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TiO₂ Thin Films Produced by Ultrasonic-Agitation Assisted Sol-Gel for Propane Gas Sensor

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Abstract

TiO₂ films were deposited by the sol–gel dip coating method assisted by ultrasonic agitation, for their use as propane gas sensors. XRD analysis revealed the TiO₂ anatase phase for all samples. The film thickness was controlled with the number of the dip-coating immersion cycles, obtaining thicknesses from 10 to 130 nm and a growing rate of 18 nm per immersion. Surface morphology shows that films grow more compact and densely packed as the number of immersion cycles increase. Gas sensing studies indicate that work temperatures above 300°C are needed for sensing activation of the films. Gas sensors sensitivity as a function of propane concentration and film thickness revealed a two-regime behavior: for partial pressures of propane above 400 ppm the sensitivity is not dependent of the film thickness, whereas it is dependent on this parameter at lower partial pressures. Such behavior is attributed to a space charge region and a change in surface structure. For the low concentration regime, the maximum sensitivity was obtained for a film thickness of 110 nm or 5 immersions.

Keywords: titanium dioxide, thin films, sol–gel, gas sensors

1. Introduction

Propane gas, found in natural gas and produced in the petroleum refining process among other alkanes, is widely used as combustible in the whole world. Propane is one of the main components of the liquefied petroleum gas, which is distributed to homes and buildings for water heating systems and cooking; it is also distributed by fuel stations to be used in transport vehicles, included public transport. Due to its low cost in the last years the use of natural gas as fuel has increased. Propane is used in power production plants as well as a precursor to chemicals such as isopropyl alcohol and silicon carbide [1, 2]. Because of propane economical importance, its increasing use as power source and its explosiveness in presence of oxygen, it is necessary to detect and control accurately its presence in public buildings, homes and industry. Such task implies the development of several sensing mechanisms, control valves and pipes. Because of this, several propane sensors have been developed and, among many others, those based in changes in electrical conductivity are some the most promising; however, there is still too much work to do when it comes to sense propane in more cheap, accurate and quick ways.

Metal oxides such as NiO, ZnO, SnO₂ and TiO₂ are widely used in several applications, in particular as gas sensors based in electrical conductivity modification; among them titanium dioxide is one of the favorites. Because of its large dielectric constant, its chemical stability, its durability, its biocompatibility and its band gap, titanium dioxide has been exploited to build capacitors for microelectronic systems [3–5], optical materials, including white paint and sunscreen, photocatalytic systems [6–8], and have given it, potential applications in medicine due to its antibacterial properties [9, 10]. TiO₂ and the metal oxides mentioned also changes its electrical resistance as a function of the chemical composition of its surrounding atmosphere, making them suitable for gas sensing [11, 12].

Titanium dioxide gas sensing properties have been widely studied and modified by doping it with metals and supported catalysts such as Pt [13–15]. Still, several efforts have to be done to produce more effective gas sensors: since they present disadvantages in response and recovering times, and in gas selectivity. Thus, studies on the response of these oxides must be realized in order to determine particular responses for each gas and improve, in this way their selectivity. Titanium dioxide response to CO, CH₄ and H₂ has been studied [16–19] and in some articles the response to alcohols such as ethanol, methanol and propanol has been reported [20–22]. In the literature, few works report about the response of the electrical conductivity of titanium dioxide, when it is exposed to propane gas [23].

Many synthesis routes have been used to obtain titanium oxide, either as a powder and as a thin film. Some are complex and expensive as is the case of sputtering and electron beam deposition [24, 25]. Some others are cheap and easy to work with, as is the case of spray pyrolysis, spin coating, dip coating and chemical bath deposition [26–29]. Also, new techniques or modified versions of the existing techniques are being explored, as is the case of the sol–gel ultrasonically assisted that has been used to obtain pure rutile phase powders and to obtain smaller grain sizes and larger surface areas when compared with the standard sol–gel technique [30, 31]. This last result is promising for gas sensing, since the sensor sensitivity depends directly on the surface area, it can be expected that more sensitive sensors can be made by synthesizing with ultrasonic assistance.

Therefore, in this work it TiO₂ films are obtained by the dip-coating method using the ultrasonic assistance during the crystal growth stage. The film thickness and work temperature are used as variables to explore the response to propane gas at different concentrations. The surface morphology is studied for different immersion cycles and the crystalline structure is analyzed by x-ray diffraction.

