

The Basic Properties (Morphology & Conduction) of Metal Oxide Semiconductors for Gas Sensing Application

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Abstract: Widely used gas sensor types in house and workplace are semiconductor type and catalytic type. In general, semiconductor gas sensor has good merits in sensitivity. Semiconductor metal oxide thin films have been extensively used for gas sensors as their conductivity changes due to interactions with gas molecules. Such sensors also offer low cost, easy fabrication and consistent performance with respect to other type of gas sensors. Recently, there is an increasing trend to use specifically engineered structured materials as gas sensing elements. The use of such structured materials such as belts, rods and wires in micro-, meso- or nano-dimensions, offer high surface to volume ratios and unique structural features that are expected to enhance the properties and performance of gas sensors. Such structured oxide based chemical sensors were also found to decrease the device response time due to rapid diffusion of gaseous species into the materials' micro-, meso- and nano-porosities. In this paper we have discussed regarding the basic principle of metal oxide gas sensor application.

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Introduction

Solid state gas sensors represent a remarkable application of modern nanotechnologies and complex physico-chemical processes. These devices transduce a chemical quantity, such as a gas concentration, into an electric signal. Gas sensors based on semiconductive materials have gained an increasing interest, thanks to their advantageous characteristics in comparison with traditional systems (based on optics and spectroscopic analysis), which are more cumbersome, expensive and require a careful maintenance by qualified personnel. On the other hand, solid state devices are characterized by small encumbrance, easy usage, low-cost, reliability, high sensitivity and repeatability. However, sensor electric properties are also influenced by the interaction with molecules of gases present in the atmosphere other than the target gas. It is difficult to eliminate the effect of interfering gases, whose signal may overcome that of the gas of interest. This intrinsic lack of selectivity made research in this field to come to a standstill and hindered a significant development of such sensors. Additivation of sensitive material by means of catalysts (such as Pd, Pt and Au) seems to be a viable way to promote or hinder a chemical reaction instead of another. Nonetheless, experiments have not solved this problem yet. Another solution is the usage of filters, though the number of experimental studies in this direction is meager. Semiconductor gas sensors are mainly applied to environmental monitoring, in order to keep pollutant gas concentrations under control, because of their negative effects on human

health and on monuments. Also indoor applications are very useful, e.g. for the detection of gas leaks from both heating system and gas kitchen. For these reasons, researchers have concentrated their studies towards gases like CO, CO₂, NO_x and alkanes. Light alkanes have been widely studied for many years especially in catalysis. Their behavior is relatively easy to understand because of their simple molecules. Metal-oxide semiconductors are widely studied and used as raw materials for chemoresistive gas sensors. These devices are found to be very useful in the detection of toxic and pollutant gases. Indeed, they are recognized to have established advantages such as low cost, compactness and ease of integration with integrated circuit technology. As Wagner and Hauffe [1] discovered in 1938, adsorbed atoms and molecules on the surface of a semiconductor influence its properties, such as conductivity and surface potential. Later, many researchers [2, 3, 4] studied these effects on semiconductor electric conductance. The first applications of these discoveries arrived soon after [5, 6] together with the production of the first chemoresistive-semiconductor-gas sensors. Since that moment, technology development and the problem of toxic and pollutant gas monitoring encouraged improvements in the production and in the performances of different kind of gas sensors. A large part of commercial gas sensors are built with WO₂, SnO₂, while TiO₂ and ZrO₂ are often employed for devices aimed towards combustion monitoring.

