ti and Sn started to decrease significantly. For both series there was a clear segregation of W to the surface with solid solution corresponding to the suppression of the other cation, particularly the transition metal cation.

This segregation was not found for the pure MWO₄. Titanium seemed to be present at the surface more or less in the concentration expected from the bulk composition. In the n-type range, Sn was repelled from the surface in the Fe-series; the effect was not so marked in the Co-series.
8.4. Discussion

The first level of interpretation comes from the idea that the transition metal ion from the wolframite provides localised d-states, split by the octahedral crystal field, in the band gap. The electronic properties of 3d-transition metal compound involve a complex conduction model due to the complexity of their electronic structure. It is well known that the 2s and 2p oxygen orbitals strongly overlap with the 4s and 4p orbitals of the 3d-transition metal ions in 3d-transition metal oxides. Due to this overlapping, there exists a strong hybrisation, which leads to a large energy band gap between the top of the 2p band and the bottom of the 4s and 4p bands. The 3d bands associated with transition metal cations lie within this energy gap [24]. In these oxides, the ten fold degeneracy of d-orbitals is removed partially by the crystal field splitting and exchange splitting. The 3d-orbital splits into a lower triplet of $t_{2g}$...
symmetry (xy, xz and yz orbitals) and a higher doublet of $e_g$ symmetry ($x^2-y^2$ and $z^2$ orbitals) as shown in Chapter 1 (Fig 1.5.).

Hence, the energy and number density of these states would depend upon the nature of the transition metal ion and its concentration. Furthermore, substitution of the transition metals as tungstates means that the lattice remains neutral without the need to change the oxidation state of Ti or Sn. Since W(VI) is d⁰, and the tungstates are wide band-gap materials and are not reduced, then the transition metal d-states should be the only localised gap states to consider. The literature evidence (generalising from the case of FeWO₄ [18]) is that where there is a choice the compounds are high spin. Thus, for Mn, Co, Fe, the unoccupied $t_{2g}$ states could act as acceptors from the valence band and the occupied $e_g$ states as donors to the conduction band. For Ni and Cu the $t_{2g}$ states are all filled so the most likely case for these series is that the $e_g$ states would act as donors to the conduction band. For Zn, all the d-states are filled and the effects should be dominated by defects and by Zn s-states at the conduction band edge.

Firstly, it is important to notice that, generally, the resistivity (see Fig 8.2.) of all the materials was higher along the TiO₂ than the SnO₂ series and decreased steadily for each family of compounds with increasing amount of TiO₂ or SnO₂. At the same time all p-type compounds exhibited higher resistivities than the n-type ones. In order to account for the variations with composition, one has to consider that all behaviours are due to $e_g$ states acting as donors. This leads to a formal oxidation of the cations which seems more reasonable than a formal reduction. Hence, the behaviour just reflects how far away the $e_g$ states are from the conduction band edge. The activation energy for conduction (see Fig 8.3.) gives an indication on where the localised d-states lie with respect to the conduction or the valence band. Hence, for small concentrations of Fe in FeWO₄-substituted compounds, the high conductivity and the low activation energy (see Fig 8.2. and 8.3.) could be interpreted by the fact that the $e_g$ states could be near the conduction band edge for SnO₂ and TiO₂. For NiWO₄-
substituted compounds, as the $t_{2g}$ states are full, the $e_g$ states can be considered as donors. If these states are far away from the conduction band or the valence band, the conductivity will be low and the activation will be high as observed on Fig 8.2. and 8.3. As far as the other materials are concerned, both the conductivity and the activation energy lie in between the two extremes with, interestingly, no apparent systematic variation with d-electron number. Overall, the activation energies increase with decreasing TiO$_2$ or SnO$_2$ content which indicates that positions of the d-states with respect to the conduction band edges changes across the series which is consistent with the changes of conductivity. Difficulties in interpreting the results could arise if there were surface segregation of one of the constituents. The behaviour would, then, reflect the variation of the surface composition, but not that of the bulk. The results (Fig 8.9 and 8.10) show that a general tendency is observed for segregation of W to the surface and an inverse segregation of the transition metal away from the surface. Another complication, which is hard to quantify, is the effect of minor amounts of unreacted compounds or of other phases.