2. Experimental

Titanium dioxide films were grown on glass substrates. Previous to deposition, substrates were cleaned in an ultrasonic bath with soap water, methanol and acetone, in an ultrasonic bath, and were dried under nitrogen gas flow. The start solution was prepared from two separated solutions (A and B). Solution A consisted of 1.04 ml of titanium isopropoxide dissolved in 10 ml of alcohol; while solution B consisted of 0.14 ml of deionized water dissolved in the same amount of alcohol. Once obtained, solution B was dropwise added to solution A while ultrasonically stirring, finally 0.4 ml of acetic acid was added to maintain a neutral pH. The solution was ultrasonically stirred for 10 min after both solutions were mixed.

A set of seven TiO₂ films with different thickness was produced by immersion of glass substrates in the starting solution. The films thicknesses was controlled with the number of immersion cycles, each cycle consisting of an immersion and

extraction of the substrate in the solution at a speed of 0.122 cm/s. All samples were dried for 10 min in a furnace at 400°C after each immersion cycle. Once all cycles were carried out, samples were treated at 400°C for 3 hr. TiO₂ thin films with different thickness were obtained systematically after 1 to 7 immersion cycles.

Film thicknesses were determined using both a Bruker Dektak XT profilometer and a Filmetrics F20 analyzer. The F20 was operated from 380 to 1100 nm and an ultra clean glass substrate was used as a reference. The crystalline structure was determined by X-ray diffraction analysis using a Bruker D8 diffractometer with a CuK_α (1.54056 Å) wavelength, at an incidence angle of 1° and varying 2θ from 20° to 80°, and a recording time of 1.5 hrs to reduce noise. The X-ray diffraction patterns were interpreted in reference to the PDF card: 21-1272 from the ICDD data base. Samples surfaces were analyzed with a LV 5600 JEOL Scanning Probe Microscope operated in tapping mode.

Sensitivity tests were performed in a vacuum chamber equipped with a mechanical vacuum pump, a temperature-controlled sample holder, and a propane gas inlet; tungsten wires were used to establish a series connection of the sensor with a Keythley 2001 multimeter used to measure changes in sensors electrical resistance. Diagrams of the sensing chamber have been reported elsewhere [32]. Previous to start the sensing tests, two silver contacts were painted on films surface to allow a direct measurement of their electrical properties. To control samples temperature the sample holder is equipped with an electrical resistance as heater and a K-type thermocouple, both connected to a temperature controller. Sensors' temperature was set to take values of ambient, 100°C, 200°C and 300°C. At each temperature electrical resistance was recorded at different propane concentrations: 0%, 1%, 10%, 50%, 100%, 200%, 300%, 400% and 500%.

In order to study sensors sensitivity as a function of film thickness, sensitivity was obtained through the following equation:

$$S = \frac{|R - R_0|}{R_0} \quad (1)$$

Where S is expressed in percentage, R is the electrical resistance of the film in presence of propane gas and R_0 is the resistance registered at 0% of propane concentration.

3. Results and discussion

3.1 Film thickness

Table 1 presents the results of film thickness measurements obtained by both optical and mechanical profilometry. In some cases, film thickness could not be measured by mechanical profilometry because of a substrate deformation, attributed to mechanical stress generated after the annealing process. However, the values obtained are in the same range as those obtained by optical profilometry (20–150 nm); thus, giving support to the values obtained optically. Such support is needed since optically obtained values are generated from a theoretical model of the reflectance spectra generated during tests; these values range from 23 to 134 nm and have a correlation coefficient above 0.99, indicating an appropriate modeling and determination of film thickness. Because of this, the values obtained optically are used in the following analyses.

When plotting film thickness of TiO₂ as a function of immersion cycles an increasing trend with a linear behavior is obtained (**Figure 1**). The values varied from 22 nm to 130 nm and the linear fit yields a deposition rate of 18 nm per

Number immersions	Profilometry (nm)	Filmetrics (nm)
1	—	23.73
2	48.6	49.80
3	87.0	60.74
4	137.4	74.32
5	142.9	108.40
6	150.0	112.00
7	—	133.80

Table 1.
Results of the film thickness of TiO₂ samples, measured by profilometry and optical methods, as a function of the number of immersion cycles.

