Nanosized Nb-TiO_2 Gas Sensors Derived From Alkoxides Hydrolization

Ana Ruiz, Albert Calleja, Ferran Espiell, Albert Cornet, and Joan Ramon Morante

***Abstract*—Nanocrystalline TiO_2 modified with Nb has been produced through the sol-gel technique. Nanopowders have been obtained by means of the hydrolysis of pure alkoxides with deionized water and peptization of the resulting hydrolysate with diluted acid nitric at 100 °C. The addition of Nb stabilizes the anatase phase to higher temperatures. XRD spectra of the undoped and the Nb-doped samples show that the undoped sample has been almost totally converted to rutile at 600 °C, meanwhile the doped samples present still a low percentage of rutile phase. Nanocrystalline powders stabilized at 600 °C with grain sizes of about 17 nm have successfully been synthesized by the addition of Nb with a concentration of 2% at., which appears to be an adequate additive concentration to improve the gas sensor performances, such as it is suggested by the catalytic conversion efficiency experiments performed from FTIR measurements. FTIR absorbance spectra show that catalytic conversion of CO occurs at lower temperatures when niobium is introduced.**

The electrical response of the films to different concentrations of CO and ethanol has been monitored in dry and wet environments in order to test the influence of humidity in the sensor response. The addition of Nb decreases the working temperature and increases the stability of the layers. Also, large enhancement of the response time is obtained even with lower working temperatures. Moreover, humidity effects on the gas sensor response toward CO and ethanol are less important in Nb-doped samples than in the undoped ones.

***Index Terms*—Gas sensors, niobium, sol-gel, titanium dioxide.**

I. Introduction

In VIEW of increasingly strict legal limits in emission of harmful gases [1], there is a great interest in developing materials and devices with enhanced electronic properties to control the level of air pollution. Semiconducting metal oxides have been widely investigated for that purpose. Among them, transition metal oxides, such as TiO_2, appear to be one of the best candidates for gas detection due to its surface characteristics, specially as anatase phase and temperature working range, being able to operate under harsh environments [2]–[5].

TiO_2 crystallizes in three different structures: brookite, anatase, and rutile, rutile being the thermodynamically stable phase. Semiconductor gas sensors based on rutile-TiO_2 have primarily been used as oxygen sensors for the control of high temperature (>800 °C) combustion processes, mainly in the automotive industry [6]–[8]. Moreover, anatase phase has been reported to be an excellent support in catalytic measurements and to pronounce selective oxidation of some molecules [2], [3].

Key points to achieve better suitable sensitive materials are both the crystalline structure and the grain size of the powders [9], [10]. However, sensing devices require thermal treatments at a sufficient high annealing temperature to ensure the stability of the layer, and this thermal stabilization often produces an excessive grain coarsening of the sensing powders, which results in a lower surface-to-volume ratio yielding a poor sensitive response. Moreover, in the case of TiO_2, calcination temperatures over 600 °C lead to a crystallographic phase transition to the rutile type. As anatase is more suitable than rutile for ambient monitoring of harmful gases [2], [3]; it is, therefore, necessary to stabilize the anatase phase at higher temperatures and hinders its transition to rutile. To prevent this change in the titania structure, it has been shown that the addition of pentavalent atoms (Nb, Ta) [11]–[14], or trivalent atoms (La) [2], [3] to titania avoids or diminishes the anatase to rutile transformation probability and hinder the grain growth.

In this work, nanocrystalline TiO_2 and Nb-TiO_2 with different Nb contents have been obtained by an easy low-cost sol-gel process. As precursors, high purity alkoxides solutions have been used. To analyze the sensing performances of TiO_2 and Nb-doped TiO_2, the powders were deposited by screen-printing on alumina substrates. Screen-printing is a well established thick-film technology, which allows small sensor to sensor differences between production lots [15]. Thick-film sensors with well-characterized anatase structure have been fabricated for gas sensitivity measurements. Many of the commercial sensors for CO monitoring using semiconducting metal oxides are based on SnO_2. However, the sensitivity of most of these sensors is strongly influenced by humidity [16]. Keeping in mind this problem, our research group was interested in study humidity effects on gas sensors. For that purpose, in gas test measurements, we have also examined the behavior of TiO_2 under humid ambients.

