

1

Importance of the Nanostructured Ceramic Materials on Gas Sensing

Rafael Vargas-Bernal* and Gabriel Herrera-Pérez

Materials Engineering Department, Higher Technological Institute of Irapuato (ITESI), Irapuato, Guanajuato, Mexico

Outline

Introduction.....	2
Basic Aspects of Nanostructured Ceramic Materials	3
Resistive or Conductometric Gas Sensors	5
How to Optimize the Sensitivity	6
How to Optimize the Selectivity	11
How to Optimize the Stability	13
How to Optimize the Response Time	16
How to Optimize the Operating Temperature	20
Effects of Synthesis of the Nanostructured Materials on Gas Sensing	23
Effect of Morphology on Gas Sensing	26
Conclusions	29
Acknowledgements	29
References.....	29

Introduction

A *gas sensor* is a device which detects the presence and/or quantifies the concentration of one or various gases within a specific volume by means of chemical and/or physical interaction of the gas or gases with matter (ceramics or polymers) for determining any change in a physical property before and after of this action. For example, in an electrochemical gas sensor, the concentration of a target gas is measured by means of oxidizing or reducing at an electrode, through resulting electrical current. Chemical sensors can be classified as: optical, electrochemical, electrical, magnetic, thermometric and based on other physical properties such as radiation [1-2]. Within chemical sensors, electrical sensors (For example, metal oxide semiconductor (MOS) sensors, organic semiconductor sensors, electrolytic conductivity sensors, or electric permittivity sensors.) are based on reversible redox processes produced between a gas or gases to be sensed and their interaction with a sensible material, which produces a change in their electrical properties. A variety of semiconductor gas sensors can be found in the market, but they can be classified according with the type of transducer used as: resistor, diode, MIS (metal-insulator-semiconductor) capacitor, MIS FET (metal-insulator-semiconductor field effect transistor), and oxygen concentration cell [3-7]. Each type of gas sensor has a specific structure, working principle and sensing mechanism. Actually, the most successful type in the market is the resistive, since only two terminals are used in the circuit, wide area of sensing is available, and a nonlinear response of large amplitude is obtained without necessity of an embedded electronic amplifier in the sensor design. Although, a lot of parameters can be used to characterize sensor performance [2], here only are considered those whose effect can be controlled by matter used as sensible material. These are listed as defined as follows:

- *Sensitivity* is the change in measured output signal per gas concentration unit, that is, the slope of its calibration curve.
- *Selectivity* is the quality that determines whether a sensor can react selectively to a certain group of gases or even specifically to a single gas.
- *Stability* is the ability of a sensor to keep reproducible performance in a specific period of time of parameters such as sensitivity, selectivity, amplitude and form of response, and recovery time.
- *Detection limit* is the lowest concentration of gas that can be detected by the sensor under established operating conditions, for example, at a particular temperature.
- *Response time* is the time required by the material used in the sensor to react to a step concentration changing from zero to a certain concentration value.
- *Recovery time* is the time that takes to the output signal of the sensor returning to its initial value without gas, after that a concentration change from a certain value to zero was applied to the sensor.
- *Operating temperature* is the temperature at which the maximum sensitivity of the sensor is achieved.
- *Resolution* is the lowest concentration difference of gas that can be discriminated by sensor.
- *Life cycle* is the period of time that will continuously operate the sensor without fault and to its maximum capacity.
- *Hysteresis* is the maximum difference in output signal when the value is reached either with an increase or a decrease of the gas concentration range to be measured.

- *Repeatability or test-retest reliability* is the variation in value of measurements taken by a gas sensor on the same item and under the same conditions.
- *Dynamic range* is the gas concentration range between the lowest detection limit and the highest limiting concentration.

Different morphologies of ceramic nanomaterials have been synthesized and functionalized by different physicochemical processes. Desirable response a different gases with good stability, sensibility, selectivity, lower operating temperature, and fast response time are attributed to nanostructured ceramic materials that have been developed until now. The gas sensing mechanism and the advantages of these nanomaterials depends of the several technical aspects such as morphology, compositions, dimensions, physicochemical properties, etc. Recently, interest in different morphologies of ceramic nanomaterials has been greatly stimulated due to their large aspect ratio, less agglomerated configuration, and slow electron/hole recombination rate. This chapter has as aim analyzing and understanding how these technical aspects, involved in the ceramic nanomaterials, have improved and optimized the gas sensing mechanism in practice. All figures in this chapter are original and were developed by the first author.

Basic Aspects of Nanostructured Ceramic Materials

A ceramic material can be defined as an inorganic, nonmetallic solid prepared by the action of heat and subsequent cooling, and it has a crystalline, partially crystalline, or amorphous structure. Ceramic materials can be classified as: structural, refractories, white wares, or technical (engineering, advanced, special or fine ceramics). In addition, technical ceramics which are used in emerging applications can be classified as: oxides, non-oxides, or composites. For gas sensing, semiconductor oxides based on metals are the most exhaustively materials used as active materials in this application. Actually, oxides based on actinides, lanthanides, and other metals have demonstrated their potential application in the design of gas sensors.

Nanostructured materials are objects of intermediate size between microscopic and molecular structures. Nanostructures can have one dimension, two dimensions or three dimensions on the nanoscale, that is, their type is associated with the number of dimensions of the object between 0.1 and 100 nm. In this way, nanotextured surfaces are unidimensional, nanotubes are bidimensional, and nanoparticles are tridimensional. Between nanomaterials that have been used to design gas sensors are found metal oxides, metal nanoparticles, metal complexes, polymers, and carbon nanotubes [8]. More recently, graphene offers another possibility to develop nanostructured gas sensors. In [8], they described a set of advantages and disadvantages related with the use of nanomaterials in gas sensors design. The main advantages are: higher sensitivity, smaller size and quantity of sensing material, shortest response and recovery times, lower working temperatures and power consumption. Moreover, they are relative inexpensive, and easy of preparing in the ultra-dispersed state. On the other hand, the main disadvantages are: they require post-treatment after of their synthesis, advanced characterization and synthesis techniques, and low repeatability and reproducibility. Ceramic nanomaterials are ideal options of semiconducting materials for fabricating high-performance gas sensors due to their extraordinary combination of physical and chemical properties, and also valuable additives that provide new functionality to gas sensors to increasing and optimizing their sensitivity, selectivity, stability, response time, and operating temperature [2-28], as shown in Figure 1.1.

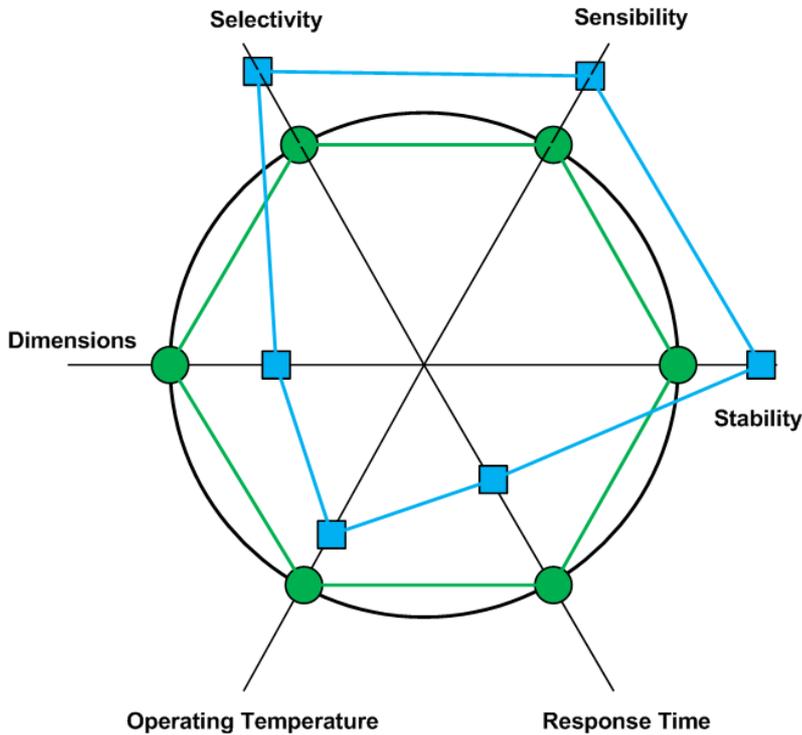


FIGURE 1.1

Web-chart that illustrates the advantages achieved in gas sensors based on nanomaterials (depicted as blue lines) on those based on bulk and/or micro-materials (illustrated with green lines)

These can be sub-classified as surface sensitive and bulk sensitive. High-performance resistive gas sensors can be prepared using simple ceramic nanomaterials such as Cu_2O [12], CdO [21], ZnO [13], Fe_2O_3 [10], In_2O_3 [9], SnO_2 [14], TiO_2 [18], MoO_3 [25], WO_3 [15], etc. and compounds such as ZnO-SnO_2 [20], $\text{Ni}_2\text{O}_3\text{-SnO}_2$ [26], LaNbO_4 [16], NiMn_2O_4 [22], NiV_2O_6 [13], potassium hollandite (barium oxide and manganese oxide) [19], cobalt titanates (titanium oxides) [24], etc. Among morphologies that have been fabricated (under different materials) until now, can be found nano-structures such as nanofibers [9, 28], nanotubes [18], nanorods [10, 13, 20, 28], nanoflowers [13], nanospheres [22, 24], nanoflakes [25], nanopowders [16, 28], nanoparticles [12, 14-16, 26], nanozeolites [19], nanosheets [21], etc. Physicochemical processes of chemical synthesis such as electrospinning [28, 29], chemical precipitation [28, 30], hydrothermal [10, 11, 13, 14], grinding-sonication [25, 31], solution-evaporation [22, 32], sol-gel [15, 33], spray pyrolysis [21, 34], etc. can be used to fabricate gas sensors. Appropriate donors or acceptors modify surface of the sensitive materials under oxygen partial pressures, and therefore, the electrical conductivity of semiconductor metal oxides can be increased or reduced. Ceramic nanomaterials have increased sensitivity, selectivity, and stability, and in addition, reduced operating temperature and response time of gas sensors. Through of morphology, composition, dimension, and physicochemical properties, it is possible improving performance of gas sensors using ceramic nanomaterials.

Resistive or Conductometric Gas Sensors

The electrical behavior of gas sensors have been widely studied using different electrical parameters such as electrical current, voltage, resistance and/or capacitance. The basic gas sensing mechanism implies redox reactions at the surface of the sensitive material, which lead to changes in the depletion layer of material that produces a change in electrical resistance due adsorption of gases on the material surface. Electrical conductivity can be defined as a measure of ability of materials to conduct an electrical current, expressed in Siemens (S). Electrical resistivity is the opposed. In nanostructured materials, large fraction of atoms in the surface involves oxygen vacancies available, and therefore, enhanced gas sensing properties can be achieved. Here, resistive or conductometric are analyzed since interaction with target gas can produce a change of conductivity or resistivity of the sensitive material to gas of interest [35]. They are used to monitor toxic gases such as carbon monoxide (CO), hydrocarbons (methane (CH₄), etc.), nitric oxide (NO), nitrogen dioxide (NO₂) and hydrogen (H₂). Semiconductors can be classified as: (1) *n*-type semiconductors when majority charge carriers are electrons, reducing gases increase the conductivity of the sensitive material, and (2) *p*-type semiconductors when main charge carriers are holes, oxidizing gases increase the conductivity of the sensitive material [36]. In Table 1.1, a summary of the behavior of electrical conductance versus type of measured atmosphere is given.

TABLE 1.1

Type of effect on electrical conductance of gas sensors in accordance to measured gas atmosphere

Type of Gas Sensor	Detection of Reducing Gases	Detection of Oxidizing Gases
<i>p</i> -type	Conductance increase	Conductance decrease
<i>n</i> -type	Conductance decrease	Conductance increase

Different analytical approaches have been proposed for describing the dependence of the responses of gas sensors based on semiconductor metal oxides [37]. The ideal gas sensor output signals can be approximated as a periodic function $f(t)$ based on Fourier series mathematically expressed as:

$$f(t) = A + \frac{4A}{\pi} \left(\frac{\text{sen}(t/T)}{1} + \frac{\text{sen}(3t/T)}{3} + \frac{\text{sen}(5t/T)}{5} + \dots \right) \quad [1]$$

where A is the amplitude of the output signal, and T is the period of the input signal, and t is the time. In Figure 1.2, it is depicted the ideal output signal obtained of a gas sensor for different number of elements n in the Fourier series, where it is obvious that a high number of n allows a better approach.