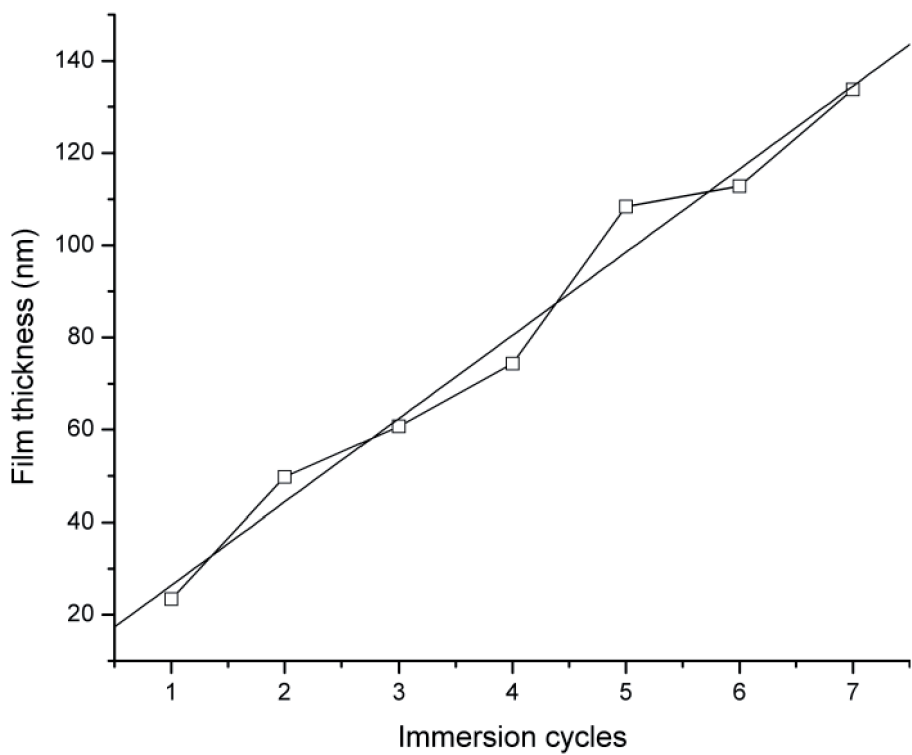


Figure 1.
Relation between the film thickness and the number of immersion cycles. A linear trend is obtained with a growing rate of 18 nm/cycle.

immersion cycle. When comparing our results to those reported by Hossein [21], where TiO₂ films were grown by the same method, a difference in film thickness is observed. Such difference is attributed to a larger solution molarity used by Hossein (0.4 M), that implies a larger number of particles available at the interphase for film growing.

It is well known that the electrical resistance of chemical gas sensors changes because of the exchange of charge carriers between the film surface and the chemisorbed species. Since the surface to volume ratio increases as the film thickness decreases, the amount of chemisorbed species, as well as the number of exchanged charge carriers, becomes larger than the number of charge carriers produced intrinsically in the bulk. At this point the output signal of the sensors becomes a function of the film thickness. Due to this effect and to the great control of film thickness obtained by this method, it could be possible to produce sensors with an optimized response. Considering that film thickness also depends on the solution

molarity, which is due to the larger number of particles available close to the substrate surface, it is left for further work to analyze sensors response as a function of this parameter in order to optimize the deposition conditions.

3.2 X-ray diffraction

Figure 2 shows the X-ray spectra obtained for selected samples. In all spectra it is observed a diffraction peak at $2\theta = 25.23^\circ$ indicating the presence of a crystalline structure corresponding to (101) planes of TiO₂ anatase structure, according to reported data in PDF 21-1272. Diffraction peaks corresponding to other titanium dioxide phases were not obtained. Given the deposition process, lattice distortions could be expected; however, from the lack of displacement of the diffraction peaks it can be inferred that there are no such distortions. This indicates that the temperature and annealing time were adequate. Such results agree with others reported elsewhere, where the anatase structure is obtained when heating TiO₂ films at 400° [33–35].

3.3 Surface morphology

2D and 3D atomic force micrographs of samples growth with one, three and five immersion cycles are displayed in **Figure 3**. From these figures it can be observed that the film growth becomes more compact and densely packed as the number of immersion cycles is increased; being the average grain size measured from the sample presented in **Figure 3e** and **f** of 50 ± 10 nm. Such differences in surface structure are of great importance for sensors behavior, since they are correlated to the exposed area, the number of available chemisorption sites, and the change in electrical resistance. The compactness of films also implies a better charge carrier transport because of the increased contact surface and the reduced spacing between grains. The observed surface structure will be used in the next section in order to explain the sensors behavior.