Bulk and band model

Electrons in a crystal can only adopt energy values which stay inside certain ranges or more specifically bands of energy. Energy bands are separated from prohibited energy bands, called band gap [7]. In a semiconductor the highest energy band occupied by fundamental state electrons is called valence band, while the upper band, in which electrons can be promoted, is called conduction band. Conduction band would be completely empty in a perfect crystal at 0 K. However, we remark that solids have an imperfect structure; as a consequence electrons are present in the conduction band or miss in the valence one. Therefore, semiconductors applied on gas sensing are based on the fact that electrons could be transferred or removed from the conduction band, in order to induce consistent variations in the conductivity of the material. Semiconductor band model is depicted in Fig. 1, where electron energy is on the x-axis, while the distance inside the crystal is on the y-axis. The energy gap E_g represents the demanded energy for valence electron excitation (promotion to conduction band). Electron distribution in the different energy levels under thermal equilibrium condition is given by the function of Fermi f :

$$f = \frac{1}{1 + e^{\frac{E - E_F}{kT}}} \tag{1}$$

Where k is the Boltzmann constant and T is the absolute value of temperature. This function expresses the probability that an energy level E is occupied by an electron. The energy of Fermi is that value of energy E_F where $f=1/2$, that is to say that an energy level equal to E_F has the same probability of being full or empty. SnO_2 is a semiconductor with an energy gap of 3.6 eV. n-type conductivity is due to the oxygen vacancies derived from the typical stoichiometric defects of the material. These vacancies can be singly or doubly ionized and they act as donor states with energy levels positioned at 0.03 and 0.015 eV under the bottom of the conduction band. Therefore, they give electrons to the conduction band and enhance the conductance of the material. As a consequence of this overpopulation of electrons in the conduction band, the Fermi level is raised. Assuming $E_C - E_F > 2kT$, where E_C is the lower limit of the conduction band, the electron density, n , can be written (employing Boltzmann approximation, for which f is reduced to a simple exponential, if $E - E_F \gg kT$) [7]:

$$n = N_C \cdot e^{-(E_C - E_F)/kT} \tag{2}$$

where N_C is the effective density of the states next to the bottom of the conduction band.

Intrinsic surface states

A sudden interruption of the crystal lattice periodicity occurs on the surface. Thus, surface atoms or ions have an incomplete coordination number (number of first neighbours), which causes a rearrangement and a greater reactivity in comparison to that of bulk atoms or ions. The perturbation of lattice periodicity is enough to create intrinsic localised electronic states at surface level [9].

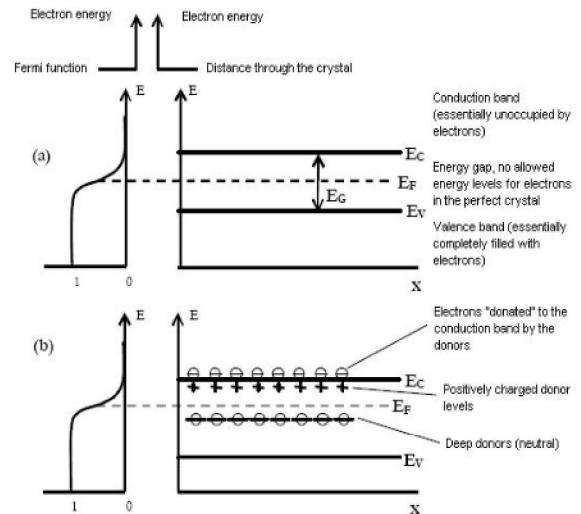


Figure 1: Fermi function and band diagram for semiconductors; (a) intrinsic semiconductor; (b) n-type semiconductor with deep and shallow donors.

In ionic materials, as many metal oxide semiconductors are, every surface ion, having incomplete coordination, is even not coupled with the opposite charge ion. In a metal oxide, metal cations tend to catch electrons behaving as acceptors, while oxygen anions tend to release electrons behaving as donors. In this last case, one can visualise the electron as not coupled in an orbital, which extends up till outside the surface. Now, it is ostensible that this electron could both accept another electron to create a couple and enter in the bulk, leaving a unoccupied surface state. In the end, it is possible to say that both energy levels, acceptors and donors, are present on the surface of the crystal. Fig. 2 shows a band model which includes the surface of the crystal and indicates the presence of surface states [7]. The case when there is no net charge is used for simplicity. This is the so-called flat-band case. As one can observe, all surface states are not at the same energy.