II. Experimental Setup

A. Film Preparation

Undoped and Nb-doped TiO_2 powders have been prepared following an alkoxide sol-gel method. For the production of crystalline anatase, an appropriate quantity of titanium (IV) isopropoxide was rapidly added to pure water at ambient temperature, with gentle stirring, to produce a fresh and amorphous

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hydrolysate, which settled rapidly. A critical step in sol-gel processing is the de-aggregation of the hydrolysate. This process needs to disperse it by peptization with appropriated acids or bases, to form stable sols. In our case, the precipitate was washed free of isopropanol with pure water, and then peptized with diluted acid nitric. This procedure leads to obtain colloidal dispersions (sols) of hydrous oxides of titanium. The resulting sol undergoes a condensation process under reflux at boiling conditions. The gels produced were dried at 120 °C and then calcined to get structural stabilization of the semiconductor powders. Further details of the preparation method can be found in [17].

In the case of the Nb-doped samples, niobium ethoxide was previously mixed with titanium isopropoxide in the required amount to achieve additive concentrations of 1% at. and 2% at. of Nb versus Ti. The mixed solutions were then added to pure water and the same powder production procedure than for the undoped samples was followed.

In order to study the evolution of the crystalline structure of the powders with the temperature, several samples have been produced by calcination at temperatures from 400 to 1000 °C over 4 h. Once the sensing powder is obtained, a paste is formed by dissolving powders with an organic solvent; in our case, diethanolamine mixed with ethanol was used. Thick-film deposition of the pastes was carried out by the screen-printing technique. Alumina substrates with printed Pt heater and electrodes were used.

B. Structural and Electrical Characterization

Structural characterization by X-ray diffraction was carried out with a Siemens D-500 X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å), with operating voltage of 40 kV and current of 30 mA. To identify crystalline phases present in the samples, general spectra were collected in steps of 0.05° from 5 to 80° (2θ) during 3 s of measurement time per step. More detailed spectra were collected in steps of 0.02° from 20° to 33° with 5 s of measurement time per step. The latter spectra allow us to study the crystallinity and the grain size of the nanopowders.

For catalytic combustion measurements, the powders were placed in a temperature-controlled reactor that allows the sample to be heated. A continuous gas flux of 20 ml/min was passed through the chamber. The gas test used has been 1000 ppm of CO on synthetic air from certified bottles. CO is catalytically oxidized to CO_2 at the different material surfaces. FTIR analyzes of the residual gas mixture were done in a Bomem MB-120 spectrometer. Before each measurement at a fixed temperature, the gas atmosphere in the chamber was stabilized for 30 min.

Gas test measurements have been carried out in a test station where the appropriated gas concentration is introduced in a stainless steel test chamber by means of mass flow controllers. Electrical responses of the sensors in dry and wet synthetic air as carrier with different concentrations of CO and ethanol were monitored.

III. Results and Discussion

Due to the high resistivity of TiO_2, the electrical response data processing becomes sometimes difficult. The addition of donor type atoms, such as Nb, decreases its resistance making possible working at lower temperatures, which also leads to lower power consumption.

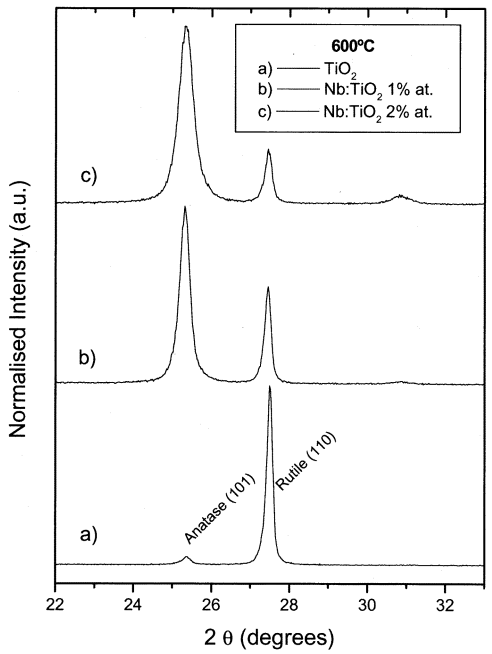

Fig. 1. XRD spectra in the region from 22° to 33° of the samples stabilized at 600 °C.