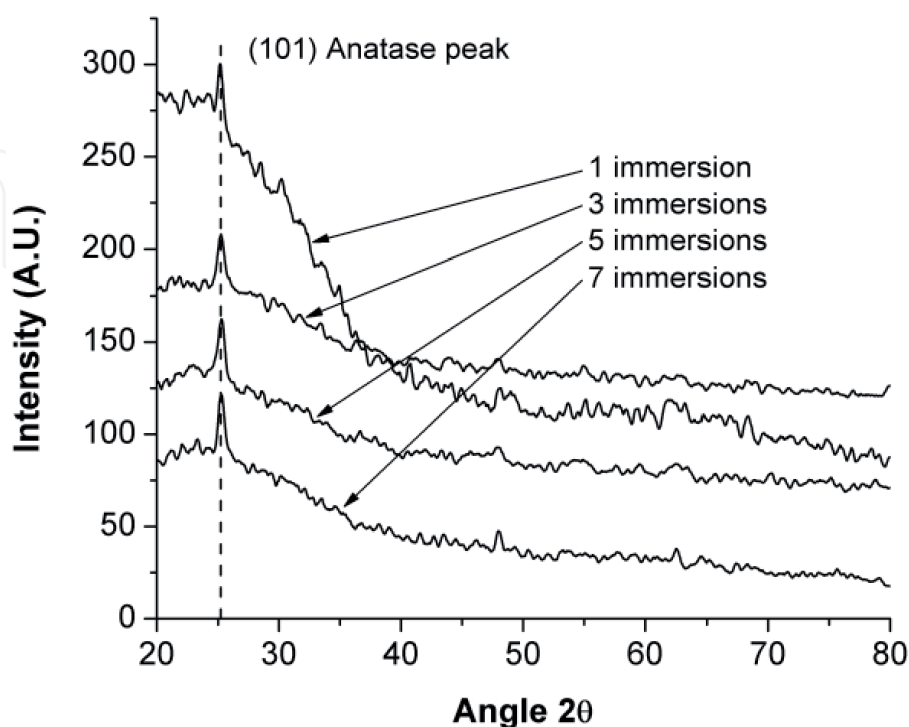


Figure 2.
XRD patterns from samples with different number of immersions.