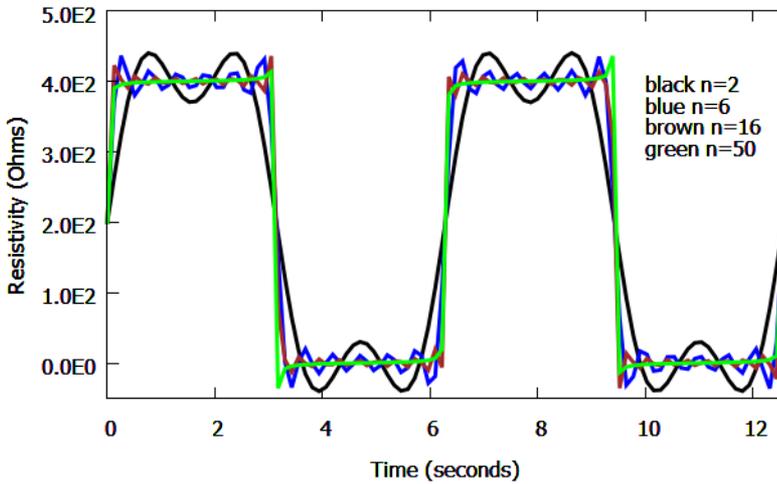


FIGURE 1.2

Ideal output signal of a gas sensor expressed as a function based on Fourier series

In practice, instantaneous transitions between the high and low levels are never achieved due to physical limitations of the electrical circuits that generate the waveform applied to gas sensors. Thus, a time is required to rise from the low level to the high level which is called *rise time*. In reverse mode, the time required to fall from the high level to the low level is called *fall time*. Two behaviors directly related with transitions can be distinguished: 1) *overdamping*, where waveform may never in reality reach the theoretical high and low levels, and 2) *underdamping*, in whose case waveform oscillate about the high and low levels before settling down. Both behaviors can be visualized in Figure 1.2, where a higher number of sinusoidal waveforms with different amplitudes and frequencies are required to achieve an ideal square wave. Therefore, rise and fall times are measured between particular transitional levels, such as 5% and 95% or 10% and 90%.

How to Optimize the Sensitivity

The main parameter related with response of a gas sensor is called sensitivity. The classical interpretation about sensitivity establishes that it is the slope of the graph that represents the change of the electrical parameter (involved in the measurement) such as resistance, current or voltage versus the gas concentration [38]. In this manner, sensor's sensitivity determines the rate of change between sensor's output and the measured quantity. Mathematically, it can be evaluated by dimensionless parameters such as sensor signal, response ratio, or sensor response, which are expressed as a ratio such as

$$S = \frac{R_a}{R_g} \quad [2]$$

in the case of reducing gases (Equation 2), or

$$S = \frac{R_g}{R_a} \quad [3]$$

for oxidizing gases (Equation 3), where R_a is the resistance of gas sensor to the reference gas (commonly the air) and R_g is the resistance when both reference gas and target gases are applied to the sensor. Other ratios for reducing gases [12, 16, 24] (Equation 4) have been also used such as

$$S = \frac{R_a - R_g}{R_a} \text{ or } S = \frac{\Delta R}{R_a} \quad [4]$$

or

$$S = \frac{R_g - R_a}{R_g} \text{ or } S = \frac{\Delta R}{R_g} \quad [5]$$

for oxidizing gases (Equation 5), are found in the literature. Therefore, since a unique definition for sensitivity has been not established, one must be very careful at using and comparing the sensitivities reported by different researchers around the world.

Alternative mathematical expressions for sensitivity in function of electrical current are [11]:

$$S = \frac{I_g - I_a}{I_a} \text{ or } S = \frac{\Delta I}{I_a} \quad [6]$$

for reducing gases, and

$$S = \frac{I_a - I_g}{I_g} \text{ or } S = \frac{\Delta I}{I_g} \quad [7]$$

for oxidizing gases, where I_a is the electrical current of the gas sensor when reference gas (commonly the air) is applied, and I_g is the electrical current when both reference gas and target gases are applied to the sensor.

Making use of the Table 1.1 and applying Equations 2 and 4 was obtained a curve where is shown the behavior of the sensitivity of p -type gas sensors in reducing atmospheres. It can be concluded that Equation 2 presents an increasing exponential behavior as R_g increases and therefore, it is necessary that ratios as large as 20 times between R_a and R_g occurs to achieve high sensitivity. Equation 4 presents a linear behavior and values less than 1 in sensitivity are obtained for sensitivity. The results of Equation 4 were scaled to can appreciate the shape of the curve. Similar behaviors can be predicted to n -type gas sensors in oxidizing atmospheres.

Equations 3 and 5 together with Table 1.1 were used to estimate the behavior of the sensitivity for n -type gas sensors in oxidizing atmospheres. Sensitivity calculated using Equation 3 has a linear behavior, therefore, since R_g will be increased then sensitivity will be higher. A logarithmic behavior can be viewed for Equation 5, it was scaled to know the shape of the curve. Similar behaviors can be predicted to p -type gas sensors in reducing atmospheres.

Sensitivity can be expressed in function of concentration for gas sensors using p -type materials as:

$$S = C_0 \ln(k_C C) \quad [8]$$

and, for gas sensors based on n -type materials as:

$$S = C_0 \exp\left(\frac{C}{k_C}\right) \quad [9]$$

where S is the sensitivity, C_0 and k_C are constants, and C is the concentration applied. In Figure 1.5, behavior of the sensitivity S as a function of the concentration C of the gas applied for both types of semiconductor materials.

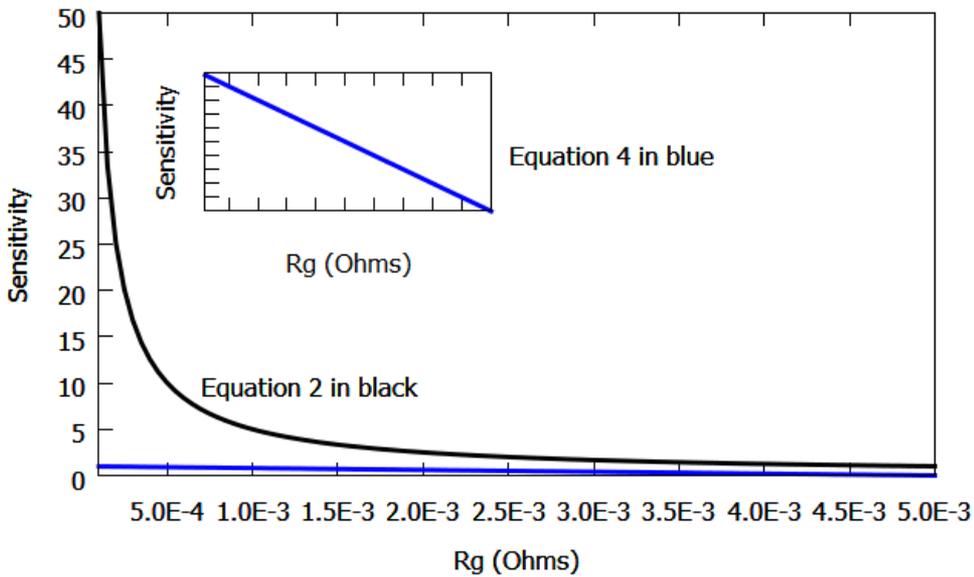


FIGURE 1.3

Behavior predicted of the sensitivity for p -type gas sensors in reducing atmospheres

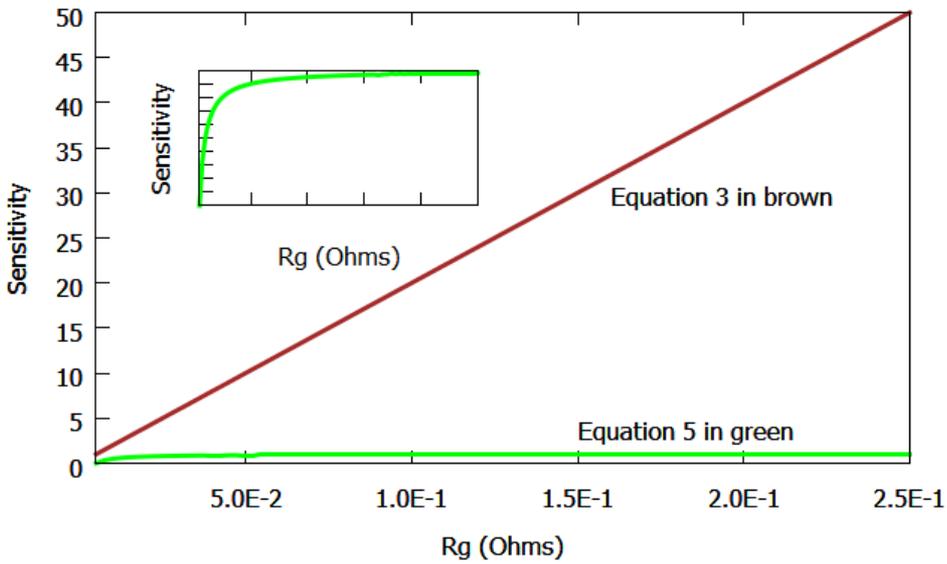


FIGURE 1.4
Behavior predicted of the sensitivity for *n*-type gas sensors in oxidizing atmospheres

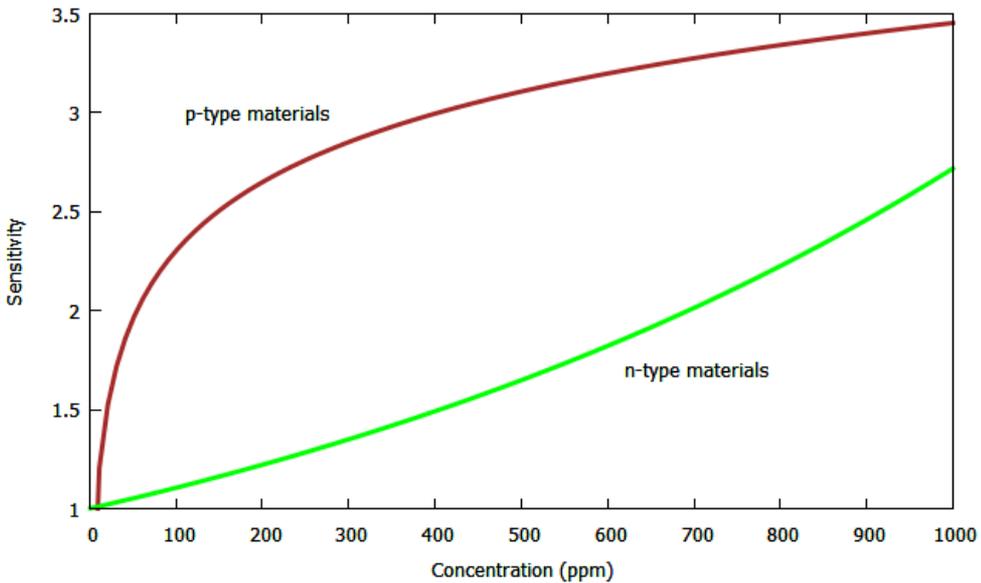


FIGURE 1.5
Behavior of the sensitivity as a function of the concentration of gas applied

The sensitivity of semiconductor oxides is guaranteed by reversible effects of chemisorption of gas molecules, formation of space charge areas, and variation of the concentration of the charge carriers on the subsurface layer [38]. The amplitude of output signal is mainly determined by structural characteristics of the oxide such as: size, structure, and degree of agglomeration of

nanocrystallites, which modifies the nature and concentration of surface reactive centers, specific surface area, and pore geometry. The electrical conductivity of semiconductor oxides is greatly sensitive to the surface composition of the active material of the sensor, which favors surface reactions between chemisorbed oxygen (O_2^- , O^{2-} , O^-) and the gas mixture to be analyzed at higher temperatures to room temperature.

