Impedance spectroscopy analysis of TiO2 thin film gas sensors obtained from water-based anatase colloids

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\textbf{A B S T R A C T}

In this work impedance spectroscopy technique was employed in order to characterize the gas-sensing behavior of undoped titanium dioxide (TiO\textsubscript{2}) polycrystalline thin films. The electrical measurements were performed in a sensor-testing chamber that allows independent control of temperature, pressure, gas composition and flow rate. Frequency measurements, in the range from 40 Hz to 110 MHz, were performed in order to evaluate the gas sensor response of the samples as a function of temperature (50–350 °C) and surrounding atmosphere (vacuum or air at atmospheric pressure). Impedance spectroscopy is a very useful and important technique due to the possibility of using this method for discriminating between grain boundary capacitance ($C_{gb}$) and grain boundary resistance ($R_{gb}$) contributions. Therefore, a simple model taking into account variations in the intergranular potential barriers is proposed in this work.

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1. Introduction

The increasing concern in the detection of toxic and flammable gases calls for the development of highly sensitive devices as well as for the understanding and determination of simplified models of sensor operation mechanisms. The interest has long been focused in wide band-gap semiconducting metal oxides such as SnO\textsubscript{2}, ZnO and TiO\textsubscript{2}, which suffer changes in the conductance when oxidizing or reducing species in air chemisorb onto the oxide particle or film surface [1,2]. In view of the importance in monitoring industrial, home and automobile pollution, today the development of nanostructured sensing films is not only an attractive trend toward miniaturization, but the alternative to maximize the surface-to-volume ratio and sensitivity [3].

Titanium dioxide has attracted much attention in the past decades and found applications of environmental interest in self-cleaning and energy efficient windows [4], dye-sensitized solar cells [5], photocatalysts for the degradation of water and air pollutants [6] and gas-sensing devices [7]. Moreover, the functionalization of titania mesoporous films is an interesting alternative toward highly selective bio-sensors [8]. TiO\textsubscript{2} presents two metastable polymorphs, anatase and brookite, and the stable phase rutile. Since the transition from anatase to rutile takes place at around 600–700 °C, rutile is the desired phase for high temperature applications (>800 °C) [7]. Anatase is characterized by high electron mobility responsible for its elevated sensitivity and faster response as a gas sensor [9]. Rutile and anatase exhibit further differences: the former is a p-type semiconductor while the latter shows n-type semiconductivity [10]. The n–p-transition regime for TiO\textsubscript{2} is displayed below 1200K at oxygen partial pressures near atmospheric conditions. As far as the electronic properties are concerned, TiO\textsubscript{2} behaves in these conditions like an intrinsic semiconductor in which densities of electrons and holes are very similar. Therefore, a very low electronic conductivity must be expected. The loss of oxygen may be accompanied by the movement of Ti ions onto interstitial sites [11].

Significant advances have been achieved lately for the use of TiO\textsubscript{2} in gas-sensing devices. A great sensitivity to H\textsubscript{2} and ethanol has been found for undoped anatase films at 400 °C, whereas Sr, Tb and Y-doped films were barely sensitive to those gases [7,12]. The response of TiO\textsubscript{2} was also tested against NO\textsubscript{2}, CO, ammonia, O\textsubscript{2} and water vapor, and the use of nanoscaled particles was observed to be critical in order to achieve sensitivity [3,13–17]. Anatase films on glass substrates also showed reproducibility and stability when exposed to CO at temperatures between 100 °C and 300 °C, apart from complete regeneration after the CO removal [18]. Akbar and co-workers discussed the electrical response of doped and undoped anatase gas sensors in several comprehensive papers [19–21]. They correlated the electrical properties with the microstructure and proposed, on the basis of dc and ac admittance spectroscopy measurements, an equivalent circuit that represents the grain boundary dominant response and considers trapping relaxations originated by the defects within the grain boundary region. The authors found consistency between the grain boundary ac response and changes

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in the barrier thermal activation induced by the heat-treatment of TiO$_2$ bulk samples in the 700–900 °C temperature range [20]. The influence of additives such as Al [19], Fe [19,22], Y [19,20], Sr and Tb [7], Cr [23–25], Nb [13,24–28], Pt [9], Ta [13] and Li [29], on the performance of TiO$_2$-gas sensors has been extensively studied.

In this work, we report the fabrication of undoped-TiO$_2$ nanostructured films from sol–gel anatase colloids and their application as gas sensors. The films have a porous structure, being composed of small grains in the 20–40 nm range. The impedance spectroscopy technique was used in order to evaluate the electrical behavior of the samples under different atmospheres and temperatures. Our interpretation of the electrical response is slightly different from the one reported by Akbar and co-workers. The results allow us to explain the modifications in the intergranular potential barriers induced by different testing conditions and to contribute for a better understanding of the sensing mechanisms in anatase-based gas sensors.