Structural characterization has been performed by XRD analyzes. The main purpose was to verify the effects of the Nb introduction in the grain size and in the crystallographic structure of TiO_2. Three sets of samples were produced: TiO_2, TiO_2 with a Nb content of 1% in atomic concentration of Nb over Ti, and TiO_2 with Nb in a concentration of 2% at. Each set was submitted to stabilization temperatures ranging from 400 to 1000 °C.

XRD spectra allow us ti study the crystallinity and the grain size of the different powders. Only the three titania phases are seen in XRD spectra; reflections produced by different oxides of niobium were not observed. In the Nb-doped samples, brookite phase is found until 600 °C. The presence of this phase is related with the quantity of anatase with respect to rutile. The more brookite we have in the samples, the lower presence of rutile stable phase is observed, as it is shown in Fig. 1, where the detailed XRD spectra in the region from 20° to 33° of the different samples calcined at 600 °C are presented. This fact can be explained assuming that brookite phase crystallizes on the surface of the anatase grains hindering the formation of rutile when the calcination temperature increases. The undoped sample has been almost totally converted to rutile at 600° C, meanwhile the Nb-doped samples present still a low percentage of rutile phase, as shown in Fig. 2, where the transition from anatase to rutile as a function of the temperature is presented. Fig. 3 points out the evolution of grain sizes with the temperature calculated from the fitting of the anatase (101) XRD peak using Scherrers equation. The mean crystallite size seems to be correlated with the percentage of each crystallographic phase, since the more percentage of rutile is observed, the bigger anatase grain size is found. Nanocrystalline powders stabilized at 600 °C with grain

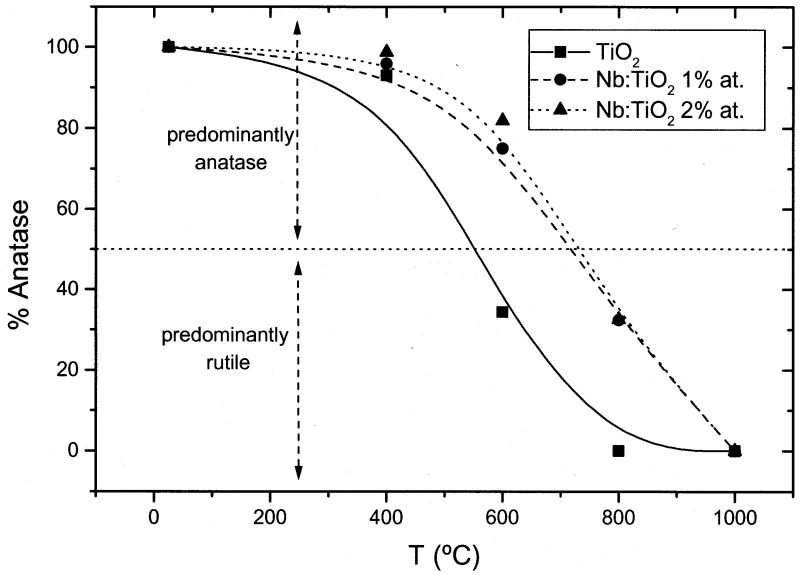

Fig. 2. Percentage of anatase phase present in the samples as a function of stabilization temperature.