Semiconductor metal oxides have strong influence on surface reactions of gas sensors, since they are sensitive to chemical components, surface-modification and microstructures of sensing layers, temperature and humidity [40]. Sensitive materials to gases must be favorable to adsorption ability, catalytic activity, sensitivity, selectivity, thermodynamic stability, etc. Unfortunately, very few of them are suitable to all technical requirements for a maximum performance. Thus, the use of composite oxides, hybrid oxides, oxides based on heterojunctions, mixed oxides, or polycrystalline oxides can increase such technical capabilities. They are formed by ternary, quaternary and n -ary metal oxides, and therefore, multiple qualities are incorporated into a sensitive material. The enhanced performance of these oxides is attributed to novel hierarchical structures that can be produced with oxides and synergetic effect between different oxides. A hierarchical nanostructure is an assembly of one-dimensional (1D) and two-dimensional (2D) nano-building blocks with exceptional physical and chemical properties [11]. These structures can be formed by same oxide with different morphologies or different oxides with similar or different morphologies. The synergetic effect in mixed oxides can be defined as an increased intensity in any characteristic such as sensitivity, selectivity, etc. caused by the combination of two or more metal oxides.

Hierarchical structures based in the same oxide but with different nanostructures have been reported. ZnO nanowires and nanodisks were prepared from sequential nucleation and growth following a hydrothermal process [11]. These structures can sense acetone with high sensitivity compared when a unique nanostructure is used. SnO₂ nanorods and nanocrystals were obtained by chemical precipitation method [41]. Enhanced response to isopropanol vapor, a good selectivity, and a fast response and recovery time were achieved with these structures for gas sensing.

For example, gas sensors based on ZnO-SnO₂ have higher sensitivity than those sensors based uniquely on tin oxide (SnO₂) or zinc oxide (ZnO) under identical conditions [42, 43]. Other composite oxides have been used such as ZnO-CdO [44, 45], PdO-TiO₂ [46], WO₃-SnO₂ [47], NiO-ZnO [48], In₂O₃-ZnO [49], etc. Responses until 7 and 59 times as high as those of the pure ZnO and the pure CdO, respectively have been reported in [44].

More than one metal oxide involved in the gas sensing material increases the surface area thanks to additional active sites for gas adsorption [46]. In addition, the possibility of improving catalyzing of the reaction associated reduces the electrical resistance of the sensor and increasing the sensor response to the analyte or target gas. Mixed oxides must combine oxides in specific proportions to increase specific surface area and adsorption oxygen to high responses. For example, a ZnO-CdO composite oxide with a content of 10 at% CdO achieved high specific surface area and high concentration of adsorbed oxygen in [45].

The sensitivity is a function of the operating temperature due to the kinetics and mechanics of gas adsorption and desorption on the surface of semiconducting metal oxides [11]. Thanks to high surface-to-volume ratio of the nanostructured materials, they increase sensitivity to different gases

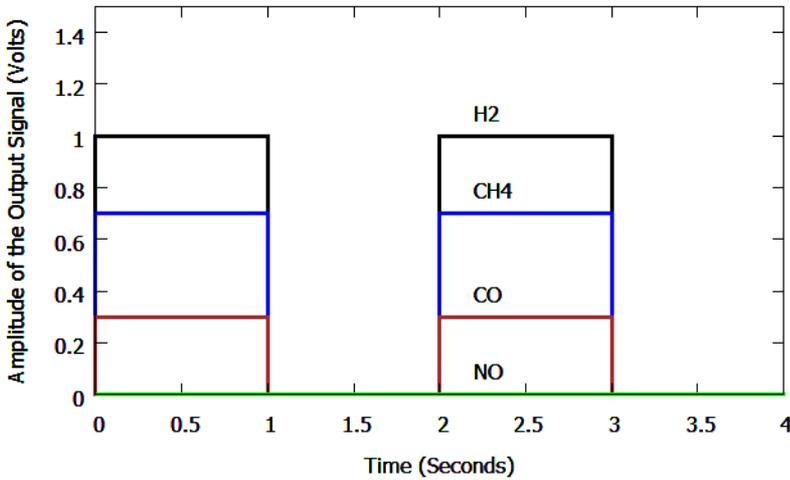
when operating temperature is adequately adjusted. For low temperatures, the chemical activation is small leading to insignificant responses. At very high temperatures, adsorbed gas molecules escape before all charge transfer can be realized, and the response is lesser. Thus, there is a specific range of temperatures in which nanostructures can absorb oxygen species to detect gases.

Surface-modification can be realized by means of impregnation, sol-gel, sputtering and thermal evaporation of noble metals on semiconducting metal oxides. Each deposition method can produce different doping states, which can be exploited in gas sensing of different target gases. The properties of catalysts depend on their composition, structure, phase, shape, size, and size distribution [40]. Thus, reactivity and selectivity of nanocatalysts is tailored through its shape, since it determines the crystallographic facets that will be exposed in the surface of the sensitive material to the target gas.

At present, researchers on gas sensors are focused in searching the optimal sensing materials and in the design of theoretical models with the aim of promoting optimization of gas sensors [3]. The optimization involves achieving high sensitivity, selectivity, stability and fast response and recovery times in the performance of gas sensors. Actually, the combined use of metal oxides and other materials such as carbon nanotubes [50], graphene oxide [51], graphene [52], or polymers [53] have been also researched actually.

How to Optimize the Selectivity

A chemical sensor can be considered ideal when it possesses high sensitivity, dynamic range, selectivity and stability; low detection limit; good linearity; small hysteresis and response time; and long life cycle [2]. Regularly, sensitivity can be easily achieved, however, selectivity is much harder to attain, since it is obtained through an increased system complexity going from simple devices or desktop analytical instruments [6]. One of the most important parameters that must be optimized in a gas sensor is its selectivity. It can be defined as the ability of a gas sensor to react to a certain gas in the presence of other gases [38]. Regularly, sensors are sensitive to different gases and it implies that a comparison on the effects achieved by each target gas is required to monitor the performance waited. Considerable difference in this parameter is achieved when reduced or oxidizing gases are applied to gas sensor. Care must be taken when cross sensitivity is presented (see Figure 1.6), since it implies different species can present self-reactivity, and therefore, the presence of target species can be hidden [54]. It is shown in Figure 1.6 that, hydrogen (H_2) has larger response, and then methane (CH_4), and finally, carbon monoxide (CO); nitric oxide (NO) is not detected. Thus, this gas sensor is selective to certain gases. A very high selectivity implies that a unique gas must be detected by a sensor and a maximum response is highly desirable.

**FIGURE 1.6**

A gas sensor can detect different gases (at the same measurement) or even nothing

The main strategies used to improve the selectivity of semiconductor oxides are [39]:

1. Changing the composition and size of nanocrystallites of oxides.
2. Using a catalyst to increase and/or modifies the chemical activity in the solid-gas interphase [55].
3. Modifying the catalyst density or concentration to improve the reactivity of the active material and gas molecules.
4. Opting for a “catalyst-oxide” pair with the aim of using d electrons of surface-localized transition metals and thus altering the surface activity of the oxide.
5. Making use of doping to modify the surface of the active material used in the sensor.
6. Mixing two or more oxides to increase the surface activity of the sensor.
7. Controlling the sensor operating temperature [55].
8. Using passive and catalytically active filters [55].
9. Changing sensitive material's morphology and the sensor architecture [56].

The greatest disadvantage of the semiconductor oxides is their low selectivity to gas molecules, thus different strategies have been proposed with the aim of increasing their selectivity [39]. Their selectivity can be improved by surface modification through the use of catalytic additions (simple or combined) and by means of complex inhomogeneous systems [6, 39]. Simple catalysts are based on chemical elements such as: gold (Au), platinum (Pt), palladium (Pd), ruthenium (Ru), or rhodium (Rh). Combined catalysts are based on oxide catalysts such as: iron(III) oxide (Fe_2O_3), lanthanum(III) oxide (La_2O_3), chromium(III) oxide (Cr_2O_3), cobalt(II,III) oxide (Co_3O_4), vanadium(V) oxide (V_2O_5), nickel(II) oxide (NiO), molybdenum(VI) oxide (MoO_3), and ceria or cerium(IV) oxide (CeO_2). When one oxide is used as catalyst, it performs the receptor function or chemically active material, while the first oxide acts as transducer [6]. At being used semiconductor metal oxides as additives, faster responses, and high sensitivity, selectivity and stability are straightly achieved. Thus, it is possible a unlimited number of possibilities of combination of sensitive materials that can be used to

strategically exploit particular physicochemical properties of each semiconductor metal oxide for designing gas sensors.

Selectivity is tested to one operating temperature establishing a specific concentration level. Different gases are tested and the highest responses indicate to which gases the sensor is selective. Any gases cannot be detected, and then sensor is insensitive to them or has not selectivity to these gases. Among practical problems in chemical sensing is solving poor selectivity of individual gas sensors [57]. With the aim of improving selectivity, it is recommended the use of devices with partially overlapping sensitivities in the form of sensor arrays [6], which can be directly obtained by means of nanostructured based on semiconductor metal oxides. Commonly, gas sensors present selectivity and sensitivity dependent on operating temperature and choice of semiconductor metal oxide [3].

Gas sensing mechanisms are highly controllable at the nanoscale level, and thus, direct benefits on the three "S" of sensor technology (sensitivity, selectivity, and stability) are possible [6]. Researchers have reported that the use of mixed oxides such as ZnO-SnO₂ enhance selectivity to carbon monoxide (CO) and ethanol (C₂H₅OH), while it suppresses the response to methane (CH₄) [43].

A lot of applications require gas sensors with high selectivity and therefore, the selection of the sensitive materials must be carefully realized [3]. It is important pointing that high selectivity implies low reversibility due to high binding energies are involved. In change, full reversibility is easily achieved since weak interactions between the analyte and the sensitive material are associated [57].

Fundamental selectivity problem can be solved using a tripartite strategy that involve sensitive material, transducer, and signal generation and processing techniques [57]. Therefore, the optimization must be worked as a whole, where materials science, instrumentation and signal processing can be grouped. Thus, selectivity can be improved through novel design of sensitive materials, the integration of individual devices into arrays, and the development of systems including air-sampling modules and data processing algorithms.

Two megatrends to solve the optimization of selectivity have been considered by researches [57]. First, it implies the development of sensitive materials whose selective response to determined analyte be unique and have suppressed response to other interferences. Second, it makes use of arrays of sensors with partially selective sensing materials and processes their outputs of individual sensors together.

How to Optimize the Stability

Another of the main parameters that determines high quality of a gas sensor is its stability. It can be defined as the quality or state of sensor of not so easily changed, moved or likely of changing. In the case of market sensors, these must exhibit a stable and reproducible performance by a period of 2-3 years [58]. Semiconductor oxides have stability in air [39]. The field experience has shown that gas sensors based on semiconductor metal oxides have long term application of more than 1 year of continuous work [59]. The low repeatability of gas sensors entails different behaviors of

identical sensors with the same history of application under identical conditions. Therefore, there exists a necessity for developing and applying corrective models after few days of running or after sensor replacement to optimize the performance of the gas sensor.

It can be distinguished two types of sensor stability: First, it is associated with the reproducibility of sensor characteristics during a certain period of time under determined work conditions, and which is called *active stability*, and second, it is implied in retention of sensitivity and selectivity during a period of time at normal storage conditions such as environmental that receives the name of *conservative stability* [2].

Gas sensors present drift (i.e., the amount the gas sensor output may change over time, expressed in %) due to different technical aspects involving material's performance, design, and operating conditions that are described by Korotcenkov and Cho [58]:

- Phase transformation (structural changes such as grain growth, cracking, diffusion, etc.) of the sensitive material, and degradation by thermal shock of contacts and heaters.
- Interference defects, nonspecific adsorption, variations on flow rate, etc.
- Changes of temperature, humidity in the surrounding environment, poisoning, etc.

Sensor drift remains as a specific challenge in chemical sensing, due sensor's performance is degraded over a long period of time independently of the technology [60]. Romain and Nicolas [59] tested three types of solutions with the aim of attempting to compensate the sensor drift: signal pre-processing (response variable including the base line signal) [61], univariate sensor correction [62] and multivariate array correction [63]. In this study, they found that a univariate multiplicative factor on output signal is necessary to obtain best results used to compensate drift as a change of self-calibration. This factor is specific for each sensor, and therefore, it is very difficult to identify the particular correlation with drift found in each gas sensor. Unfortunately, these methods require long field monitoring and learning phases, time-consuming and besides expensive, which leads users to prefer buying a new instrument.