Double layer

Considering again Fig. 2 for n-type semiconductor, it must be underlined that the flatband case cannot be an equilibrium situation. The electrons in the conduction band are at a much higher energy level than the energy level of the acceptor surface states. Thus, they will move from the conduction band to those lower-energy states, forced by this new energetically more favorable configuration. With the upper levels (acceptors) completely empty and the lower levels (donors) completely full, by definition the Fermi energy must be in between. Therefore, the electrochemical potential of the electrons at the surface states is lower than that in the conduction band. Thereby, electrons will have to move towards the surface states.

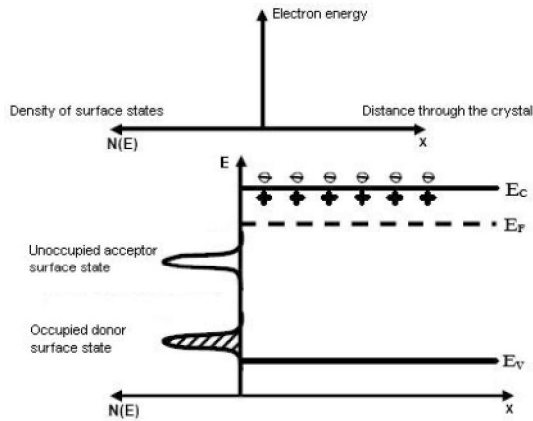


Figure 2: Surface states bands at the n-semiconductor surface. In the diagram, the surface states are assumed to be neutral (acceptor states are unoccupied and donor states are occupied). For simplicity in many arguments, the bands of surface states can be represented as single energy levels.

When such transitions occur, a charge builds up at the surface and a countercharge in the bulk (the countercharge being that of the donor ions). Fig. 3 shows an n-type semiconductor after the charge has moved from the donor ions to the surface states. A double layer is formed, with the positively charged donors in the semiconductor as space-charge layer on the one side, and the negatively charged surface states as a sheet of charges on the other side. Thus, an electric field develops between these two charge layers. The term space-charge layer refers to the region, where the uncompensated donor ions are the only important charged species. The charge density from such ions is $N_i = N_D - N_A$, where N_D is the donor density and N_A is the acceptor density. The term depletion layer is used to describe this region, because all the mobile carriers (in figure 3, the electrons) have

been exhausted from the region and moved to the surface [7]. A scheme of two grains of metal-oxide powder is depicted in Fig. 4, where the space-charge region around the surface and at the contact point is shown. The oxygen species adsorbed create the surface-charge layer, which is responsible for the intergranular potential barrier that conduction electrons have to overcome, in order to go from a grain to another.

The equation of Poisson

The one-dimensional equation of Poisson states:

$$\frac{d^2 \Phi}{dx^2} = q \frac{N_i \epsilon_0}{\epsilon} \tag{3}$$

where Φ is the potential, N_i is the net density of ions in the space-charge region, ϵ is the dielectric constant of the semiconductor, and ϵ_0 is the permittivity of free space. The donor density N_D (for n-type material) or acceptor density N_A (for p-type material) is independent of x (the distance into the crystal), in general, because the donors or acceptors have been introduced into the material in such a way as to make them independent of distance (homogeneous doping). A change in coordinates is helpful in relating the mathematics to the band diagram, where, rather than potential, the energy of an electron is plotted. We define to that end the parameter V as:

$$V(x) = \Phi_b - \Phi(x) \tag{4}$$

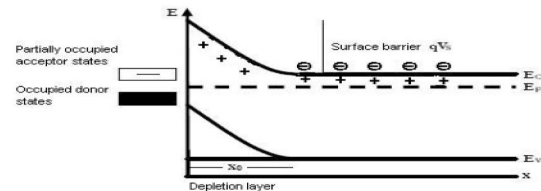


Figure 3: Double layer. Electrons from the conduction band are captured by surface states, leading to a negatively charged surface with the counter-charge the positively charged donors near the surface.