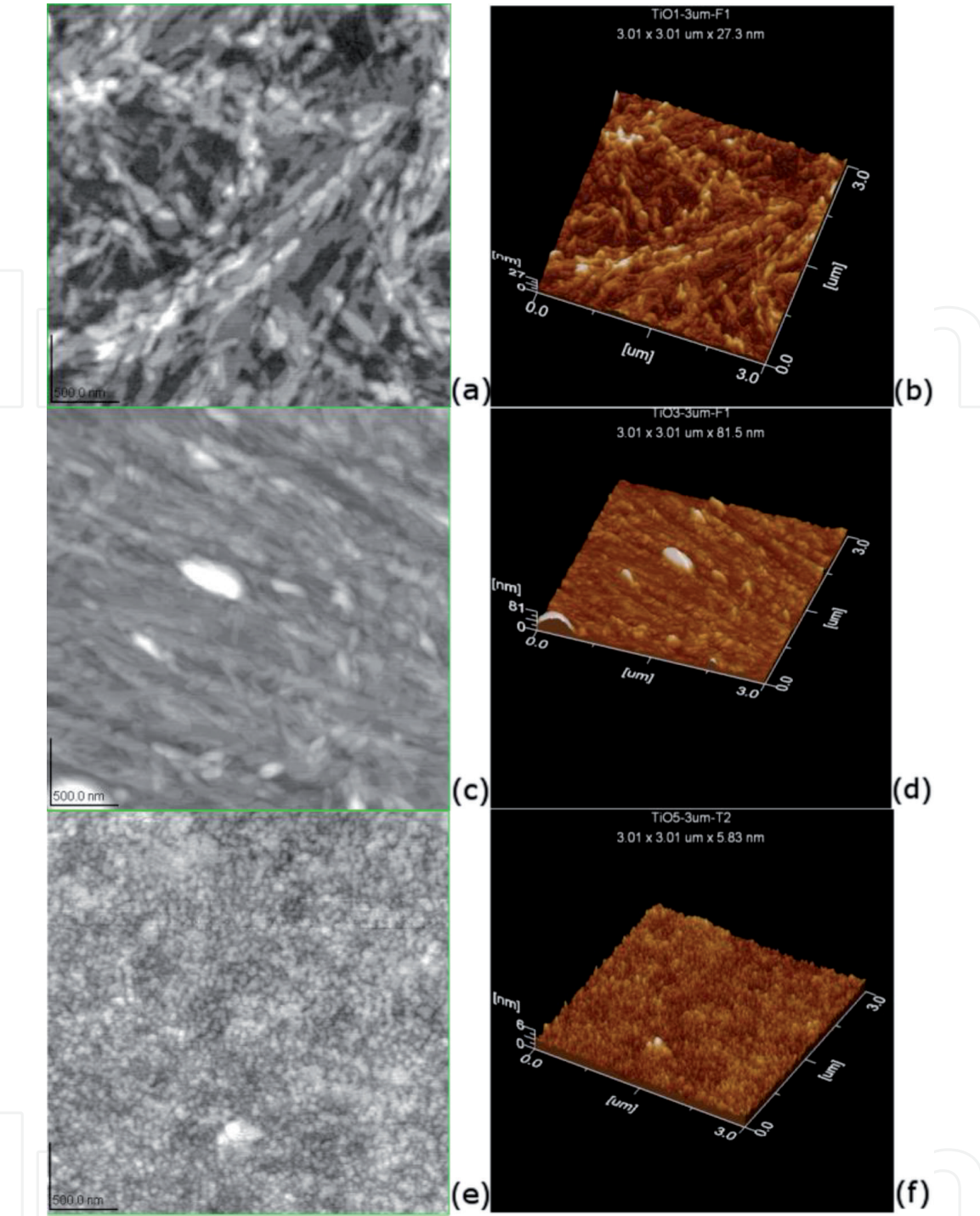


Figure 3. 2D and 3D AFM micrographs of TiO_2 thin films with one (a, b); three (c, d) and five immersion (e, f). cycles.

3.4 Sensing properties

Figure 4 shows graphs corresponding to samples grown with 1, 3, 5, and 7 immersions. In these graphs resistance versus gas concentration is plotted at different work temperatures. When analyzing the results it is observed that at temperatures of 200°C and below, changes in electrical resistance due to an increase of propane gas concentration are negligible and it can be considered as constant; however, when working at a temperature of 300°C all samples present important changes in electrical resistance, whose differences can be of an order of magnitude. As can be seen from all graphs, when temperature changes from 200 to 300°C , a drop in electrical resistance is obtained at a propane concentration of 0% ; such drop is due to a thermal activation of electrical conductivity where a large number