The temporal drift of n -type gas sensors can be mathematically expressed as a change of conductance versus operating time as follows:

$$G_{oxi} = G_0 \exp(-k_t t) \quad [10]$$

or

$$G_{red} = G_0 \exp(k_t t) \quad [11]$$

where G_{oxi} is the conductance for oxidizing gases in operating time t , G_{red} is the conductance for reducing gases in operating time t , k_t is a aging constant, and G_0 is the initial conductance of the sensor. In Figure 1.7, electrical conductance of n -type gas sensors as a function of time has been plotted for oxidizing gases (during a period of 2 years). The effect of aging time on gas sensors for reducing gases is illustrated in Figure 1.8. Equations 10 and 11 must be inversed in the case of p -type gas sensors. Aging constants have very small values, but maximum degradation can be viewed as k_t and t increase. A value of $k_t = 0$ implies that zero aging or degradation is presented during

operation of a gas sensor. In these expressions, it is considered that k_t is constant with time, which in real life is not necessarily true.

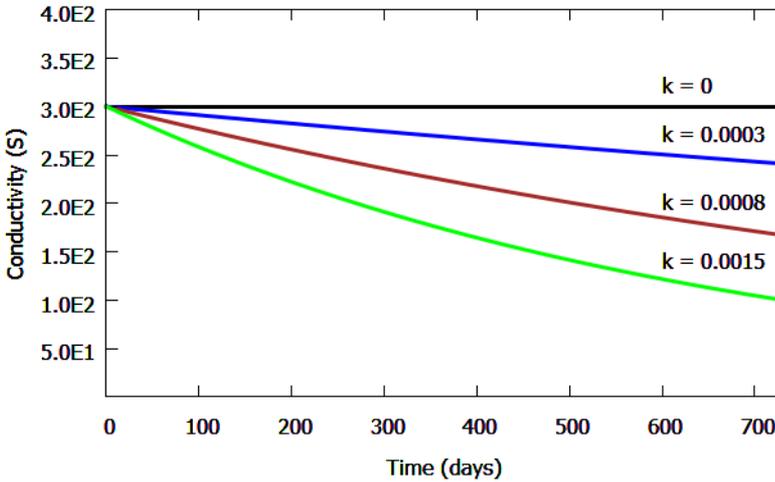


FIGURE 1.7 Aging effect in *n*-type gas sensors visualized as conductance versus operating time for oxidizing gases

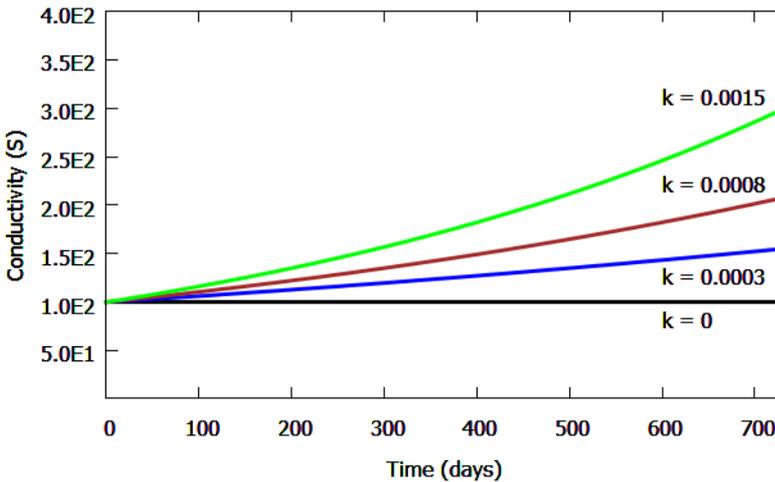


FIGURE 1.8 Aging effect in *n*-type gas sensors visualized as conductance versus operating time for reducing gases

The long-term stability of a gas sensor is mainly dependent upon the humidity of the ambient gas stream; therefore, an appropriate housing is required to eliminate this effect [64]. Water absorption will not donate electrons to sensing layers, it leads to a decrease in baseline resistance (initial resistance or resistance at air) of the gas sensor, and thus, to a lesser stability of the gas sensor [40].

One-dimensional materials have lengths comparable with Debye length, and therefore, they are more thermodynamically stable than nanograins which favors stable operation of gas sensors over a long time period [65]. Nanostructured materials such as nanobelts, nanorods, nanowires and other nanostructures can be facile of fabricating, have open surfaces, present high gas sensitivity and long-term stability, which make them excellent design platforms for the new generation of gas sensors.

How to Optimize the Response Time

Response time can be defined as the time that a system or device requires to react to a given input, and it is often measured in seconds. Moreover, it is considered as time required for injecting the mixture of the target gas and air directly into the sensor head until obtaining an output signal in the gas sensor [66]. Using mathematical values, *response time* (t_r) represents the period of time required for that resistance of the gas sensor to reach 90% of the equilibrium value after injecting the gas [11]. Moreover, *recovery time* (t_d) is the time necessary for the resistance of the sensor to return to 10% above of the original value in air after releasing the gas measured. Unfortunately, in practice, it is not necessarily the case, since gas will travel several meters before of arriving to the sensor head. Thus, response time must include the period in which gas is accumulated around of the sensor and time required to get from the leak point to the detector. Total speed of response of gas sensors can be calculated as

$$t_{total} = t_{detector} + t_{gas} \quad [12]$$

where $t_{detector}$ specifies how long time takes to gas sensor to reach 90% of the total response when a well-defined gas concentration is injected directly into the sensor head and whose value oscillates from 10 to 20 seconds, and t_{gas} represents how long time takes to certain gas concentration to travel from the leak spot to the detector, which is difficult of predicting due to changing conditions through of the length of the path traveled, and whose value oscillates from minutes to hours. Thus, only $t_{detector}$ is considered commonly to determine response time. Commercial gas sensors are numbered as T50 or T90, and the number indicates the achieved percentage of response of the test gas concentration, as illustrated in Figure 1.9. Typically, it is required an exposure of twice the T90 time to the gas sensor for getting a stable reading.

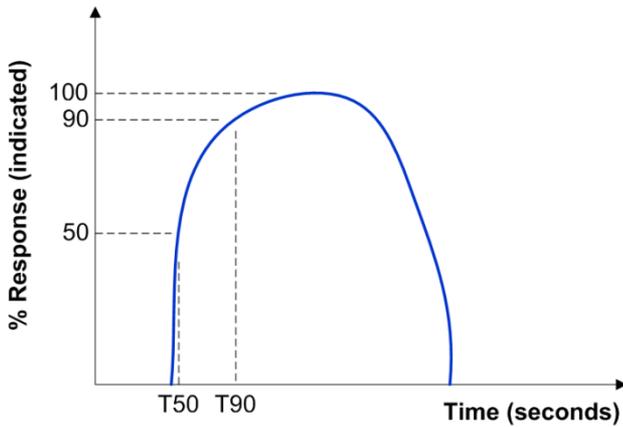


FIGURE 1.9
Response time involving the recovery times of practical gas sensors

Gas sensors respond to higher concentration faster, and to lower concentrations slower, i.e, gas molecules require long or short times to react with the oxygen species on the surface of the sensitive material. When low concentrations are measured, then response times must be significantly higher. Since diffusion is used to produce physical, chemical or physicochemical interaction between sensitive material and the target gas, diffusion rate is a key criterion to calculate the response time. In larger spaces for gas diffusion, the gas response and response time are improved. Gas diffusion into interior of bulk materials is sluggish, leading to long response and recovery times. Metal oxide semiconductors used in gas sensors have a fast response time, which is directly related to the grain size and the size of the particle boundary in the material [36]. Mixed oxides produce sensitive materials with fast response times and therefore, recovery times lesser (response times below 10 s) [11]. Response time values in tens and hundreds of seconds are reported in almost all technical papers about gas sensors based on microsensors [67]. The response time and recovery time for simple metal oxides are long with respect to hybrid oxides, due to its hierarchical structure behaves as tunnel barriers whose response is faster [11]. The tunneling current across the barriers is exponentially related to the barrier height and carrier density is increased. In Table 1.2, values of barrier height for different mixed oxides are given. It is clear that barrier height has an intermediate value between those to individual oxides.

TABLE 1.2
Barrier height for different mixed oxides used to build gas sensors

Mixed Oxide	Band Gap of the First Oxide	Band Gap of the Second Oxide	Band Gap of the Mixed Oxide
SnO ₂ -ZnO	3.7 eV	3.20 eV	3.23 eV
SnO ₂ -TiO ₂	3.7 eV	3.20 eV	3.60 eV
SnO ₂ -WO ₃	3.7 eV	2.60 eV	3.20 eV
SnO ₂ -CdO	3.7 eV	2.16 eV	3.08 eV
In ₂ O ₃ -CdO	3.0 eV	2.16 eV	2.50 eV

The interests for using nanostructured materials is directly associated with the reduction of response and recovery times in the gas sensing. In addition, hierarchical structures have large specific surface area and surface permeability almost ideal, which favors abundant adsorption and fast diffusion of target gases to sensitive material used in the gas sensor.

The effect of humidity on the response of SnO₂ thin films was studied in [68], they found that a decreased response time and larger responses in the presence of water during gas sensing. Doping of the sensitive material by means of catalysts, as well as controlling its grain size can reduce response time of the gas sensor [36, 69].

It is clear that models for response time must be different for *n*-type and *p*-type semiconductors due to the particular type of minority and majority charge carriers. The response time (t_{90}) for resistive gas sensors can be calculated as a function of the diffusion coefficient (D_V), and particle size (R) [70]. For small particle size the kinetics is controlled by surface reaction. It is necessary to increase D_V and/or to decrease R with the aim of shortening the response time of gas sensors. They found that t_{90} is directly proportional to R^2/D_V . In Figure 1.10, it is illustrated the behavior of the response time for different values of D_V with variations in R . Therefore, since diffusion coefficient depends on molar flux and the gradient in the concentration of the gas, it can be controlled to be injected to the gas sensor, while particle size can be optimized by means of the synthesis process used to fabricate the sensitive material to the target gas.

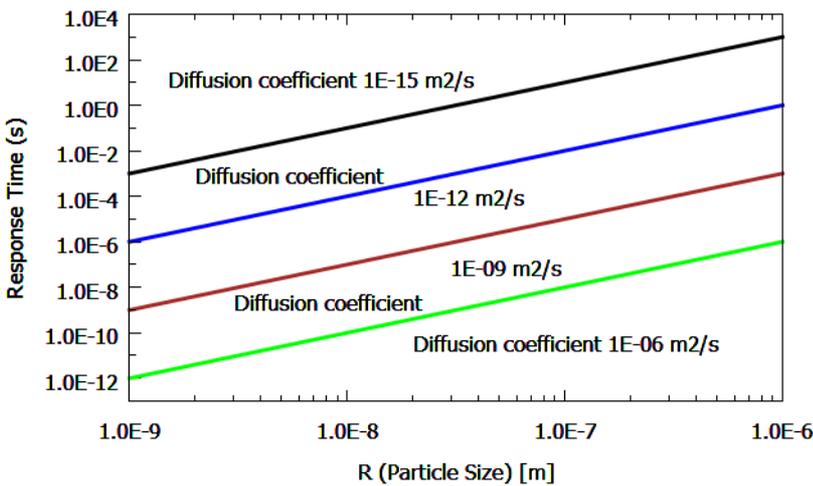


FIGURE 1.10

Response times of gas sensors as a function of particle size and diffusion coefficient

Recovery time constants of gas sensors τ have exponential temperature dependence [71]:

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad [13]$$

where E_a is the activation energy for adsorption or desorption of the gas, k_B is the Boltzmann constant, T is the temperature, and τ_0 is a prefactor that partly compensates the acceleration effect

of a lower activation energy (E_a) found in nanomaterials. Using values obtained in [70], recovery time constants versus temperature were depicted in Figure 1.11 for H_2 adsorption by means of gas sensors based on Pt-SnO₂ and SnO₂ in the range of 298 K to 1073 K. The behaviors for H_2 desorption in the same range of temperature, and gas sensors before described is illustrated in Figure 1.12. Sensitive materials (SnO₂) containing catalysts (Pt) present better characteristics of recovery time constants (shorter times) that those without catalysts either in adsorption or in desorption as visualized in Figures 1.11 and 1.12. In addition, high temperatures offer shorter recovery time constants in both types of sensors. In the case of adsorption in Pt-SnO₂ sensor, a recovery time constant of 1 second is maintained almost constant in full range of temperature. Desorption curves have the same shape for both types of gas sensors. Asymmetric behavior is presented for adsorption and desorption, i.e., a deformed shape of the output signal of the gas sensor is waited. The platinum favors adsorption on desorption, as shown in Figures 1.11 and 1.12.