Using the simple model of a surface trap-limited conductivity, outlined in Chapter 1. and developed in Chapter 6., the switch from n- to p-type response to reducing gases can be interpreted, at least in part, if one make some guesses about the local state occupancy and the energy of these states with respect to the energy associated with an oxygen atom adsorbed on the surface. Ni- and Cu-based materials were the only two families of compounds, which remained n-type across both series. If the partially occupied $e_g$ states in the Ni and Cu series lie above the oxygen surface state for all compositions, then these materials would always be n-type. For the Mn, Fe and Co series, however, at high mole fraction of tungstate, the d-states must all lie below the oxygen surface state to give the observed p-type behaviour whereas at low mole fraction of tungstate, the oxygen surface state must move above the $e_g$ states. For Zn-based materials we would expect the behaviour to be different again, which is what is observed: for the Co, Mn, Fe series, the n-p transitions occur at similar compositions along both the TiO$_2$ and SnO$_2$ branches, whereas for the Zn series they do not.
The next question is why there should be a maximum in response with composition on the SnO₂ branch for some series but no corresponding maximum on the TiO₂ branch. We showed earlier in Chapter 6., that, for the case where the gas response could be described in terms of a surface trap-limited process, the dependence of conductivity on the surface trap concentration, i.e. the gas sensitivity, could be written approximately as:

\[
\frac{d(\sigma / e)}{dN_s} \approx -\mu_e K_3 \frac{N_A + N_D}{N_s} + \mu_p \frac{K_4}{(N_A + N_D)}
\]

where: \(N_s\) denotes the surface trap concentration (the concentration of adsorbed oxygen species which mediate the gas response); \(N_A\) the bulk acceptor state density; \(N_D\) the bulk donor state density; \(K_3\) the equilibrium constant between surface acceptors and conduction band; \(K_4\) that for equilibrium between surface acceptors and valence band and \(\mu_e, \mu_p\) respectively the mobility of electrons and holes. For an n-type oxide, if substitution increases the bulk state density, \((N_A+N_D)\), then the sensitivity should increase (in the absence of effects caused by the space charge layer at the surface being thinner than the crystallite size). This is observed for the SnO₂ branch of the series studied here. Then, if on further substitution, \(K_3\) decreased and \(K_4\) increased, then the response would go through a maximum then decrease and switch to p-type, again as observed on the SnO₂ branch. Dependent on the change of \(K_3\) with composition compared with that of \((N_A+N_D)\), then the maximum in response might not be marked or might be absent, as observed on the TiO₂ branch.

In our previous discussion of the SnO₂ (n-type)-CrNbO₄(p-type)-TiO₂(n-type) series (Chapter 7. and [7]), we interpreted the p-n transition on the TiO₂ branch to the energy of the oxygen surface state moving closer to the conduction band edge as the Ti content increased. For the discussion of the behaviour of the SnO₂-TiO₂ series in Chapter 7., again, it was necessary to postulate that the energy of the oxygen surface state moved closer to the conduction band edge as the Ti content increased. These statements are equivalent to postulating a marked change of \(K_3\) with TiO₂ content, and so are consistent with the interpretation presented here for the difference in behavior between TiO₂ and SnO₂ branches. The interpretation of the variation in conductance with composition presented above is also consistent with the postulate.
that $K_3$ decreased (that is, the energy difference between conduction band edge and surface acceptor state energy increased) with increase of wolframite concentration.