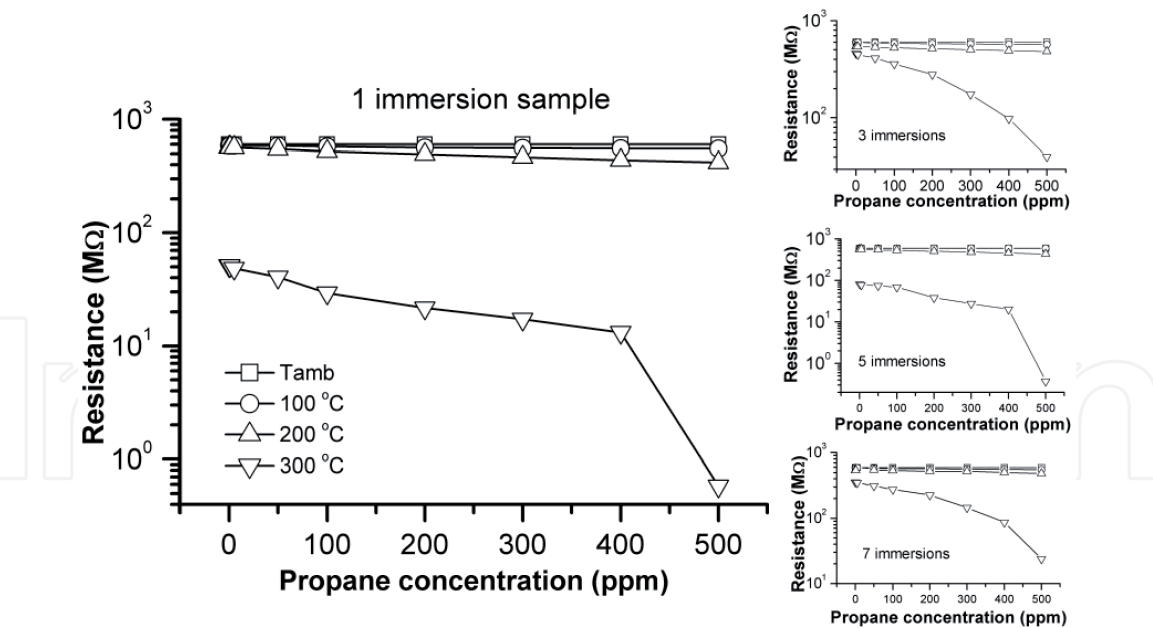


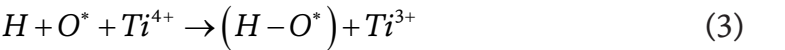
Figure 4. Resistance as a function of propane concentration for different work temperatures. At 300°C changes in resistance become important. Inserted charts show the same behavior in all sensors.

of electrons are released into the conduction band. Further changes in electrical resistance are due to the interaction of propane gas with the films surface. Since all samples present the same behavior, the work temperature of 300°C will be used in the following analyses; however, it will be left for further analyses to find the minimum temperature at which the drop occurs, in order to minimize sensors power consumption.

Based on the n-type conductivity reported for the anatase structure of TiO₂ [36], the reduction of the electrical resistance of the films when they are in presence of propane can be attributed to an injection of electrons in the conduction band. This can be explained by the detection mechanism proposed by Kerlau [37], based on the studies of K. Cheng et al. [38], where propane molecules interact with lattice oxygen (O*) to form isopropoxyde and H-O* bonds, as it is explained by the following equation:

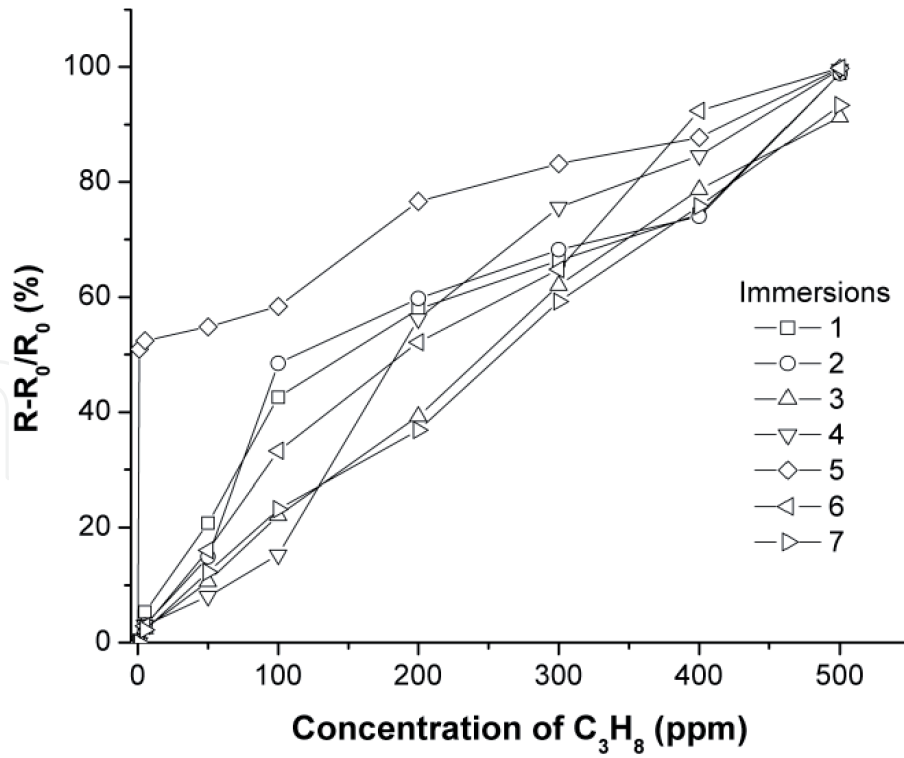


Where the partial reaction between hydrogen and the lattice oxygen produces an extra electron that becomes trapped by the positive neighboring titanium atoms, and it is released into the conduction band by thermal excitation:

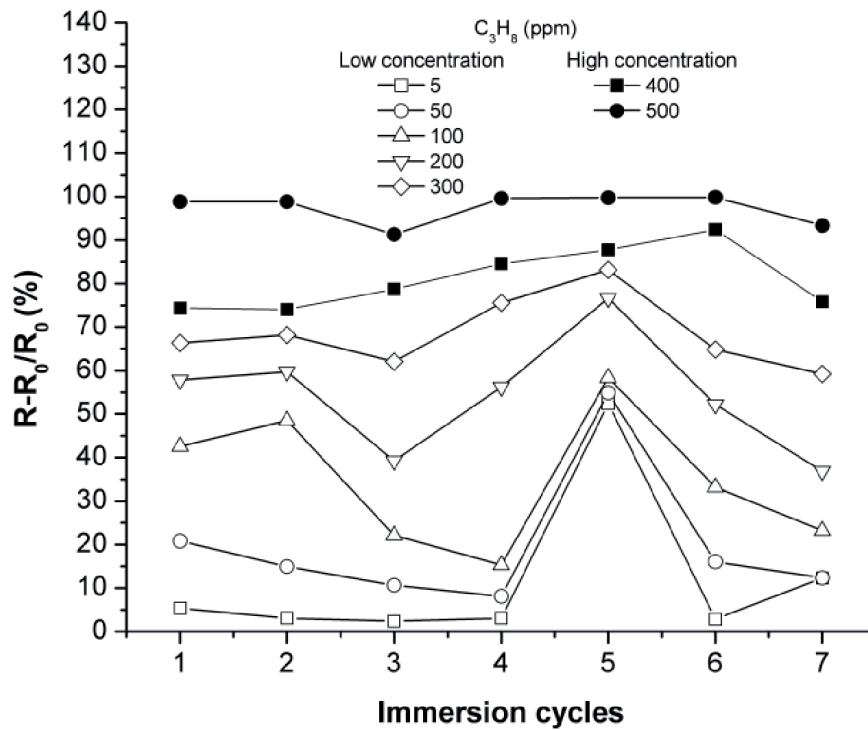


The released electron contributes to increase the electrical conductivity, since it is a function of the number of free charge carriers, thus, diminishing its electrical resistance.

Figure 5a shows graphs of the sensitivity, as defined in Eq. (1), as a function of propane concentration in parts per million (ppm). As can be seen, in the range that goes from 5 to 300 ppm the sensor produced with five immersion cycles present the highest sensitivity and at higher propane concentrations sensors sensitivity tend to have the same values. A different perspective of this behavior is presented in **Figure 5b** where the sensitivity at the same propane concentration is plotted versus the number of immersion cycles. In this figure it is observed a dependence of the



(a)



(b)

Figure 5.

Sensors sensitivity for the different films produced as a function of (a) propane concentrations and (b) as a function of the number of immersion cycles at different propane concentrations.

sensitivity not only as a function of immersion cycles (film thickness), but also as a function of propane concentration.

Based on the last, a two-regime behavior can be proposed: one at concentrations in the range that goes from 5 to 300 ppm and the other at concentrations above 300 ppm. In the first regime, or the low concentration regime, the values of sensitivity present a strong dependence of film thickness: a diminishing trend at a film thickness smaller than 60 nm, a maximum peak around 90 nm, and another

diminishing trend at higher film thickness. In the second regime, or the regime of high concentrations, the sensitivity depends no more of the film thickness and presents a constant value for different film thickness.

The low concentration regime might be explained by the presence of a space charge region (SCR), generated by adsorbed particles at the sensor surface, and the surface morphology of the samples. Since positive hydrogen atoms are adsorbed at the surface, their electric fields bend the electronic state energies of titanium oxide towards lower energies (**Figure 6**). This band bending is projected into the material and becomes less important as it goes deeper into the film. This is due to the decaying electric field tendency, which means that the energy E of free carriers in the conduction band changes with depth as:

$$E = E_c - \frac{A}{r^n} \tag{4}$$

Where E_c is the energy at the edge of the conduction band, A and n are constants that depend on crystal structure and number of chemisorbed particles, and r is the distance from the surface. If the film thickness is small enough to be comparable in magnitude to the depth of the SCR, the contribution of the SCR to the electrical conductivity of the film becomes dominant and depends directly on the number of adsorbed atoms.