Gas sensors with faster response times are desired to monitor transient in-vivo events and bedside patients [4]. More selective instruments are required to analyze ambient urban or battlefield air. Response time can be optimized with nanoporous structures due to high surface-to-volume ratio generated and decreased distance for bulk diffusion required for gas sensing. In particular, when nanowires or nanorods are used in the sensitive material, diameter of these nanostructures can control the response time of the gas sensor. Moreover, high responses imply slow response times. Covalent bonding in sensitive materials reduces sensitivity and increase response times of the gas sensors [4].

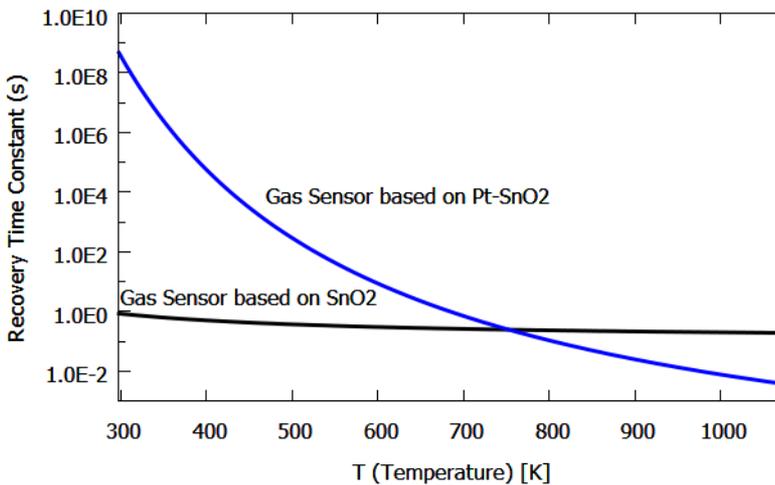
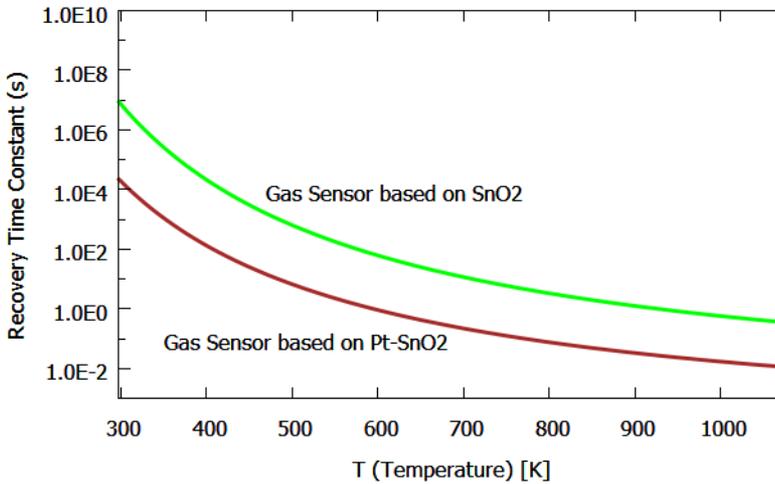


FIGURE 1.11

Behavior of the recovery time constant gas sensors based on Pt-SnO₂ and SnO₂ during adsorption of H_2

**FIGURE 1.12**

Recovery time constant of gas sensors based on Pt-SnO₂ and SnO₂ during desorption of H₂

Moreover, it must be noted that rise and fall times of gas sensors are modified by factors such as age of the sensor, chemisorption of target gas in sensor, cumulative exposure to target gas and interfering gases of the sensor, and poor maintenance to it. Other factors that can affect response time of gas sensors are the presence of weather baffles (splash guards), changes in flow rate, etc. The use of filters or permeable membranes for increasing the selectivity in gas sensing, increases the response time of the gas sensors [64].

How to Optimize the Operating Temperature

Operating temperature can be defined as temperature at which a gas sensor operates. When a gas sensor is exposed to air, oxygen molecules are adsorbed on the surface of the sensitive material [16]. This material traps electrons from the conduction band and produces negatively charged chemisorbed oxygen species O^{δ-} such as O₂⁻, O⁻ and O²⁻. Hence, the concentration of holes in valence band increases and the resistance (of the sensitive material) decreases due to increased concentration of available carriers. The type of such chemisorbed oxygen species at the surface depends on the operating temperature.

Gas sensing at low temperatures is essential for several gases with characteristics such as colorless, odorless, explosive and extremely flammable [72]. Moreover, advantages in terms of reducing energy consumption and improving the reliability and stability of the gas sensor. Redox reactions are reversible at elevated temperatures, thanks to that the baseline resistance is recovered to their original value, after exposure to air again. At relatively low temperatures, O₂ in the atmosphere produce adsorbed O₂⁻ species, which allow small responses of the gas sensor.

Regularly, a device must operate within a temperature range specified by minimum and maximum values. Outside this range, gas sensor may fail. There is significant influence of operating temperature on the sensitivity of gas sensors, all sensors must be tested at different temperatures

to find the optimum operating conditions for gas sensing. Oxygen can be chemisorbed in the following forms: O_2^- ($< 100\text{ }^\circ\text{C}$), O^- and O^{2-} (high temperatures). In the case of gas sensors, it is considered that dominant O^- chemisorbed oxygen is the responsible of operating temperatures in the range of $300\text{--}450\text{ }^\circ\text{C}$ [37]. Therefore, gas sensors operating to low temperatures can be obtained by means of the use of nanomaterials, such as semiconductor metal oxides. The use of hybrid oxides such as $\text{SnO}_2\text{-ZnO}$ has reduced operating temperature by $50\text{ }^\circ\text{C}$, when it is compared with a gas sensor fabricated uniquely of SnO_2 [43].

Nanostructured materials have a significant number of oxygen vacancies, which make them very favorable for gas sensors operating at low temperatures [72]. At room temperature, oxygen molecules take away electrons from the conduction band of the semiconductor metal oxide to form surface O_2^- and O^- species, which creates an electron depleted surface layer with high electrical resistance [73]. In n -type metal oxides, the baseline resistance requires of the formation of a depletion layer produced by dissociation and adsorption of oxygen molecules and electron transport in it [12]. The electrical resistance will be increased slowly in accordance with the O_2^- concentration due to that electrical conductivity will lower near the n -type metal oxide surface. The O_2^- chemisorption process is exponentially increased as the temperature is raised, leading to electrical current decay due to high electrical resistance at high temperatures. Well-aligned electrospun SnO_2 nanofibers for hydrogen detection have operating temperature of $150\text{ }^\circ\text{C}$ [72]. A summary of the behavior of the gas sensors related with operating temperature is given in Table 1.3.

TABLE 1.3

Behavior of gas sensors with respect to their operating temperature

Chemisorbed Oxygen Species	Operating Temperature	Response Amplitude
O_2^-	Low ($< 100\text{ }^\circ\text{C}$)	Small
O^- and O^{2-}	High ($> 100\text{ }^\circ\text{C}$)	High

The presence of oxygen vacancies in the sensitive material determines the electronic and chemical properties involved in the adsorption behaviors of metal oxide surfaces [74]. Abundance of electron donors on surface metal oxides increases responses and reduce the operating temperature in gas sensing [72, 75]. Ambient air generates oxygen vacancies that can be exploited at relatively low temperatures, which are widely guaranteed through of the use of 1D nanostructures, since they have high surface-to-volume ratio [71]. In addition, the effectiveness of 1D structures is directly related with the cross sectional dimensions that are comparable with the Debye length implied in electron depletion depth.

In [75], two main approaches can be adopted to reduce the operating temperature of gas sensors by means of semiconductor metal oxides. First, it consists in adding additives such as noble metals on the surface of the sensitive materials. Noble metals acting as catalysts can increase the response, selectivity to certain gases, and reduce the operating temperature of the gas sensors. Second, it can be reduced the grain size of the sensitive materials searching make comparable or less than its size to Debye length.

At low temperatures, gas molecules are trapped in a physisorbed state and cannot overcome the activation barrier E_A [76]. Besides, the thermal activation is too low to overcome the desorption barrier and therefore, adsorbed molecules are kinetically trapped at the surface.

The behavior of n -type gas sensors and p -type gas sensors with respect to temperature can be mathematically expressed as a change of conductance versus operating temperature as follows:

$$G_n = G_{com} \exp(-k_T T) \quad [14]$$

or

$$G_p = G_{com} \exp(k_T T) \quad [15]$$

where

$$G_{com} = \frac{G_0 G_C}{(G_0 + G_C)} \quad [16]$$

when there is catalyst and,

$$G_{com} = G_0 \quad [17]$$

without catalyst, and G_n is the conductance for n -type gas sensors in operating temperature T , G_p is the conductance for p -type gas sensors in operating temperature T , k_T is a temperature coefficient of resistance, G_C is the conductance of the catalyst, and G_0 is the initial conductance of the sensor gas. In Figure 1.13, electrical conductance of n -type gas sensors as a function of time has been plotted for a range of 0 to 500 K. The effect of temperature on gas sensors for p -type gas sensors is illustrated in Figure 1.14. Temperature coefficient of resistance has very small values, but maximum degradation of the conductance can be viewed as k_T and T increase. A value of $k_T = 0$ implies that electrical conductance is maintained during any operation temperature of a gas sensor. In these expressions, it is considered that k_T is constant with temperature, which in real life is not necessarily true.

The aging and temporal change in physicochemical properties in all materials are peculiar in the design of gas sensors without taking into account their nature and effects during their useful life [4]. The selection of a material is a complicated choice, since high stability and operating temperature for example, cannot offer good sensitivity, and fast response and recovery times in the gas sensing. Thermal stress is reduced with the use of low operating temperatures and long life times are achieved. Electrical conductance oscillations can be presented at low temperatures in the presence of reducing gases, which are not desired, since these contribute with non-awaited responses and incorrect values in the output of the gas sensor [4]. Annealing in air of the sensitive materials at temperatures exceeding the operating temperature reduces resistance drift phenomena found in sensors under operation by large periods of time.

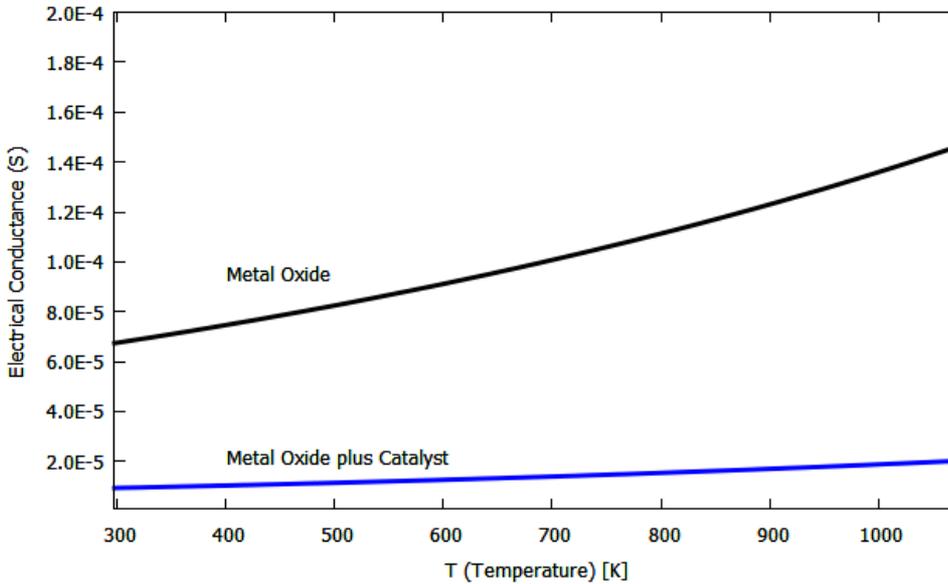


FIGURE 1.13

n-type gas sensors electrical conductance versus their operating temperature

Effects of Synthesis of the Nanostructured Materials on Gas Sensing

Researchers continue trying to develop new sensing materials with novel structures and/or morphologies for enhancing sensitivity, selectivity, and stability, as well as, new and better synthesis methods for ensuring reliability, safety, reproducibility, and cost reduction. In Figure 1.15, it is depicted different techniques that can be used to obtain nanostructured materials, some metal oxides can be synthesized by different methods as shown [77]. Following are detailed the benefits that synthesis methods can offer to the development of gas sensors based on nanostructured materials.