It remains to discuss the relative selectivity $S_{CO}/S_{CH_4}$, $S_{CO}/S_{NH_3}$ observed, and the different effects of water vapour along the different series in comparison to the effects of the reactive gases. The notable effects on selectivity are the maximum in $S_{CO}/S_{CH_4}$ for the Fe and Zn series along the SnO$_2$ branch, the uniformly higher selectivity $S_{CO}/S_{CH_4}$ for the Cu series across the whole range and the maximum in $S_{CO}/S_{NH_3}$ for the Zn series along the TiO$_2$ branch. Previous work has shown that the selectivity of porous pellets can be altered as a consequence of changes in the rate of surface catalysed combustion of the different gases. To explain the observed maximum in this way would require that the combustion rate of CO was drastically decreased for these particular compositions. Another explanation might be that there are two different types of oxygen surface state mediating the response, and that, for the series showing the maxima, the relative proportions of these two states change. This last interpretation is supported by comparing surface concentration of the Co and Fe series along the SnO$_2$ branch which show different behaviour in the way surface composition changes with bulk composition.

As stated earlier, all the reactive gases were consistent in their classification of the materials as n- or p-type. However, the sign of response to water vapour was not always consistent. Overall, the Co-, Cu- and Zn- based materials response to water behaved as expected as n-type or p-type materials. Clearly, there were some differences between water and the other gases for Mn-, Fe- and Ni-based compounds which is certainly a result of technological importance. The sign of the resistance change associated with adsorption of water by the oxides can be discussed [6, Chapter6] in terms of the surface hydroxide trap energy; in particular its position relative to the $O_{ads}$ trap state. For the n-type oxides which exhibit a resistance decrease upon exposure to water vapour or the p-type oxide which exhibit a resistance increase, the effect could be explained by assuming dissociative adsorption of water with the $OH_{ads}$ trap state produced lying higher in energy than the $O_{ads}$.
The opposite behaviour, where materials which otherwise behave as p-type give a resistance decrease with water n-type materials give a resistance increase means that the OH\textsubscript{ads} state must lie lower in energy than O\textsubscript{ads}. The fact that the introduction of some transition metal ions causes a change in sign of response to water vapour without causing a change in sign of response to other gases implies that there are surface binding sites for water vapour which are specifically associated with these substituents. Fig 8.9 shows that the behaviour may be associated with the surface excess of tungsten over tin, and there is the possibility that tungsten could be present on the surface in a lower oxidation state. In this sense, the results parallel those found for the effects of Sb(III) segregation, in Chapter 3.

Since the compounds that contain the wolframites exhibit smaller sensitivity to water than SnO\textsubscript{2} (typically S\textsubscript{H2O} \leq 0.5), the energies of the acceptor states O\textsubscript{ads} and OH\textsubscript{ads} on the substituted compounds must be closer together than for pure SnO\textsubscript{2}.

### 8.5. Conclusion

The response of gas-sensitive resistors fabricated from solid solutions compounds of Wolframites-based \((\text{MWO}_4)_x([\text{Sn-Ti}O_2])_{1-x}, 0<x<1\) and M: Mn, Fe, Co, Ni, Cu, Zn to carbon monoxide, methane, ammonia and water have been studied. The conductance and the activation energy for conductance variation with composition associated with the energy and number density of 3d-transition metal states depend upon the nature of the transition metal ion and its concentration. The resistivity behaviours of all the compounds are believed to be due to e\textsubscript{g} states acting as donors leading to the oxidation of cations. The activation energy for conduction gives an indication on where the localised d-states lie with respect to the conduction or valence band. Difficulties in interpreting the results arise upon surface segregation of one of the constituent. The surface trap-limited conductivity model can explain, at least partially, the switch from n- to p-type response to reducing gases if assumptions are made about the local state occupancy and the energy of these states with respect to the energy associated with O adsorbed on the surface. The sign of response to water was not always consistent with that expected with the other reactive gases, which clearly represents a result of technological importance. The sign of
resistance change associated with adsorption of water can be explained in terms of the surface OH trap energy relative to the O\textsubscript{ads}\textsuperscript{-} trap state. This observation implies that there are surface binding sites for water vapour which are specifically associated with particular transition metal ions.
References