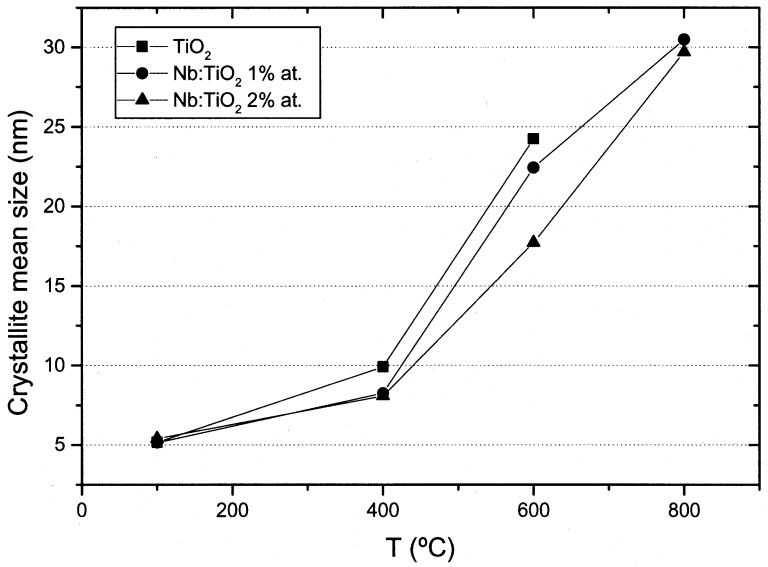

Fig. 3. Comparison of grain sizes calculated by XRD as a function of the calcination temperature.

sizes about 17 nm have successfully been synthesized by the addition of Nb with a concentration of 2% at., which as well is the sample with more predominant anatase phase (80%). In our case, this concentration seems to be the adequate additive concentration for gas sensors applications, such as it is suggested by the catalytic conversion efficiency experiments performed from FTIR measurements. However, a systematic study of the effects of the concentration of Nb in the sensor characteristics has to be performed to highlight this point.

Catalytic combustion at temperatures from room temperature to 500 °C was studied for the samples thermally treated at 600 °C. The infrared CO_2 absorption spectra of the residual gases resulting from the CO catalytic reaction on the surface of the materials are shown in Fig. 4. The temperature indicated in this figure is the one set on the temperature controller of the chamber. Due to thermal conductivity losses, the actual temperature is little lower than the temperature set at the heating element. FTIR absorbance spectra show that catalytic conversion occurs at lower temperatures when niobium is introduced. For both samples, as the temperature increases, the CO consumption is higher and the intensity of CO_2 absorption increases as indeed observed in the figure.

The electrical response of the films calcined at 600 °C to different concentrations of CO is shown in Fig. 5. The gas sensing capability has been quantified as the ration between the resistance in synthetic air and the resistance under gas exposure. In this figure, it is observed that the addition of Nb decreases the working temperature and increases the sensitivity, as correlated with catalytic measurements. At a working temperature of 400 °C, the Nb-TiO_2 film doped with 2% at. exhibits higher sensitivity and faster response time than the undoped titania film working at 500 °C. These results are in accordance with the gas

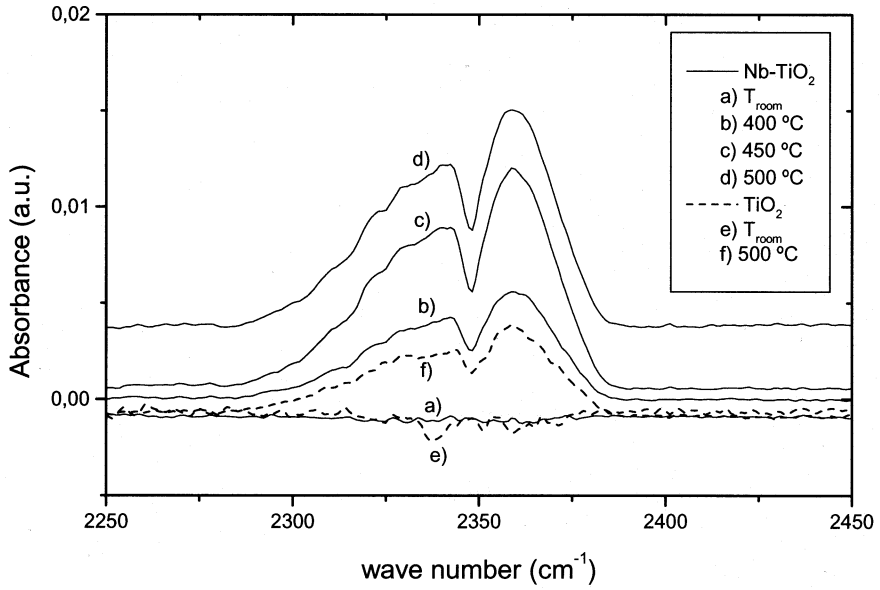

Fig. 4. Variation of the infrared CO_2 vibration with the working temperature resulting from the CO conversion by the (solid lines) Nb-TiO_2 and the (dashed lines) TiO_2 samples, both stabilized at 600 °C.