Until now, researchers are developed template-free methods with the aim of depositing one-dimensional nanostructures in a liquid environment such as hydrothermal methods, electrospinning, sonochemical and surfactant assisted [5].

The electrospinning process uses an electrical charge to draw very fine fibers to low temperatures from a liquid [5], such as polyacrylonitrile. It is simple, flexible and effective to produce nanofibers with high surface-to-volume ratio [71]. Nanofibers with diameters as small as tens of nanometers and lengths of up to several centimeters can be produced with controllable morphologies. These fibers can be produced hollow or solid depending on the precursor solution and parameters used during electrospinning [28, 29]. The interest for this method is thanks to correlation among nanofibers morphology, oxygen vacancy contents, and the gas sensing performances. The enhancement in the gas sensing properties provides of the significant oxygen vacancies associated with hollow morphologies and corrugated surfaces of the nanofibers. These oxygen vacancies allow

gas sensing at lower operating temperatures of hydrogen. In addition, high response, good stability, good selectivity and fast response-recovery times can be achieved using this synthesis process.

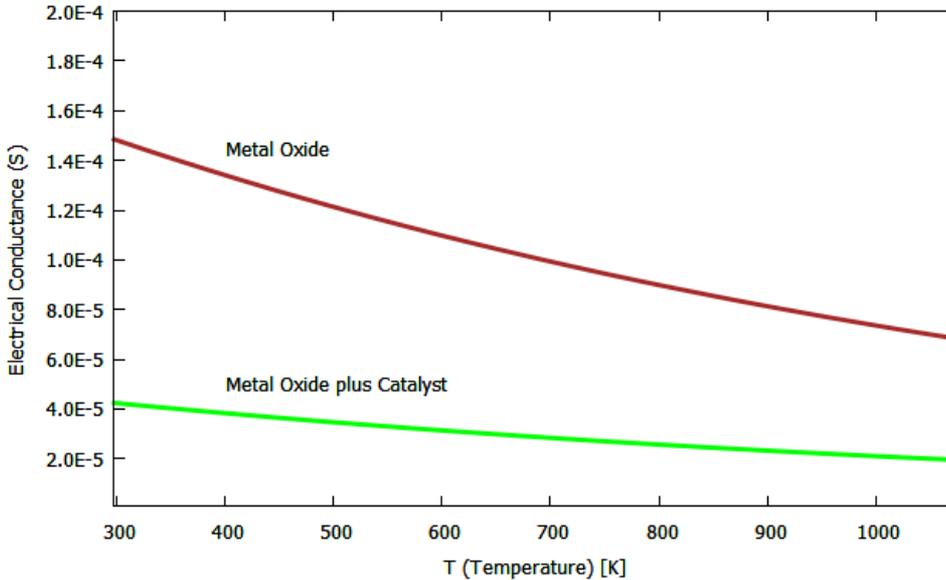
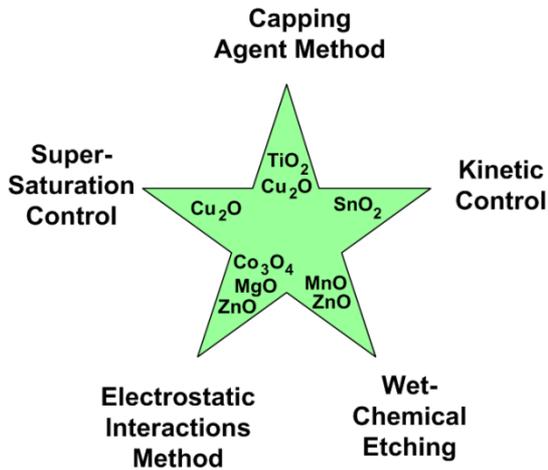


FIGURE 1.14

p-type gas sensors electrical conductance versus their operating temperature

Hydrothermal synthesis includes several techniques used for crystallizing materials from high-temperature aqueous solutions at high vapor pressures [5]. This method can be used to fabricate three-dimensional (3D) hierarchical ZnO structures with high surface-to-volume ratios and an increased fraction of (0001) polar surfaces [11]. Moreover, it has low energy requirements, safe and environmental processing conditions, low cost and large scale manufacturing are particularly attractive to produce nanoparticles, nanowires, nanorods, nanosheets, and nanodisks [13]. These characteristics and synthesis method provide an interesting route for designing nanostructured materials based on metal oxide nanostructures with superior gas sensing performance where high response amplitudes and fast response-recovery times are achieved due large surface areas [10]. Moreover, good reproducibility and repeatability, as well as long-term stability can be achieved [14].

Chemical precipitation consists in the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid [5]. When the reaction is produced in a liquid solution, the solid obtained is called the precipitate. The chemical that causes the solid can be formed is called the precipitant. Precipitation may occur if the concentration of a compound exceeds its solubility either when mixing solvents or at changing their temperature. This process can be used to produce nanostructured materials with different sizes and phases, which increases chemical activity to completely exploit oxygen vacancies found on surface of the sensitive material used in gas sensing [28, 30, 40].

**FIGURE 1.15**

Different synthesis methods that can be used to produce nanostructured materials based on semiconductor metal oxides

Sonochemical synthesis uses ultrasound to produce chemical reactions and processes, in which acoustic cavitation leads to the formation, growth, and implosive collapse of bubbles in a liquid [5]. Solids are produced after of a thermal treatment and they have nanostructured form, which increases their surface activity [31]. Sonication produces exfoliation of materials into nanostructures, which are stabilized with a solvent. The achieved hierarchical structure depends on ultrasonication time used during chemical reaction, and it is beneficial for their use in gas sensing materials due to the introduction of new surface states that generating oxygen vacancies. High responses and response and recovery times in the order of seconds can be obtained [25].

Surfactant-assisted synthesis can optimize hydrothermal synthesis, which has an excess of agglomeration of particles and a size distribution relatively wide, to offer better performance in gas sensing [5]. The surfactants at being adsorbed on the surface of particles reduce the agglomeration of particles and they operate as a soft template for the synthesis of 1D nanostructured materials. The control of agglomeration and size distribution establishes a catalytic surface morphology for gas sensing [78].

Solution-evaporation is a synthesis process that is used to remove water or other liquids from mixtures, and whose aim is concentrating chemicals to vaporize most of the water from a solution which contains the desired product. This method has been used to produce metal oxides for gas sensing to low temperatures, ease to control homogeneity, crystal size, stoichiometric ratio, and formation of determined phases [22]. The improved performance of gas sensor using materials obtained using this process synthesis can be attributed to the electronic sensitization, high thermal stability and low screening of the catalyst used [31].

The sol-gel synthesis consists in dissolving chemical compounds in a liquid with the aim of bringing it back as a solid, based on a controlled stoichiometry by mixing sols of different compounds, producing small particles that can be sinterable, and which can be used to produce sensitive materials for gas sensing. Materials with good sensitivity and high selectivity for gas sensors at

room temperature can be achieved [15, 33]. In addition, response and recovery times depend of the gas that is being sensed.

The chemical spray pyrolysis technique can be used to deposit a wide variety of metal oxides as thin films through controlling the size of the droplets and their distribution over preheated substrates [79]. The grain shape can be controlled by deposition temperature and doping concentration. In particular, substrate temperature has a direct influence on droplet pyrolysis, precursor oxidation, and crystal growth. This synthesis process increases response and offers faster response and recovery times due to smaller crystallite size and larger specific surface areas [21, 34]. Nanostructured materials that are synthesized by this method improve the sensitivity and selectivity of the gas sensors.

Effect of Morphology on Gas Sensing

In materials science, morphology is the study of shape, size, texture, spatial organization, and phase distribution of particles in a material. Different nanostructures can be obtained depending on their material composition, crystal structure and manufacturing method. Each synthesis process offers a diversity of parameters such as temperature, pressure, reagent concentration, treatment time and pH, that at be controlled allow obtain different morphologies, compositions and crystallinity of the products. Besides, a lot of tridimensional shapes can be synthesized such as spheres, rods, tubes, needles, cubes, octahedrons, etc. [80].

Morphology variation allows control its functionality in an effective way, since surface is directly related with interface that such material will have into outside. Such interface is related with the large number of atoms that determine their physicochemical properties. Moreover, most nanomaterials are thermodynamically unstable, which make that their morphologies are unbalanced, that it is different from the shape of monocrystals in a given material. Nonequilibrium morphologies correspond to local minimums of free energy of the system [81].

The main advantage of the morphology on gas sensing is called its surface-to-volume ratio (SVR). It is the amount of surface area per unit volume of an object or a cluster of objects. In addition, it is measured in units of inverse distance, that is, in the international system of units, it is given in inverse meters.

In chemical reactions using a solid material, as realized in the gas sensing, the surface area to volume ratio is one of the most important factors since it is directly related with the reactivity that is defined as the rate at which the chemical reaction will be realized. Materials with high surface-to-volume ratio can react at much faster rates than monolithic materials, due to that more surface is available to react. In the other hand, high surface-to-volume ratio serves as a very intense driving force to speed up thermodynamic processes that minimize free energy. An increased surface-to-volume ratio also implies that a better and larger exposure to the environment where target gases can be detected.

A sphere with radius r has a surface area of

$$S = 4\pi r^2, \quad [18]$$

and a volume of

$$V = \frac{4}{3}\pi r^3. \quad [19]$$

Therefore, its surface-to-volume ratio is expressed as:

$$\frac{S}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}. \quad [20]$$

The surface-to-volume ratio for a sphere of radius r was obtained for different values of r going from 1 nm to 1000 nm and depicted in Figure 1.16.

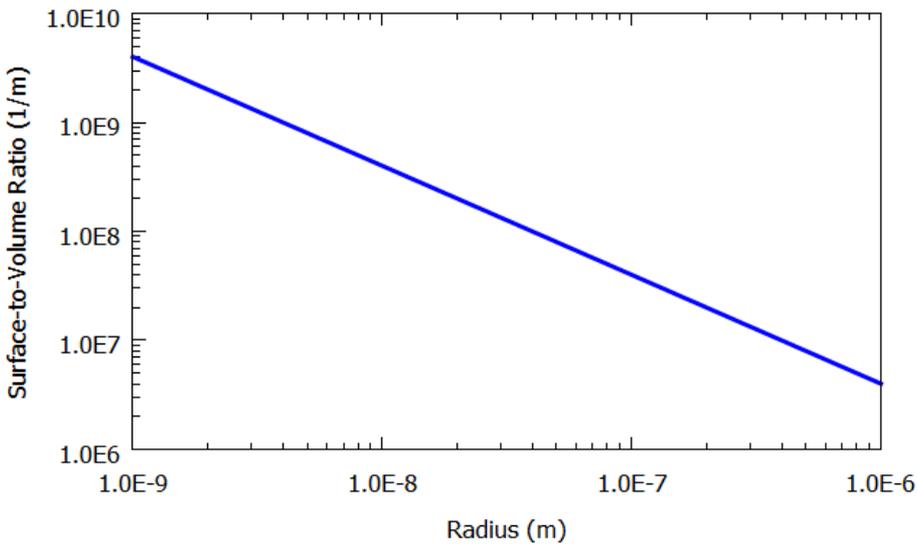


FIGURE 1.16

Graph of surface-to-volume ratio against their radius (for spherical nanomaterials)

A cube with side of length a has a surface area of

$$S = 6a^2, \quad [21]$$

and a volume of

$$V = a^3. \quad [22]$$

Therefore, its surface-to-volume ratio is expressed as:

$$\frac{S}{V} = \frac{6a^2}{a^3} = \frac{6}{a}. \quad [23]$$

The surface-to-volume ratio for cube with size of length a was obtained for different values of a going from 1 nm to 1000 nm and shown in Figure 1.17.

At comparing the results obtained, it is possible affirm that the searching for a nanostructure with larger surface-to-volume ratio and better physicochemical properties was started several years ago. Thus, the aim of developing different and multiple synthesis process to obtain nanostructured materials will continue for several years to fulfill the objective of optimizing better possible performance of this type of materials applied to gas sensing and other technical areas such as catalysis.