Based on this, it is expected a diminishing trend of sensitivity with immersion cycles, for every cycle increases films thickness and reduces the contribution to electrical conductivity of the SCR. This explains the behavior up to 70 nm (4 immersion cycles); however, it does not explain the behavior at larger film thickness. The peak at 5 immersion cycles followed by a diminishing trend in sensitivity is attributed to a combined effect of the SCR and changes in surface structure. According to AFM images, the compactness of films with larger thickness and their more uniform distribution of grains result in a better electrical contact among crystallites, not only in the bulk but also at the surface. Since electrical conduction is given in the surface due to the SCR, a more uniform surface allows a larger amount of charges at the interphase and a conduction path with an inferior amount of dislocations and vacancies contributing to diminish carriers' mobility. Since the change in surface structure allows a more adequate interaction of the sensor with the gas it is expected an increase in sensors sensitivity, and, thus, the peak observed at five cycles. This

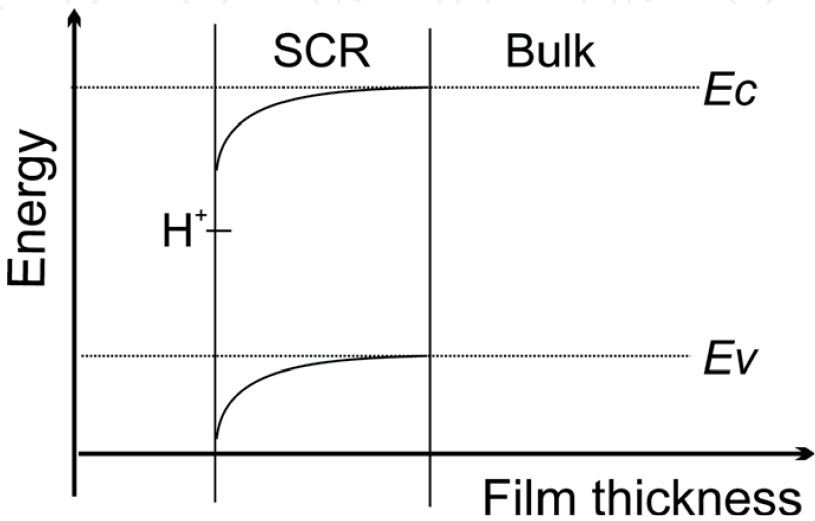


Figure 6. Energy band diagram as a function of the film thickness. The chemisorbed proton H^+ bends the energy bands towards lower energies, this bending known as the space charge region (SCR), becomes less important as it goes deeper in the film; at large film thickness the band gap equals that of the bulk.

behavior is given in samples with a larger thickness than 110 nm but, since the influence of the SCR diminishes with the thickness, the diminishing trend is maintained for a larger number of immersion cycles.

The high concentration regime, where sensitivity becomes independent of film thickness is explained by the saturation of the surface by the adsorbed species. According to Langmuir theory the number of adsorbed species is a function of gas partial pressure. This means that at high propane concentrations the number of adsorbed species is large enough that the contribution to the electrical conductivity due to differences in surface area is negligible. In this regime sensitivity depends only on propane partial pressure.

4. Conclusions

Seven titanium oxide gas sensors were produced on glass substrates by the ultrasonically assisted dip-coating method, using a 0.17 M solution of titanium isopropoxide and an immersion speed of 0.122 cm/min. Film thicknesses ranged from 20 nm to 150 nm with deposition rate of 18 nm per immersion. From X-ray diffraction analysis, sensors annealed at 400°C for 3 hrs a polycrystalline structure corresponding to the TiO₂ anatase phase.

Propane sensing tests indicate that work temperatures of 300°C cause significant changes in electrical resistance of TiO₂ gas sensors and is close to be the smallest temperature at which sensors can detect propane presence. An analysis of the sensitivity as a function of the film thickness indicates a two-regime behavior where at concentrations above 400 ppm of propane the sensitivity becomes independent of the thickness. Sensitivity becomes dependent of film thickness at lower concentrations. Its behavior is explained by a contribution of a space charge region and a change in surface structure. Such behavior indicates that film thickness values close to 120 nm are adequate to sense propane at concentrations in the range of 5 to 300 ppm of propane.

Acknowledgements

The authors thank and recognize the financial support of DGAPA-UNAM Project IN102419. Useful discussions with of Dr. Carlos Magaña and Dr. Francisco Hernández are recognized and appreciated. Also we thank the technical assistance of Manuel Aguilar in laboratory works.

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