2. Experimental details

In this work, Ti(O$^i$Pr)$_4$ (97%, Aldrich) was mixed with acetic acid (100%, Merck) and a non-ionic surfactant (Triton X-100, Aldrich) in 2-propanol (Qhemis). Then, water was added dropwise, with stirring, in a 1:1 Ti(O$^i$Pr)$_4$:H$_2$O molar ratio. The obtained gel was aged for 24 h in order to maximize condensation. The gel was peptized at 80 °C and the evaporated alcohol compensated with water. The resulting colloidal dispersion was transferred into a PTFE-lined stainless steel vessel for hydrothermal treatment at 200 °C. Afterwards, the dispersion was concentrated by evaporation until a 5 wt% TiO$_2$ paste was obtained. The paste was characterized by X-ray diffraction (XRD; Rigaku Rint2000) and thermal analysis (TG/DTA; Shimadzu TG50-DT50). The TiO$_2$ paste was doctor-bladed on insulating alumina substrates, onto which gold electrodes with an interdigitated shape had been previously sputtered, and films were heat-treated at 450 °C for 20 min. The morphology of the films was studied by field-emission scanning electron microscopy (FE-SEM; JEOL JSM 6700F).

For gas-sensing measurements, the films were tested in a chamber with temperature, pressure, gas composition and flow rate control. Electrical resistance and impedance measurements, in the 40 Hz–110 MHz frequency range, were carried out between 100 °C and 250 °C with an HP4192A impedance analyzer. The electrical behavior of the films was analyzed by means of impedance plots in which the impedance $Z$ is shown in a complex plane with the reactance ($Z''$) plotted against the resistance ($Z'$) [30]. The curves were obtained at different temperatures (25–350 °C), with heating and cooling rates of ~1 °C/min, in vacuum ($10^{-2}$ Torr) and in dry air at atmospheric pressure. In order to ensure that the system was in steady state before data acquisition, it was verified that the response was constant in time. Fig. 1 describes the conditions of temperature and pressure as well as the procedure adopted for sequential measurements.

Due to the great electrical resistance of undoped-TiO$_2$ at low temperatures, semicircular curves were only obtained at temperatures higher than 330 °C. Thus, 350 °C was the selected temperature for the analysis. Finally, the electrical resistance and capacitance were determined from fittings of the impedance diagrams with an $R$(RC) equivalent circuit using the ZView 2.1 software.

3. Results and discussion

The XRD pattern of the TiO$_2$ colloid after hydrothermal treatment at 200 °C showed that the material crystallized exclusively into the anatase phase. As expected, no phase transition was observed after thermal treatments up to 600 °C. Thermal analyses indicated that organics were completely burned above 400 °C and that the phase transition to rutile takes place around 700 °C. Anatase is usually the desired phase in gas-sensing devices for service temperatures below 800 °C since electron mobility is higher in anatase than in rutile, leading to higher sensitivity and faster response [7,9]. Fig. 2 shows a FE-SEM image of a film heat-treated at 450 °C. The TiO$_2$ films are porous, consisting of small grains in the 20–40 nm range.

The temporal response of the sensor (resistance vs. time curve) was recorded, from impedance spectroscopy measurements, when the atmosphere was changed from vacuum ($10^{-2}$ Torr) to air (at atmospheric pressure) at a constant temperature of 350 °C, as shown in Fig. 3.

After a quick increase upon oxygen exposure, the electrical resistance measured at 40 Hz is almost constant after approximately 120 s. This phenomenon could be correlated with a significant diffusion of oxygen into the grain boundaries due to the open porous microstructure and the nanoscaled grain sizes. The film exhibited a very strong increase in resistance (almost three orders of magnitude) when air was introduced in the test chamber.

The results from impedance spectroscopy measurements, carried out according to the schedules shown in Fig. 1, can be fitted with a simple $R_b$(R$_{gb}$C$_{gb}$) electrical model where $R_b$ and $R_{gb}$ reflect the bulk and grain boundary resistances, respectively, and $C_{gb}$ the capacitance across the grain boundary [31,32]. The impedance of a
resistance $R_{gb}$ in parallel with a capacitance $C_{gb}$ is given by:

$$Z_{gb} = \frac{1}{R_{gb} + j\omega C_{gb}},$$  \hspace{1cm} (1)

where $\omega = 2\pi f$.