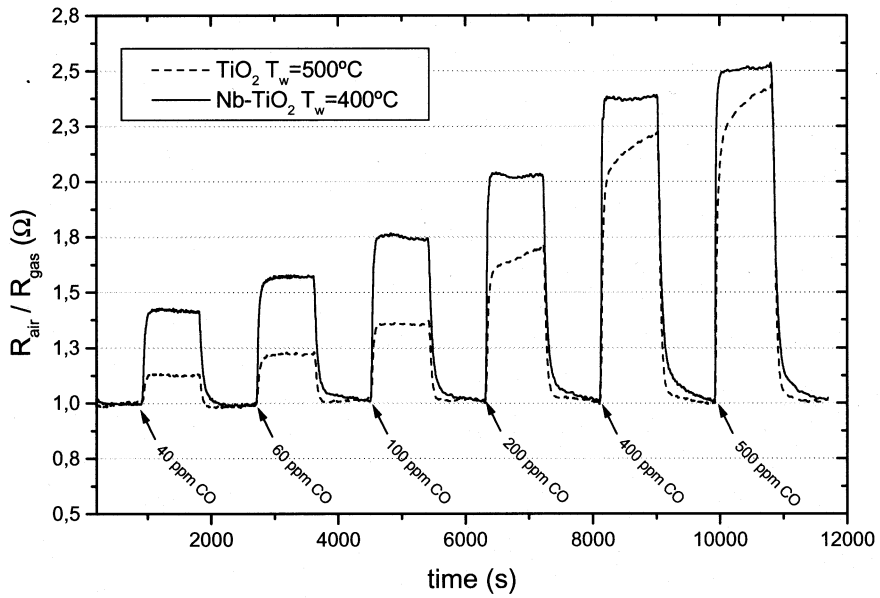

Fig. 5. Real-time sensor response to different CO concentrations for the undoped and the Nb-doped samples treated at 600 °C.

sensing capability to CO found for the same type sensors [9], [13].

The sensor response to gas in a sudden change in humidity was also monitored. In Fig. 6, the response of the sensing powders to 500 ppm of CO in dry gas mixture and in a gas mixture with a relative humidity of 50% at a working temperature of 400 °C are shown. Although the sensors are sensitive to low CO concentrations, to illustrate the changes produced by humidity, the concentration of gas was chosen as the one that gave the largest sensor response, i.e., 500 ppm. In the TiO_2 sensor response, a peak after a sudden change in humidity is observed before the profiles stabilize. This peak in the transient regime could be explained by the generation of OH^- groups that make the conductance rise, and the following recombination of the charged particles make it decrease [18]–[20]. Both sensors are sensitive to CO even in humid ambient, however the influence of the humidity in the Nb-doped sample is weaker than in the undoped one. More pronounced effects have been observed in the detection of ethanol. The sensing response toward 100 ppm of ethanol in dry and wet synthetic air at a working temperature of 400 °C is shown in Fig. 7. Though the sensitivity of the sensors is diminished in relative humidity of 50%, the powders are still sensitive. However, the response time of the Nb-TiO_2 layer is lower than the undoped one. The same happens at lower working temperature (300 °C). This poor dependence on humidity can be very useful to define gas sensors based on TiO_2 as an alternative to the higher humidity influenced gas sensors already existing in the market.

