

# Electrical conduction mechanism and gas sensing properties of Pd-doped TiO<sub>2</sub> films

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## ABSTRACT

Undoped and Pd-doped titanium oxide thin films (0.5 wt.%) were prepared by the sol-gel technique (dip-coating) on glass and silicon substrates. The as-deposited thin films were compacted by subjecting them to different annealing temperatures (300 °C, 500 °C). The dependences of the electrical conductivity vs. inverse temperature were investigated in air and in vacuum. A study of the effects of Pd-doping, annealing temperature and ambient conditions on their electrical properties was performed. The sensing behavior of titanium oxide thin films exposed to some reducing gases (methane, acetone, ethanol, formaldehyde and liquefied petroleum gas) was carried out, by means of electrical conductivity measurements. All the studied films are most sensitive to formaldehyde, with a special remark for the Pd-doped ones deposited on silicon substrates.

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## 1. Introduction

High-purity and homogeneous oxide materials can be prepared by the sol-gel method, based on hydrolysis and poly condensation of metal-organic precursors, that allows an excellent compositional control. Vitreous coatings, obtained by the sol-gel method at low-temperature processing, present promising applications, and TiO<sub>2</sub> thin films were among the first ones in this respect because of its high energy band gap, high refractive index, high dielectric constant, etc. [1,2], being versatile for various applications (gas sensors, photocatalysis, optoelectronics, etc.) [1–6]. Concerning Pd doping, generally, its dispersion by the sol-gel method was made in SiO<sub>2</sub> [7], Al<sub>2</sub>O<sub>3</sub> [8], but less in TiO<sub>2</sub>, which explains our interest on the study of the sol-gel prepared Pd-doped titanium oxide films [3,4,9]. This paper concentrates on the sol-gel bi-layer Pd-doped TiO<sub>2</sub> films, which demonstrated their superiority (regarding the sensing gas properties) over the mono-layer ones, as presented in ref. [4]. More, in this paper, a comparative study is made on the electronic and sensing gas performances as a function of the post-deposition annealing temperature, palladium doping, and ambient conditions.

## 2. Experimental

The sol-gel method (alkoxide route) was used to prepare undoped and Pd-doped TiO<sub>2</sub>. Tetraethyl orthotitanate (95%, Merck) was the source for TiO<sub>2</sub> and Pd acetylacetonate (99%, Merck) was the source for Pd. Both precursors were used to prepare Pd-doped materials (0.5 wt.%), by simultaneous gelation in the sol-gel process (other experimental details are presented in ref. [3]). The un-supported materials resulted from the gelling of the starting solutions at room temperature, were dried at 80 °C and then thermally-treated in air, for 1 h, at 300 °C and 500 °C. Supported TiO<sub>2</sub> films (mono and bi-layers) were obtained by dip coating on different substrates: glass (microscopic slides) and Si (100)p (covered by a 510 nm oxide layer). Thin films densification was performed at the same mentioned temperatures, with a heating rate of 1 °C/min. In this paper, only bi-layer TiO<sub>2</sub> films have been studied.

The structure of the obtained materials (gels and films) was investigated by X-ray diffraction (XRD), with a Bruker-AXS, D8 Advance (CuK<sub>α</sub> radiation). Using an X-RAY 5.0 program, the weight percentage of the anatase phase ( $W_A$ ), and the average crystallite size for both identified phases (anatase and rutile) have been determined (see Table 1).

Atomic Force Microscopy (AFM) was used for the morphology investigation of the films, the AFM images were being acquired in the intermittent regime, with a Nomad microscope, from Quesant. The thin film's thickness, measured by using an ellipsometric method [3], was found to be under 100 nm (see Table 1).

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**Table 1**

Annealing temperature ( $T_a$ ), thickness ( $d$ ), weight percentage of the anatase phase ( $W_A$ ), average crystallite size for the anatase phase ( $D_A$ ) and for the rutile phase ( $D_R$ ), root mean square roughness ( $R_{rms,gl}$ ) for the TiO<sub>2</sub> samples deposited on glass substrates, sensitivity in front of formaldehyde at optimum operating temperature 240 °C for films deposited on glass substrates ( $S_{240,gl}$ ) and on Si substrates ( $S_{240,si}$ ).

| Samples                   | $T_a$<br>(°C) | $d$<br>(nm) | $W_A$<br>(%) | $D_A$<br>(nm) | $D_R$<br>(nm) | $R_{rms,gl}$<br>(nm) | $S_{240,gl}$ | $S_{240,si}$ |
|---------------------------|---------------|-------------|--------------|---------------|---------------|----------------------|--------------|--------------|
| TiO <sub>2</sub> undoped  | 300           | 50          | 100          | 17.3          | 0.0           | 1.1                  | 4.25         | –            |
|                           | 500           | 49          | 74           | 44.2          | 40.5          | 1.2                  | 1.74         | –            |
| TiO <sub>2</sub> -0.5% Pd | 300           | 71          | 100          | 18.5          | 0.0           | 5.3                  | 6.92         | 8.93         |
|                           | 500           | 72          | 94           | 30.7          | 29.5          | 6.4                  | 4.2          | 6.12         |