Eq. (1) can be expressed as:

$$\left(\frac{Z'_{gb} - R_{gb}}{2}\right)^2 + \frac{Z''_{gb}^2}{(R_{gb}/2)^2} = \left(\frac{R_{gb}}{2}\right)^2$$  \hspace{1cm} (2)

where $Z'_{gb}$ and $Z''_{gb}$ are the real and imaginary components of $Z_{gb}$, respectively. The corresponding plot of the real against the imaginary component of $Z_{gb}$ is a semicircle of radius $R_{gb}/2$ centered at $(R_{gb}/2, 0)$. The addition of a series resistance $R_s$ will only shift the curve in the $R_s$ value. Thus, $R_{gb}$ and $R_s$ are derived from the low- and higher-frequency resistance values, respectively, and the capacitance can be obtained from the maximum value of the reactance.

Fig. 4 shows the impedance plots registered at 350 °C according to Schedule 1 (Fig. 1). When the sample is heated to 350 °C in vacuum ($10^{-2}$ Torr), the impedance curves become measurable because of thermal activation. In presence of air at 350 °C (Fig. 4 filled circle) there is an increase in the grain boundary resistance due to oxygen adsorption.

Furthermore, the interaction of oxygen with the surface would tend to increase the sample resistance due to the decrease of the conduction band bottom, the Fermi level is known as unpinning of the Fermi level [32–35]. Conversely, if the barriers were previously overlapped (Fig. 5b and c) and vacuum is maintained for 2 h, the reverse process takes place as can be observed in Fig. 6 (open up-triangle) and in the band diagram of Fig. 5d. The out-diffusion of oxygen and the oxygen vacancy generation increase the sample resistance due to the decrease of the conduction band bottom from $V_s$ to $V_d$. In the extreme situation of total decrease of the conduction band bottom, the Fermi level would be reached and $qV'$ would tend to $\Phi$ (where $q$ is the absolute value of the electron charge and $\Phi$ is the barrier height) returning to the conditions in Fig. 5a. At this point, barriers would not be overlapped and the overlapping process would only be possible if oxygen would be introduced into the chamber (for temperatures above 300 °C). According to the Poisson equation, and due to the small particle size of the samples under study, the overlapping of depletion regions is highly probable. This is in agreement with results previously published by other researchers [33–35].
vacuum. This process can be interpreted on the basis of Fig. 5e. Due to the short stabilization time (120 s), a change from d to e is observed rather than a change from d to b. The oxygen adsorption at the grains surface increases the barrier height but there is not enough time for oxygen to diffuse into the TiO$_2$ grains. Finally, in order to promote overlapping the sample was cooled to 35 °C in air and heated once again to 350 °C in the same atmosphere during a 4 h process. The final configuration of the barriers corresponds to that of Fig. 5b and the sample was used for the following measurements.

Fig. 7 shows the impedance spectroscopy response during Schedule 3 (Fig. 1) carried out at 350 °C in air, then in vacuum and finally in air again. The average particle size of films annealed at 450 °C in air did not increase during measurements, as expected, due to the low temperature used for testing (350 °C).

The radii of semicircles became smaller in vacuum indicating that $R_{gb}$, as well as barrier height and width, decreased due to oxygen desorption (change from Fig. 5b to f). When the sample is exposed to air again, an increase in the sensitivity is clearly observed, due to the low initial $R_{gb}$ at 350 °C. The curves in Fig. 7, fitted with an $R_b(R_{gb}C_{gb})$ equivalent circuit, yielded the resistance and capacitance values listed in Table 1. Notice the increase in $R_{gb}$ after oxygen exposure (see also Fig. 4).

For Schottky barriers (samples with non-overlapped barriers), the capacitance is related to the electron concentration in the bulk, $n$, and to the barrier height, $V_B$, as [31]

$$C \propto \left( \frac{n_{V_B}}{V_B} \right)^{1/2}.$$  (3)

Therefore, because in the initial condition barriers are overlapped, $C_{gb}$ is physically meaningful for the vacuum and for the final oxygen exposure conditions only. A decrease in the final capacitance is associated with a higher barrier and/or with a reduction of the donor concentration due to the annihilation of oxygen vacancies.

4. Conclusions

Impedance spectroscopy analysis of TiO$_2$ thin film gas sensors obtained from water-based anatase colloids was performed in this work. Hydrothermal treatment, at 200 °C, of the titanium colloidal
dispersion showed that the material crystallized exclusively into the anatase phase. TiO₂ doctor-bladed thin films heat-treated at 450 °C with nanoparticles in the 20–40 nm range were obtained. The sensor exhibited a good response time, with the electrical resistance being almost constant after approximately 120 s. The film exhibited a very strong increase in resistance (almost three orders of magnitude) when air was introduced in the test chamber. The impedance spectroscopy measurements performed on nanostructured anatase films were carried out in order to study the sensing mechanism at different atmospheres. The Schottky potential barrier height increased due to oxygen chemisorption at the intergrains, having a pronounced effect on the electrical n-type conductivity. Oxygen desorption from the TiO₂ surface due to vacuum exposure causes a decrease in the barrier height and facilitates electrical conductance.

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References


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