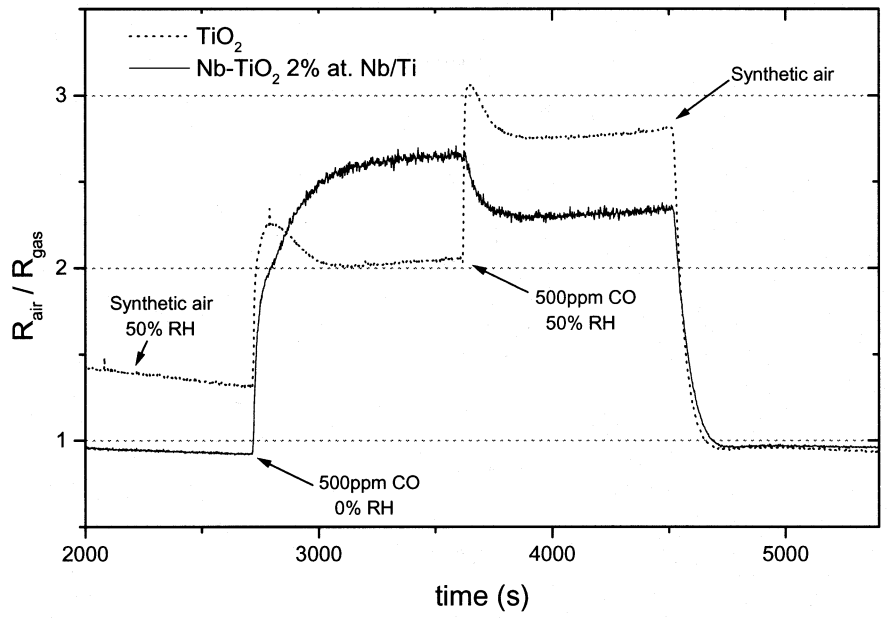

Fig. 6. Electrical response of the undoped and the Nb-doped powders to CO in dry and wet atmospheres at a working temperature of 400 °C.

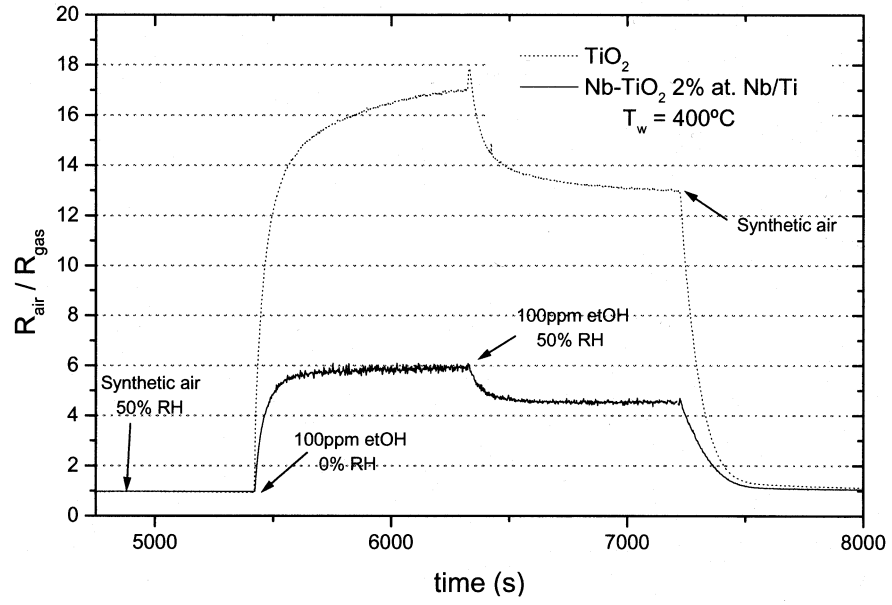

Fig. 7. Electrical response of the undoped and the Nb-doped powders to ethanol in dry and wet atmospheres at a working temperature of 400 °C.

IV. Conclusion

Nanocrystalline TiO_2 and Nb-modified TiO_2 powders have been successfully synthesized by sol-gel technique using pure alkoxides as precursors. Nb was added to stabilize the anatase phase to higher temperatures and to hinder the grain growth, as indeed observed by XRD analyzes.

Titania nanopowders stabilized at 600 °C with grain sizes about 17 nm and anatase percentage over 80% have been produced by the addition of Nb in a concentration of 2% at. This concentration seems to be adequate for many of the gas sensor applications, such as is suggested by catalytic conversion experiments and gas test measurements.

Gas test measurements show that the addition of Nb decreases the working temperature of the sensing powders and increases its sensitivity. Likewise, the dependence of these powders on the humidity is weaker than in undoped TiO_2. In summary, the adequate addition of niobium appears to be an interesting method to define gas sensors based on TiO_2 for practical applications.

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