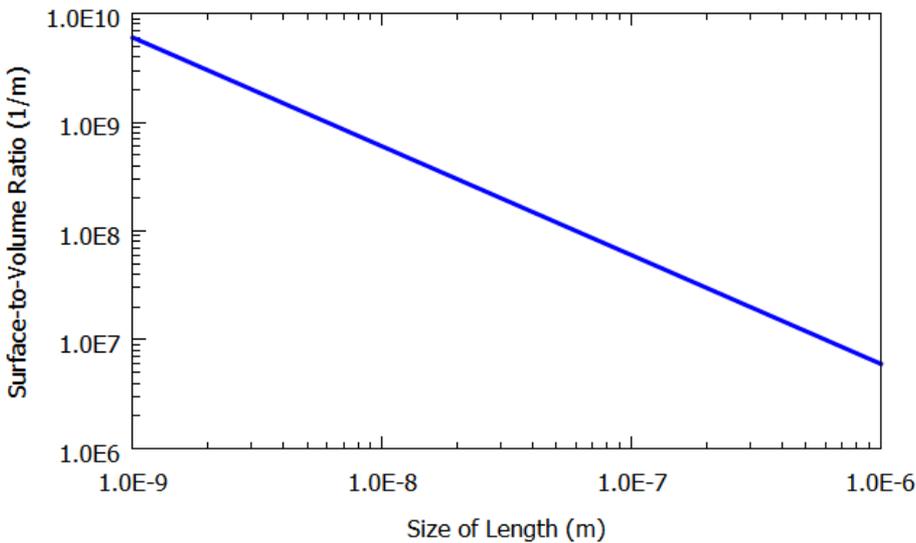


FIGURE 1.17

Graph of surface-to-volume ratio against their size of length (for cubical nanomaterials)

Polycrystalline silicon is a direct competitor of the semiconductor metal oxides, since it offers a large variety of morphologies and moreover, large values of surface-to-volume ratio [82]. Thus, designers using metal oxides must exhaustively work in the optimization of nanostructured materials to offer sensitive materials that can be very attractive to be incorporated them into novel nanometric integrated circuits.

Thanks to immense surface-to-volume ratio and the great void fraction in nanostructured materials, very high sensitivities can be achieved with porous metal oxide ceramics [3]. Also, this ratio contributes to faster response and recovery times in gas sensing. Electrospinning technique has the ability to control the diameters of nanowires and nanorods that favor high surface-to-volume ratios, and porosity which can be completely strategic to improve quality and performance of gas sensors.

Conclusions

From introduction of nanostructured ceramic materials in gas sensing, they have been considered as a strategic area in the development of chemical sensors. The main contribution of the nanomaterials to gas sensors is associated with their surface-to-volume ratio, which allows them increase efficiency from several fronts such as sensibility, selectivity, stability, response time and operating temperature. Intense surface activity can be guaranteed with the use of nanostructured materials in gas sensing due to possibility of controlling thermodynamic processes realized in the surface of the sensitive material. In this chapter is shown as the use of mixed oxides based on nanomaterials offers better results than single semiconducting metal oxides for gas sensing, because they operate under synergistic behaviors and have hierarchical structures whose electrical conductivity is increased by tunnel barriers. It is illustrated as selectivity, sensibility, and stability of gas sensors can be increased by means of nanostructured materials. Besides, it is analyzed as response and recovery times, operating temperature and dimensions of gas sensors are reduced using nanostructured materials. Mathematical expressions to determine sensitivity versus concentration of target gases for *n*-type and *p*-type materials, temporal drift of *n*-type and *p*-type gas sensors as a change of electrical conductance versus operating time (to study stability), change of electrical conductance versus operating temperature *n*-type gas sensors and *p*-type gas sensors (to analyze the effect of the operating temperature), were introduced and depicted by means of graphical results. In general, it was studied how optimize different parameters associated with gas sensing using nanostructured materials with the aim of achieving the better performance. This work widens and corroborates the knowledge developed by several researchers around of the world with respect to the importance of nanostructured ceramic materials in the development of gas sensors.

Acknowledgements

Authors thank to Instituto Tecnológico Superior de Irapuato its economic support to publish this chapter as scientific research realized in Departamento de Ingeniería en Materiales through of the project PIFOCA-03-2013, and to the Departamento de Desarrollo Académico of the same institution.

References

1. Hulanicki A, Głab S, Ingman F. Chemical Sensors Definitions and Classification. *Pure and Applied Chemistry* 1991; 63(9) 1247-1250.
2. Bochenkov VE, Sergeev GB. Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures. In: Umar A, Hahn YB (eds.) *Metal Oxide Nanostructures and Their Applications* Vol. 3. California: American Scientific Publishers; 2010. p 31-52.
3. Korotcenkov G. *Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications* Vol. 1 Conventional Approaches. New York: Springer; 2013.
4. Korotcenkov G. *Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications* Vol. 2 New Trends and Technologies. New York: Springer; 2014.

5. Jaaniso R, Tan OK (eds.). *Semiconductor Gas Sensors*, Palo Alto: Woodhead Publishing; 2013.
6. Comini E, Faglia G, Sberveglieri G. *Solid State Gas Sensing*. New York: Springer; 2009.
7. Zhuiykov S. *Electrochemistry of Zirconia Gas Sensors*. Boca Raton: CRC Press; 2008.
8. Jiménez Cadena G, Riu J, Rus FX. Gas Sensors based on Nanostructured Materials. *Analyst* 2007; 132(11) 1083-1099.
9. Gao J, Wang L, Kan K, Xu S, Jing L, Liu S, Shen P, Li L, Shi K. One-Step Synthesis of Mesoporous Al₂O₃-In₂O₃ Nanofibers with Remarkable Gas-Sensing Performance to NO_x at Room Temperature. *Journal of Materials Chemistry A* 2014; 2(4) 949-956.
10. Wang S, Zhang H, Wang Y, Wang L, Gong Z. Facile One-Spot Synthesis of Au Nanoparticles decorated Porous α -Fe₂O₃ Nanorods for *in situ* Detection of VOCs. *RSC Advances* 2014; 4(1) 369-373.
11. Alenezi MR, Henley SJ, Emerson NG, Ravi S, Silva P. From 1D and 2D Nanostructures to 3D Hierarchical Structures with Enhanced Gas Sensing Properties. *Nanoscale* 2014; 6(1) 235-247.
12. Rai P, Khan R, Raj S, Majhi SM, Park KK, Yu YT, Lee IH, Sekhar PK. Au@Cu₂O Core-Shell Nanoparticles as Chemiresistors for Gas Sensor Applications: Effect of Potential Barrier Modulation on the Sensing Performance. *Nanoscale* 2014; 6(1) 581-588.
13. Luo X, Lou Z, Wang L, Zheng X, Zhang T. Fabrication of Flower-like ZnO Nanosheet and Nanorod-assembled Hierarchical Structures and Their Enhanced Performance in Gas Sensors. *New Journal of Chemistry* 2014; 38(1) 84-89.
14. Zhang Z, Song H, Zhang S, Zhang J, Bao W, Zhao Q, Wu X. Selective Epichlorohydrin-Sensing Performance of Ag Nanoparticles decorated Porous SnO₂ Architectures. *CrystEngComm* 2014; 16(1) 110-115.
15. Yan W, Hu M, Zeng P, Ma S, Li M. Room Temperature NO₂-Sensing Properties of WO₃ Nanoparticles/Porous Silicon. *Applied Surface Science* 2014; 292 551-555.
16. Balamurugan C, Lee DW, Subramania A. Preparation and LPG-Gas Sensing Characteristics of *p*-Type Semiconducting LaNbO₄ Ceramic Material. *Applied Surface Science* 2013; 283 58-64.
17. Khandekar MS, Tarwal NL, Mulla IS, Suryavanshi SS. Nanocrystalline Ce doped CoFe₂O₄ as an Acetone Gas Sensor. *Ceramics International* 2014; 40(1) Part A 447-452.
18. Kiliç N, Şennik E, Işık M, Ahsen AS, Öztürk O, Öztürk ZZ. Fabrication and Gas Sensing Properties of C-doped and un-doped TiO₂ Nanotubes. *Ceramics International* 2014; 40(1) Part A 109-115.
19. Fort A, Addabbo T, Vignoli V, Bertocci F, Mugnaini M, Atrei A, Gregorkiewitz M. Gas-Sensing Properties and Modeling of Silver doped Potassium Hollandite. *Sensors and Actuators B: Chemical* 2014; 194 427-439.
20. Mondal B, Basumatari B, Das J, Roychaudhury C, Saha H, Mukherjee N. ZnO-SnO₂ based Composite Type Gas Sensor for Selective Hydrogen Sensing. *Sensors and Actuators B: Chemical* 2014; 194 389-396.
21. Deokate RJ, Lokhande CD. Liquefied Petroleum Gas Sensing Properties of Sprayed Nanocrystalline Ga-doped CdO Thin Films. *Sensors and Actuators B: Chemical* 2014; 193 89-94.
22. Guan Y, Yin C, Cheng X, Liang X, Diao Q, Zhang H, Lu G. Sub-ppm H₂S Sensor based on YSZ and Hollow Balls NiMn₂O₄ Sensing Electrode. *Sensors and Actuators B: Chemical* 2014; 193 501-8.

23. Balamurugan C, Lee DW. A Selective NH₃ Gas Sensor based on Mesoporous *p*-Type NiV₂O₆ Semiconducting Nanorods synthesized using Solution Method. *Sensors and Actuators B: Chemical*, 2014; 192 414-422.
24. Belle CJ, Wesch GE, Neumeier S, Lozano-Rodríguez MJ, Scheinost AC, Simon U. Volume-doped Cobalt Titanates for Ethanol Sensing: An Impedance and X-Ray Absorption Spectroscopy Study. *Sensors and Actuators B: Chemical* 2014; 192 60-69.
25. Alsaif MMYA, Balendhran S, Field MR, Latham K, Wlodarski W, Ou JZ, Kalantar-Zadeh K. Two Dimensional α -MoO₃ Nanoflakes obtained using Solvent-assisted Grinding and Sonication Method: Application for H₂ Gas Sensing. *Sensors and Actuators B: Chemical* 2014; 192 196-204.
26. Vuong NM, Hieu NM, Hieu HN, Yi H, Kim D, Han YS, Kim M. Ni₂O₃-decorated SnO₂ Particulate Films for Methane Gas Sensors. *Sensors and Actuators B: Chemical* 2014; 192 327-333.
27. Kim HJ, Lee JH. Highly Sensitive and Selective Gas Sensors using *p*-Type Oxide Semiconductors: Overview. *Sensors and Actuators B: Chemical* 2014; 192 607-627.
28. Wei S, Wang S, Zhang Y, Zhou M. Different Morphologies of ZnO and Their Ethanol Sensing Property. *Sensors and Actuators B: Chemical* 2014; 192 480-487.
29. Landau O, Rothschild A. Microstructure Evolution of TiO₂ Gas Sensors produced by Electrospinning. *Sensors and Actuators B: Chemical* 2012; 171-172 118-126.
30. Senguttuvan TD, Srivastava V, Tawal JS, Mishra M, Srivastava S, Jain K. Gas Sensing Properties of Nanocrystalline Tungsten Oxide Synthesized by Acid Precipitation Method. *Sensors and Actuators B: Chemical* 2010; 150(1) 384-388.
31. Bai S, Zhang K, Wang L, Sun J, Luo R, Li D, Chen A. Synthesis Mechanism and Gas-Sensing Application to Nanosheet-assembled Tungsten Oxide Microspheres. *Journal of Materials Chemistry A* 2014; 2(21) 7927-7934.
32. Jin C, Kim H, An S, Lee C. Highly Sensitive H₂S Gas Sensors based on CuO-coated ZnSnO₃ Nanorods Synthesized by Thermal Evaporation. *Ceramics International* 2012; 38(7) 5973-5978.
33. Hazra A, Das S, Kanungo J, Sarkar CK, Basu S. Studies on a Resistive Gas Sensor based on Sol-Gel grown Nanocrystalline *p*-TiO₂ Thin Film for Fast Hydrogen Detection. *Sensors and Actuators B: Chemical* 2013; 183 87-95.
34. Shinde SD, Patil GE, Kajale DD, Gaikwad VB, Jain GH, Synthesis of ZnO Nanorods by Spray Pyrolysis for H₂S Gas Sensor. *Journal of Alloys and Compounds* 2012; 528 109-114.
35. Williams DE. Semiconducting Oxides as Gas-Sensitive Resistors. *Sensors and Actuators B: Chemical* 1999; 57(1-3) 1-16.
36. Fine GF, Cavanagh LM, Afonja A, Binions R. Metal Oxide Semi-Conductor Gas Sensors in Environmental Monitoring. *Sensors* 2010; 10(6) 5469-5502.
37. Barsan N, Schweizer-Berberich M, Göpel W. Fundamental and Practical Aspects in the Design of Nanoscaled SnO₂ Gas Sensors: A Status Report. *Fresenius Journal of Analytical Chemistry* 1999; 365(4) 287-304.
38. Korotcenkov G, Cho BK. Engineering Approaches for the Improvement of Conductometric Gas Sensor Parameters Part 1: Improvement of Sensor Sensitivity and Selectivity (Short Survey). *Sensors and Actuators B: Chemical* 2013; 188 709-728.
39. Romyantseva MN, Kovalenko VV, Gas'kov AM, Pagnier T. Metal-Oxide based Nanocomposites as Materials for Gas Sensors. *Russian Journal of General Chemistry* 2008; 78(5) 1081-1092.