where Φ_b is the potential in the bulk of the semiconductor. Then the first integration of Poisson's equation is straightforward:

$$\frac{dV}{dx} = \frac{qN_i(x - x_0)}{\epsilon \epsilon_0} \tag{5}$$

where x_0 is the thickness of the space-charge region. The thickness of the space-charge region is determined by the distance necessary to compensate all the surface charge. At $x \geq x_0$ the semiconductor is

uncharged, so we use the boundary condition that $dV/dx=0$ at $x=x_0$. For n-type material $N_D x_0 (=N_i x_0)$ is the number of electrons (per unit area) extracted from the surface region of thickness x_0 , and this equals the number of electrons (per unit area) moved to the surface:

$$N_i x_0 = N_s \tag{6}$$

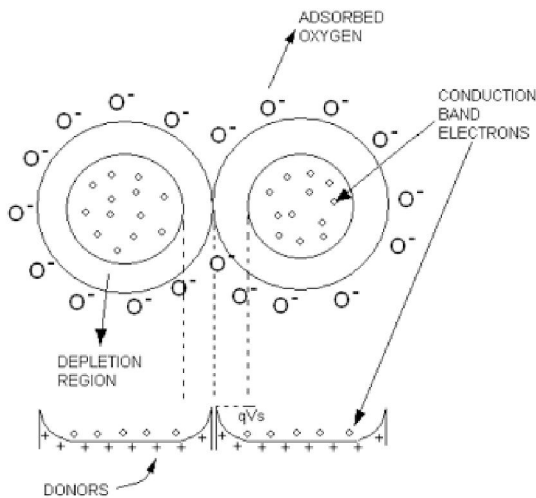


Figure 4: Potential barrier between grains

where N_s is the density of charged surface states. The integration of equation 6 leads to:

$$V = \frac{qN_i(x - x_0)^2}{2\epsilon\epsilon_0} \tag{7}$$

because V was defined zero at $x=x_0$. This leads to the relation of Schottky; the value of the surface barrier V_s (V at $x=0$) is

$$V_s = \frac{qN_i x_0^2}{2\epsilon\epsilon_0} \tag{8}$$

The energy qV_s is the energy that electrons must attain before they can move to surface energy levels. In the end, using equation 5 to eliminate x_0 from equation 7, the following expression is obtained:

$$V_s = \frac{qN_s^2}{2\epsilon\epsilon_0 N_i} \tag{9}$$

An important relation describing the potential difference between the surface and the bulk (or, as

qV_s , the energy difference of electrons between the surface and the bulk) as a function of the amount of charge N_s on the surface. In the above calculus, the charge was assumed to be on clean surface, but equally well the charge can be associated, for example, to the density of negatively charged adsorbed oxygen (e.g., O^{2-}), of critical interest for semiconductor gas sensors operating in air.

A chemoresistive sensor is able to respond to an external stimulus (e.g., a gas concentration) with an electric signal (usually, a conductance change). Indeed, when a gas arrives at the surface of a sensor, it interacts both physically and chemically. Adsorption from the gaseous phase leads to charge exchanges between the adsorbate layer and the material itself, meaning a variation of the free electron concentration and, therefore, of the total number of electrons available for conduction.

Conductance variation

Two kind of working processes can be distinguished for chemoresistive sensors [7]: the first one concerns bulk conductivity variations, the second one is connected to surface conductivity variations. Bulk conductivity variations are very important in oxygen partial pressure measurements. In this case, bulk chemical defects play a fundamental role, because the bulk has to be in equilibrium with atmospheric oxygen. On the other hand, the second class of sensors is even able to detect different gases from oxygen. Indeed, the equilibrium value of surface conductance, which is reached in conditions of constant oxygen partial pressure, is influenced by the perturbing presence of surrounding gases. This class of sensors is sensitive to the variations of oxygen concentration too, but bulk chemical defects are less important for the measurements of atmospheric gases. The study of this second class of sensors will be mainly deepened. They are relatively simple and low-cost devices, consisting in a heater and a layer of a nanostructured semiconductor in contact with two electrodes, which are necessary to measure the conductance of the material. There are different ways to build the sensor, but two fundamental aspects still remain: the possibility of heating the device up to the desired temperature and of measuring the conductance. Metal oxides are the most suitable semiconductors in the implementation of this kind of sensors. In effect, while other kind of semiconductors may undergo irreversible chemical changes, after extended or cyclic heatings in ambient, creating stable layers of oxide, metal oxides bind surrounding oxygen in a reversible way. The simplest and most common application of sensors consists in identifying a particular gas in the atmosphere, when there are not other kind of gases, that can generate a significant