Chapter 9. General Conclusion

This thesis has had as its theme the effects of surface composition on response of gas sensitive resistors. Surface composition was altered in two ways: by inducing surface segregation; and by varying bulk composition in solid solution series. The series were chosen so that transition metal ions in both high and low oxidation states could be studied. Superimposed upon the effects of surface composition were the effects of changing microstructure and of gradients of gas composition caused by surface catalysed combustion. It was important to separate out all these effects in order to be clear about the effects of changing surface composition.

Firstly, the effect of firing temperature of the well-studied (Sn-Sb)O₂ materials (prepared by co-precipitation) on Sb segregation were demonstrated. The consequences for water adsorption, for sensitivity and for surface-catalysed combustion were shown. From the experimental results a correct formulation of ‘adsorbed oxygen’ on SnO₂ could be given. An oxygen molecule is believed to be trapped in or on a surface oxygen vacancy, and it is proposed that the combustion reaction proceeds partly through these species and partly through lattice oxygen at the surface. Water competes with oxygen for the surface vacancies, blocking this route which accounts for the diminution in the rate of the surface catalysed reaction in the presence of water. To account for the effect of antimony segregation on the reaction, we presume that the surface vacancy is correctly formulated as an association of Sn(II) with the vacancy in the absence of antimony, and of Sb(III) with the vacancy in the presence of surface segregated antimony. As the binding energy of water to the Sb(III).V₀ surface defect complex is less than that to the Sn(II).V₀ complex, the temperature variation of combustion rate would then correspond simply to the desorption of water from the defect complex. The apparent activation energy for combustion on the Sb-segregated sample would measure the heat of adsorption of water onto the surface defect. A dissociative adsorption of water onto the surface defect complex is proposed, and replacement with water of oxygen adsorbed at the defect results in an increase of conductivity. Where Sb is surface segregated, the surface defect complex is different and a similar formulation for the surface reactions
can then be made. If the energy difference between OH state and oxygen state is bigger on this site, then the effect of water vapour on the conductivity would be larger. Such a statement is consistent with water being less strongly bound at this state than at the tin defect state represented, and is thus consistent with the interpretation of the effect on combustion kinetics advanced above. Hence, the study of the effect on electrical response and on combustion kinetics of Sb segregation in SnO₂ has identified consequences linked to the adsorption of water. Discussion of these has suggested formulations for the surface defect states which mediate the electrical behaviour.

The effects of microstructure, and especially the particle size, on the behaviour (sensitivity and selectivity) of these compounds to carbon monoxide and methane were also observed and discussed. By using a co precipitation method starting from pure metals (Sn and Sb), the crystallite size \( D \) of Sn(Sb)O₂ can be controlled in the range 16 to 180 nm. For undoped SnO₂ the electrical conductivity in air and in CO or CH₄ containing air do not exhibit the same characteristics with a change in \( D \). An interpretation based on the variation in surface potential, \( \phi_s \) has been proposed. For Sb-doped SnO₂ the variation in conductance in air and in gas show a particle-size threshold dependence, which can be well understood by assuming a classical grain boundary contact model. Effects of water vapour on gas response are due to the effect of water adsorption upon the thickness of the space charge layer, \( I_s \), since H₂O is electrically active and adsorbed independently on different sites than the reactive ionosorbed O species.

Computer simulation methods of the surface properties of stoichiometric SnO₂ rutile with special emphasis on the surface defect chemistry of antimony dopants and in particular, the effects of segregation of both the dopant (Sb) and point defects (\( V_{O}^{**} \)) to the surface have been analysed. Discussion of these have suggested formulations of the surface defect states which seem to be in agreement with our experimental XPS results and could confirm our interpretation concerning the effect on electrical response and on combustion kinetics based on experimental data.
Secondly, the properties of certain complex solid solution series and systematic cation substitution as a way of understanding the gas response mechanism linked to the surface chemistry has been investigated.