40. Wang C, Yin L, Zhang L, Xiang D, Gao R. Metal Oxide Gas Sensors: Sensitivity and Influencing Factors. *Sensors* 2010; 10(3) 2088-2106.
41. Hu D, Han B, Deng S, Feng Z, Wang Y, Popovic J, Nuskol M, Wang Y, Djerdj I. Novel Mixed Phase SnO₂ Nanorods Assembled with SnO₂ Nanocrystals for Enhanced Gas-Sensing Performance toward Isopropanol Gas. *The Journal of Physical Chemistry C* 2014; 118(18) 9832-9840.
42. Le DTT, Trung DD, Chinh ND, Binh BTT, Hong HS, Van Duy N, Hoa ND, Van Hiue N. Facile Synthesis of SnO₂-ZnO core-shell Nanowires for Enhanced Ethanol-Sensing Performance. *Current Applied Physics* 2013; 13(8) 1637-1642.
43. Nikan E, Khodadadi AA, Mortazavi Y. Highly Enhanced Response and Selectivity of Electrospun ZnO-doped SnO₂ Sensors to Ethanol and CO in Presence of CH₄. *Sensors and Actuators B: Chemical* 2013; 184 196-204.
44. Zhou L-J, Li C, Zou X, Zhao J, Jin P-P, Feng L-L, Fan M-H, Li G-D. Porous Nanoplate-assembled CdO/ZnO Composite Microstructures: A Highly Sensitive Material for Ethanol Detection. *Sensors and Actuators B: Chemical* 2014; 197 370-375.
45. Cai X, Hu D, Deng S, Han B, Wang Y, Wu J, Wang Y. Isopropanol Sensing Properties of Coral-like ZnO-CdO Composites by Flash Preparation via Self-Sustained Decomposition of Metal-Organic Complexes. *Sensors and Actuators B: Chemical* 2014; 198 402-410.
46. Lai H-F, Wu R-J, Lu C-S. Promotion Effect of Palladium Oxide on TiO₂ Sensing of Gaseous Formaldehyde. *Science of Advanced Materials* 2014; 6(5) 1074-1080.
47. Kida T, Nishiyama A, Hua Z, Suematsu K, Yuasa M, Shimano K. WO₃ Nanolamella Gas Sensor: Porosity Control using SnO₂ Nanoparticles for Enhanced NO₂ Sensing. *Langmuir* 2014; 30(9) 2571-2579.
48. Xu L, Zheng R, Liu S, Song J, Chen J, Dong B, Song H. NiO@ZnO Heterostructured Nanotubes: Coelectrospinning Fabrication, Characterization, and Highly Enhanced Gas Sensing Properties. *Inorganic Chemistry* 2012; 51(14) 7733-7740.
49. Zang W, Nie Y, Zhu D, Deng P, Xing L, Xue X. Core-Shell In₂O₃/ZnO Nanoarray Nanogenerator as a Self-Powered Active Gas Sensor with H₂S Sensitivity and Selectivity at Room Temperature. *The Journal of Physical Chemistry C* 2014; 118(17) 9209-9216.
50. Mao S, Cui S, Yu K, Wen Z, Lu G, Chen J. Ultrafast Hydrogen Sensing through Hybrids of Semiconducting Single-Walled Carbon Nanotubes and Tin Oxide Nanocrystals. *Nanoscale* 2012; 4(4) 1275-1279.
51. Deng S, Tjoa V, Fan HM, Tan HR, Sayle DC, Olivo M, Mhaisalkar S, Wei J, Sow CH. Reduced Graphene Oxide Conjugated Cu₂O Nanowire Mesocrystals for High-Performance NO₂ Gas Sensor. *Journal of the American Chemical Society* 2012; 134(10) 4905-4917.
52. Huang Q, Zeng D, Li H, Xie C. Room Temperature Formaldehyde Sensors with Enhanced Performance, Fast Response and Recovery based on Zinc Oxide Quantum Dots/Graphene Nanocomposites. *Nanoscale* 2012; 4(18) 5651-5658.
53. Singhal A, Kaur M, Dubey KA, Bhardwaj YK, Jain D, Pillai CGS, Tyagi AK. Polyvinyl Alcohol-In₂O₃ Nanocomposite Films: Synthesis, Characterization and Gas Sensing Properties. *RSC Advances* 2012; 2(18) 7180-7189.
54. Moos R. A Brief Overview on Automotive Exhaust Gas Sensors based on Electroceramics. *International Journal of Applied Ceramic Technology* 2005; 2(5) 401-413.
55. Morrison SR. Selectivity in Semiconductor Gas Sensors. *Sensors and Actuators* 1987; 12(4) 425-440.
56. Göpel W, Hesse J, Zemel JN (Eds). *Sensors: A Comprehensive Survey Vol. 3 Chemical and Biochemical Sensors Part II*. Weinheim, Germany: Wiley-VCH; 1991.

57. Potyrailo RA, Surman C, Nagraj N, Burns A. Materials and Transducers toward Selective Wireless Gas Sensing. *Chemical Reviews* 2011; 111(11) 7315-7354.
58. Korotcenkov G, Cho BK. Engineering Approaches to Improvement of Conductometric Gas Sensor Parameters Part 2: Decrease of Dissipated (Consumable) Power and Improvement Stability and Reliability. *Sensors and Actuators B: Chemical* 2014; 198 316-341.
59. Romain AC, Nicolas J. Long Term Stability of Metal Oxide-based Gas Sensors for E-Nose Environmental Applications: An Overview. *Sensors and Actuators B: Chemical* 2010; 146(2) 502-506.
60. Vergara A, Vembu S, Ayhan T, Ryan MA, Homer ML, Huerta R. Chemical Gas Sensor Drift Compensation using Classifier Ensembles. *Sensors and Actuators B: Chemical* 2012; 166-167 320-329.
61. Padilla M, Perera A, Montoliu I, Chaudry A, Persaud K, Marco S. Drift Compensation of Gas Sensor Array Data by Orthogonal Signal Correction. *Chemometrics and Intelligent Laboratory Systems* 2010; 100(1) 28-35.
62. Haugen J-E, Tomic O, Kvaal K. A Calibration Method for Handling the Temporal Drift of Solid State Gas-Sensors. *Analytica Chimica Acta* 2000; 407(1-2) 23-39.
63. Di Carlo S, Falasconi M. Drift Correction Methods for Gas Chemical Sensors in Artificial Olfaction Systems: Techniques and Challenges. In: Wang W. (ed.) *Advances in Chemical Sensors*. Rijeka, Croatia; Intech; 2012. p 305-326.
64. Tierney MJ, Kim H-O L. Electrochemical Gas Sensor with Extremely Fast Response Times, *Analytical Chemistry* 1993; 65(23) 3435-3440.
65. Sysoev VV, Schneider T, Goschnick J, Kiselev I, Habicht W, Hahn H, Strelcov E, Kolmakov A. Percolating SnO₂ Nanowire Network as a Stable Gas Sensor: Direct Comparison of Long-Term Performance versus SnO₂ Nanoparticle Films. *Sensors and Actuators B: Chemical* 2009; 139(2) 699-703.
66. Kornbech M, Olesen MT. Fixed Gas Detectors - Total Speed of Response. *World Pipelines* 2010; 34.
67. Kugishima M, Sakai G, Shimano K, Yamazoe N. Development of SnO₂-based Gas Sensor Sensitive to Dilute Ethylene Oxide in Air. *Sensors and Actuators B: Chemical* 2005; 108(1-2) 130-133.
68. Korotcenkov G, Blinov I, Brinzari V, Stetter JR. Effect of Air Humidity on Gas Response of SnO₂ Thin Film Ozone Sensors. *Sensors and Actuators B: Chemical* 2007; 122(2) 519-526.
69. Izu N, Nishizaki S, Itoh T, Nishibori M, Shin W, Matsubara I. Gas Response, Response Time and Selectivity of a Resistive CO Sensor based on Two Connected CeO₂ Thick Films with Various Particle Sizes. *Sensors and Actuators B: Chemical* 2009; 136(2) 364-370.
70. Izu N, Shin W, Murayama N. Numerical Analysis of Response Time for Resistive Oxygen Gas Sensors. *Sensors and Actuators B: Chemical* 2002; 87(1) 99-104.
71. Helwig A, Müller G, Sberveglieri G, Faglia G. Gas Response Times of Nano-Scale SnO₂ Gas Sensors as Determined by the Moving Gas Outlet Technique. *Sensors and Actuators B: Chemical* 2007; 126(1) 174-180.
72. Kadir RA, Li Z, Sadek AZ, Rani RA, Zoolfakar AS, Field MR, Ou JZ, Chrimes AF, Kalantar-Zadek K. Electrospun Granular Hollow SnO₂ Nanofibers Hydrogen Gas Sensors Operating at Low Temperatures. *Journal of Physical Chemistry C* 2014; 118(6) 3129-3139.
73. Rout CS, Kulkarni GU, Rao CNR. Room Temperature Hydrogen and Hydrocarbon Sensors based on Single Nanowires of Metal Oxides. *Journal of Physics D: Applied Physics* 2007; 40(9) 2777-2782.

74. Ahn MW, Park KS, Heo JH, Park JG, Kim DW, Choi KJ, Lee JH, Hong SH. Gas Sensing Properties of Defect-Controlled ZnO-Nanowire Gas Sensor. *Applied Physics Letters* 2008; 93(26) 263103.
75. Zhang L, Yin Y. Hierarchically Mesoporous SnO₂ Nanosheets: Hydrothermal Synthesis and Highly Ethanol-Sensitive Properties operated at Low Voltage. *Sensors and Actuators B: Chemical* 2013; 185 594-601.
76. Batzill M. Surface Science Studies of Gas Sensing Materials: SnO₂. *Sensors* 2006; 6(10) 1345-1366.
77. Wang X, Jiang ZY, Jiang YQ, Lin HX, Kuang Q, Xie ZX. Shape-Controlled Synthesis of Metal Oxides Micro/Nanocrystals enclosed by Crystal Facets of High Surface Energy. *Scientia Sinica Chimica* 2013, 43(12) 1630-1639.
78. Pawar RC, Shaikh JS, Moholkar AV, Pawar SM, Kim JH, Patil JY, Suryavanshi SS, Patil PS. Surfactant assisted Low Temperature Synthesis of Nanocrystalline ZnO and Its Gas Sensing Properties. *Sensors and Actuators B: Chemical* 2010; 151(1) 212-218.
79. Patil PS. Versatility of Chemical Spray Pyrolysis Technique. *Materials Chemistry and Physics* 1999; 59(3) 185-198.
80. Pu, Z, Cao M, Yang J, Huang K, Hu C. Controlled Synthesis and Growth Mechanism of Hematite Nanorhombhedra, Nanorods and Nanocubes. *Nanotechnology* 2006; 17(3) 799-804.
81. Moriarty P. Nanostructured Materials. *Reports on Progress in Physics* 2001; 64(3) 297-381.
82. Korotchenko G, Cho GK. Porous Semiconductors: Advanced Material for Gas Sensor Applications. *Critical Reviews in Solid State and Materials Sciences* 2010; 35(1) 1-37.