signal. However, an efficient and reliable device requires a certain selectivity, in order to detect and measure the presence of a single constituent in a random gas mixture. Selectivity can be obtained by adding catalysing elements, such as noble metals, to the semiconductor, even if, till now, the comprehension of the role of these dopants on the selectivity is not very deep and clear. Some general aspects were assigned for the functioning and employing of these materials in their different shapes, being single crystals, homogeneous thin films, porous thick films or partially synthesized grain layers [8]:

- the presence of oxygen is even necessary, in order to detect burner gases;
- as the temperature becomes higher, the sensitivity to a particular gas increases until it reaches a maximum value, afterward it decreases, approaching to zero for higher temperatures;
- the response in function of temperature is a logarithmic curve in a wide range of concentration, therefore low gas concentrations give an high differentiation, while this does not occur with greater concentrations;
- the response time to a rapid variation of concentration depends on both the nature of the gas and the working temperature; a quick starting response is often followed by a slower approach to the equilibrium (several hours in some cases);
- the response to burner gases is generally non selective;
- the presence of water vapour ponderously affects the response.

Conduction and morphology of the sensitive layer

Chemical reactions occurring on the surface are transduced to electric signals by means of the electrodes in contacts with the sensitive material. Reactions may occur at different points of the sensors, depending on its morphology. Two cases may be distinguished: compact and structurally homogeneous sensitive layer, in which the electron flow is parallel to the solid-gas interface, or even to the space charge layer; thus, the interaction with the gases occurs just on the top of the surface (see Fig. 5, such layer is obtained by most of the techniques used for thin film deposition); porous and not thin sensitive layer, made of partially sinterised grains, where electrons are forced to overcome the intergranular barrier; therefore, in this case, a certain thickness of material is available for reactions, because of the porosity, and the active

surface is higher in comparison with the first case (see Fig. 6, such layer is typically a thick film).

In the compact layer case, we may consider two different configurations: partially and completely depleted layer [11]. In the first case, when surface reactions do not influence the conductance of the whole layer ($z_g > z_0$ case, in Fig. 6), the conduction process takes place mainly in the bulk ($z_g - z_0$ thick), which turns out to be much more conductive than the depleted surface layer. This situation can be presented schematically with two parallel resistances: one influenced by surface reactions and the other not. Thus, the conduction is parallel to the surface and the reduced sensitivity is explained. The two configurations, partially and completely depleted layers, can switch one into the other, when in contact.

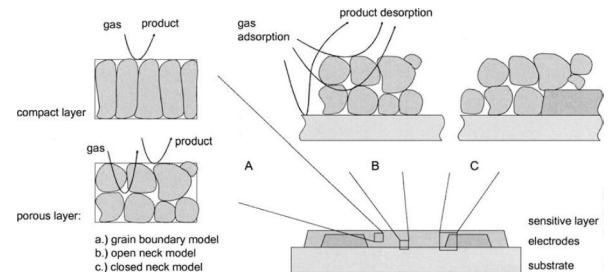


Figure 5: Schematic layout of a typical resistive gas sensor. The sensitive metal oxide layer is deposited over the metal electrodes onto the substrate. In the case of compact layers, the gas cannot penetrate into the sensitive layer and the gas interaction is only taking place at the geometric surface. In the case of porous layers the gas penetrates into the sensitive layer down to the substrate. The gas interaction can therefore take place at the surface of individual grains, at grain-grain boundaries and at the interface between grains and electrodes and grains and substrates.