For the \((\text{CrNbO}_4)_{0.5}(\text{Sn}_{1.2}\text{Sb}_0.8\text{O}_2)_{0.5}\) compounds an n-p transition occurred at a \(\text{CrNbO}_4\) stoichiometry that increased with the level of \(\text{Sb}^{5+}\). The n-type compounds exhibited higher sensitivity to CO and \(\text{C}_3\text{H}_8\) than the p-type compounds, which was rationalised by a model in which both the energy of the surface acceptor state (formulated as \(O_{\text{ads}}\)) relative to the conduction band and the surface acceptor state density determined the sensitivity. The response of the compounds to water (resistance decrease for both n-type and p-type materials) was similarly described in terms of the relative energies of the trap states \(O_{\text{ads}}\) and \(\text{OH}_{\text{ads}}\). \(\text{OH}_{\text{ads}}\) lies higher in energy than \(O_{\text{ads}}\) in the n-type but lower in the p-type compounds. The sensitivity to water would then be determined by the energy difference between the two trap states. The compound \((\text{CrNbO}_4)_{0.5}(\text{Sn}_{0.95}\text{Sb}_0.05\text{O}_2)_{0.5}\) exhibited sensitivity to carbon monoxide and propane comparable to \(\text{SnO}_2\) but much reduced sensitivity to water, a result of potential practical and technological importance.

The variation of both conductance and conductance activation energy with composition for the single phase materials \([\text{Ti}_x(\text{Sn}_{1.2}\text{Sb}_y)_{1-x}\text{O}_2]\) has been explained using a model which is either a surface trap limited conductance for undoped materials or a Schottky barrier controlled conductance for Sb-doped materials. The effect of dopant density and surface composition on the gas response was explained using the same compensated semiconductor conduction model. The different sensitivity to water vapour compared to other gases, especially in the range \(0.8 < x < 1\), was thought to be due to different value of the surface state energy equilibrium constant with respect to the conduction band edge, \(K_3\), for states associated with water, \(K_{3,\text{H}_2\text{O}}\). The compounds \(\text{Ti}_x(\text{Sn}_{0.99}\text{Sb}_{0.01})_{1-x}\text{O}_2\) in the range \(0.8 < x < 1\) exhibited reduced sensitivity to water compared to pure \(\text{SnO}_2\) with a high sensitivity and selectivity to carbon monoxide and methane, which is the main requirement for a good gas sensor.

For the Wolframite-based \([\text{MWO}_4]_x([\text{Sn-Ti}]\text{O}_2)_{1-x}, 0 < x < 1\) and \(M: \text{Mn, Fe, Co, Ni, Cu, Zn}\) compounds the conductance and the activation energy for conductance variation with
composition associated with the energy and number density of 3d-transition metal states depend upon the nature of the transition metal ion and its concentration. The resistivity behaviour of all the compounds are believed to be due to $e_g$ states acting as donors leading to the oxidation of cations. The activation energy for conduction gives an indication on where the localised d-states lie with respect to the conduction or valence band. Difficulties in interpreting the results arise upon surface segregation of one of the constituent. The surface trap-limited conductivity model can explain, at least partially, the switch from n- to p- type response to reducing gases if assumptions are made about the local state occupancy and the energy of these states with respect to the energy associated with O adsorbed on the surface. The sign of response to water was not always consistent with that expected with the other reactive gases which clearly represents a results of technological importance. The sign of resistance change associated with adsorption of water can be explained in terms of the surface OH trap energy relative to the $O_{ads}^-$ trap state. This observation implies that there are surface binding sites for water vapour which are specifically associated with particular transition metal ions.

Finally, even if the problems associated with robustness and reproducibility have not been considered, it is hoped that this study will provide an incentive to use these materials for commercial gas sensors as they are simple and inexpensive to manufacture and operate.