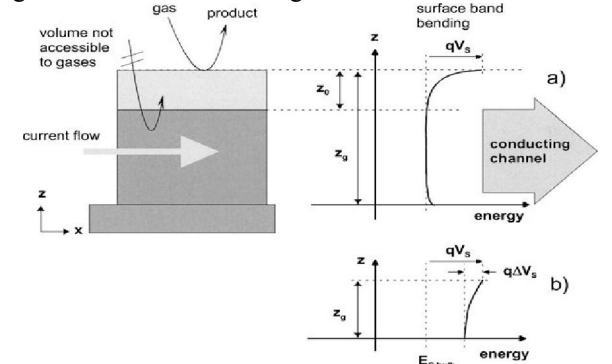


Figure 6: Schematic depiction of a compact layer with geometry and energy band representations: the thicker partially depleted layer (a) and the thinner completely depleted layer (b). z_0 is the thickness of the depleted layer, z_g is the total thickness and qV_s is the band bending.

With oxidizing and reducing gases, respectively, because withdrawal or injection of free charge carriers occur. For porous layers, the presence of necks between grains complicates the situation. Three contributions may be present in a porous layer: surface/bulk, grain boundary (for large grains not sintered together) and flat bands (for small grains and small necks). The switching mentioned above for compact layers is also possible for porous ones. In Fig. 7, we may observe the depletion area around grain surface and among intergranular contacts. The space charge region, depleted by charge carriers, is much more resistive than bulk, thus the layer close to the intergranular contacts is the main responsible for the resistance of the device. Considering the large grain model in Fig. 7, one notices that the charge carriers must overcome a potential barrier qV_s , in order to move from a grain to another. This means that the electric flow is limited by the density of

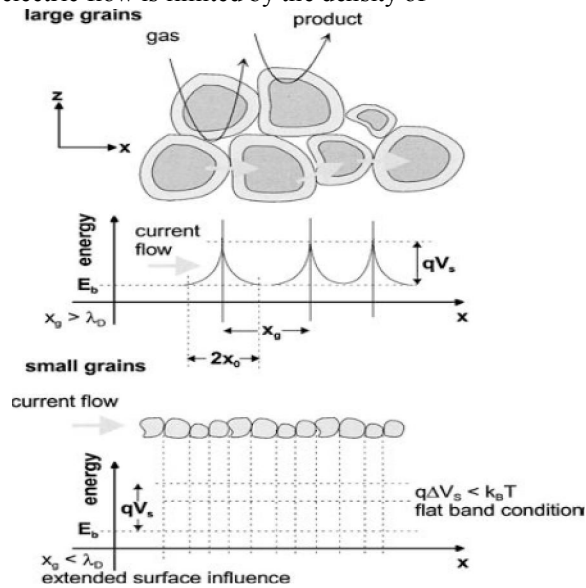


Figure 7: Schematic depiction of a porous layer. λ_D is the Debye length and x_0 is the grain thickness. electrons with energy at least equals to:

$$n_s = N_C e^{-(qV_s + E_C - E_F)/KT} = N_D e^{-qV_s/KT} \quad (10)$$

where N_C represents the effective density of the states close to the bottom of the conduction band. Recalling Eq. 7, we may write:

$$n_s = N_D e^{q^2 N_S / 2\epsilon\epsilon_0 k T N_i} \quad (11)$$

In the end, oxygen atoms adsorbed on the surface capture electrons from the bulk of the material, leading to the formation of a considerable potential, V_S , which causes conduction variation, monitored for gas detection. The intermediate case between compressed particle and thin films occur when particles are synthesized, as can be seen in Fig.7. The formation of necks occurs between synthesized particles. The more the neck diameter grows, the more the control of material conductance is assumed by the necks, rather than the surface states. This effect happens when neck size is comparable to the thickness of the space charge layer, that is to say that the diameter of necks must be 10 nm as order of magnitude. Therefore, an accurate control of grain morphology is necessary, in order to have reliable sensors for their quantitative use in real conditions [12].

Conclusion:

In this Review we have discussed regarding the Intrinsic surface states, Double layer, Conductance variation and Conduction and morphology of the sensitive layer of the Metal oxide semiconductor. In future we will be discussed about the W_o_3 Metal oxide semiconductor .

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