For the electrical resistance measurements, silver vacuum deposited electrodes, placed parallel to each other at a distance of 0.8 mm, have been used. The temperature dependent electrical conductivity was investigated, for the studied TiO<sub>2</sub> films, in a vacuum cryostat ( $10^{-2}$  Pa), in the temperature range of 273–440 K (Oxford ITC4 temperature controller) [10] and in ambient air in the temperature range of 373–623 K. To test the samples' gas sensing performance, the films were mounted on a heater placed in a glass enclosure capable of controlling the different gas concentrations [4]. The tests were performed in the temperature range of 373–623 K. The gas sensitivity ( $S = \frac{|R_a - R_g|}{R_g}$ ) was determined for the different test gases (acetone, ethanol, methane, formaldehyde and liquefied petroleum gas (LPG)), by measuring the electrical resistances of the thin film sensor in the test gases ( $R_g$ ) and in air ( $R_a$ ) (with the maximum 5% error in the mentioned temperature range). The gas concentration was varied from 400 ppm to 3000 ppm. During the cooling process, the samples continued to be exposed to the test gases.

### 3. Results

The films deposited on glass substrates are characterized by smooth surfaces (Table 1, Fig. 1), even that they are rougher than their counterparts deposited on silicon substrates, as reported in ref. [4] (the root mean square roughness ( $R_{rms}$ ) of about 2.2 nm for 500 °C thermally-treated samples). Referring to the films deposited on glass, we have to mention that  $R_{rms}$  does not exceed 7 nm (see Table 1).

Annealing determines an increase in  $R_{rms}$ , and the same effect has the palladium doping.

The un-supported films have polycrystalline structures, as revealed from the X-ray diffractometry studies. In the case of the double-layer films deposited on glass and silicon substrates, due to the fact that they are very thin (under 100 nm—see Table 1), the XRD patterns of the films are covered by those of the substrates. The XRD measurements were made on the un-supported films, in which the crystalline phase evolution is maintained.

To obtain information on how the electrical properties of TiO<sub>2</sub> films are influenced by the annealing temperature, Pd-doping, or the ambient conditions, a study on the temperature dependent resistivities was performed in air and in vacuum. The electrical transport in polycrystalline materials is dominated by grain boundary effects. In the grain boundary model, resistivity ( $\rho$ ) of thermally activated band conduction is expressed by [11,12]:

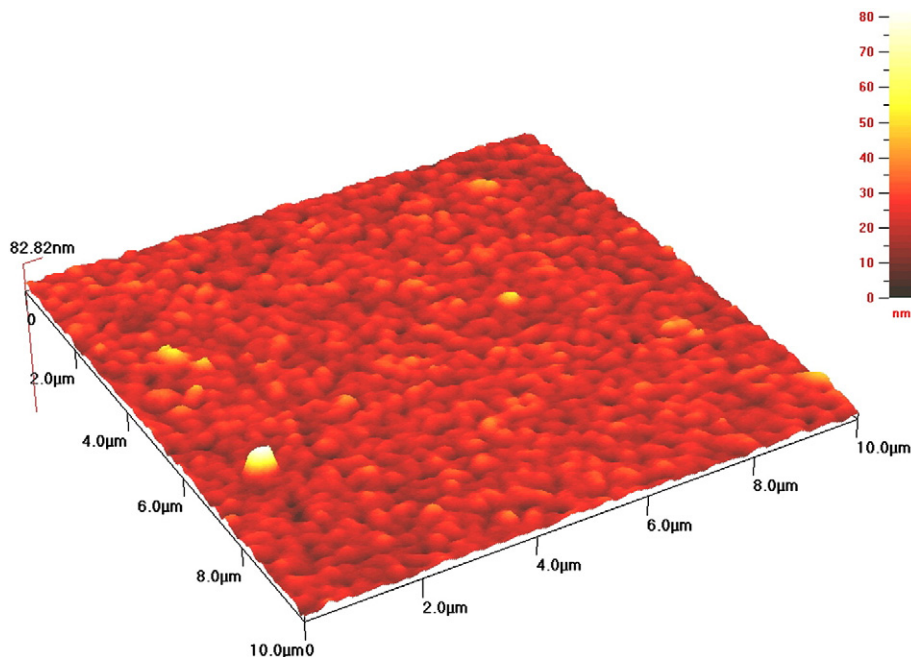
$$\rho = \left( \frac{(2\pi m^* k_B T)^{1/2}}{Le^2 n} \right) \exp\left(\frac{E_b}{k_B T}\right) \quad (1)$$

where  $e$  is the electron charge,  $n$  is the electron concentration in neutral region of the crystallites,  $L$  is the mean size of the crystallites,  $k_B$  is the Boltzmann's constant,  $m^*$  is the effective mass of charge carriers and  $E_b$  is the energy barrier height at the grain boundary, which can be expressed as [11,12]:

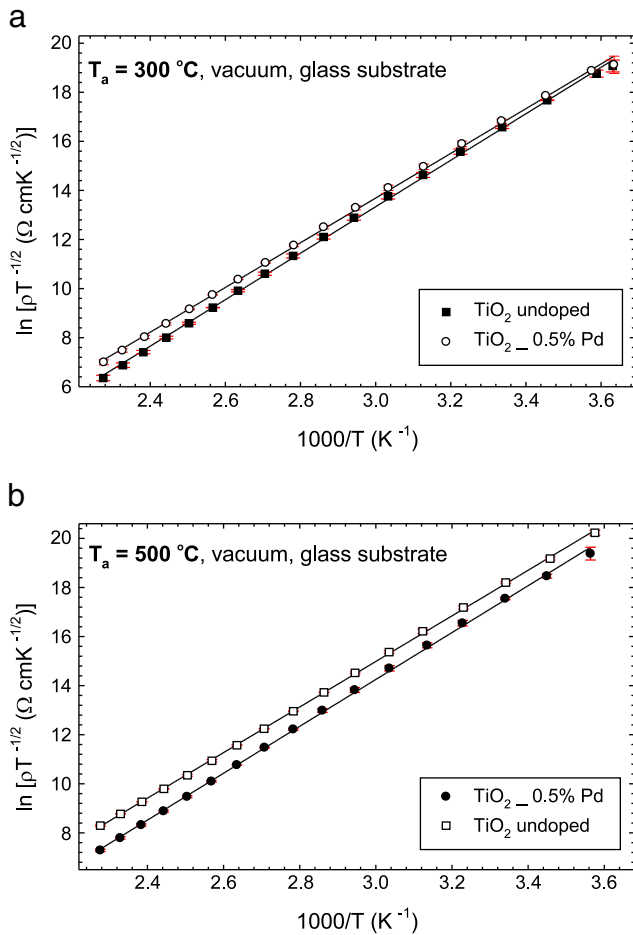
$$E_b = \frac{L^2 e^2 N_d}{8\epsilon} \quad (2)$$

where  $\epsilon$  is the low frequency dielectric constant (taken as 41.4, for the anatase phase [13]) and  $N_d$  is the donor concentration.

We have examined the plots of  $\ln(\rho T^{-1/2})$  vs.  $10^3/T$  in air and in vacuum, for samples deposited on glass substrates. The solid lines in Fig. 2 represent the best fitted values. The linearity of the plots observed in Fig. 2 reveals that, for the studied domain of the temperature, the grain boundary scattering of the charge carriers dominates in the investigated samples. The values of  $E_b$ , calculated from the slopes of these linear dependences, and the values of  $N_d$ , obtained from relation (2), are listed in Table 2. The lowest value of  $E_b$



**Fig. 1.** AFM images of Pd-doped TiO<sub>2</sub> films, deposited on glass and thermally-treated at 300 °C.



**Fig. 2.** Temperature dependence of the electrical resistivity (in vacuum) plotted as  $\ln(\rho T^{-1/2})$  vs.  $10^3/T$  for the samples thermally-treated at 300 °C (a) and 500 °C (b). The solid lines are the best-fit lines. The error bars account for the standard deviation.

is observed for the Pd-doped titania films deposited on silicon substrate and is thermally-treated at 300 °C.

The electrical conductivity of the metal-oxide films depends on the composition of the ambient atmosphere, which makes them useful as gas sensors. Metal-oxide gas sensors can detect reducing gases such as  $H_2$ , CO, etc., as well as oxidizing gases such as  $NO_2$ ,  $O_3$  etc. The presence of the reducing gases in the atmosphere leads to an increase in the electron concentration in the surface layer, decreasing the intergrain barrier height, and finally increasing the electrical conductivity. In the present work, the sensing behavior of  $TiO_2$  thin films exposed to some reducing gases (methane, acetone, ethanol,

formaldehyde and liquefied petroleum gas) was carried out. We have tested the sensitivity of the films deposited on glass and Si substrates (undoped and 0.5% Pd doped  $TiO_2$ ) to these test gases, by measuring their electrical resistance in air and in the corresponding gas atmospheres. To maintain the stability of a sensor, the choice of an optimal operating temperature is necessary. It was found that the optimum operating temperature (where the sensitivity reaches its maximum) is 240 °C (Fig. 3) for the samples under study. In fact, this paper continues the research presented in ref. [4], on the sensitivity of bi-layer Pd-doped  $TiO_2$  films, thermally-treated at 500 °C. Here we refer to the samples thermally-treated at 300 °C.

These films show almost the same behavior as the ones thermally-treated at 500 °C [4], namely, formaldehyde followed by ethanol, and acetone, is the test gas that produces the most significant changes in the electrical resistance of the studied films. An enhancement in the sensitivity in front of all the test gases can be observed for the samples thermally-treated at 300 °C (Figs. 3 and 4). It also could be seen (Fig. 4) that, for the annealing temperature  $T_a = 300$  °C, the samples are more sensitive to methane than to LPG, compared with the samples thermally-treated at  $T_a = 500$  °C (see ref. [4]).

By plotting the dependences of the studied sample sensitivities (at 240 °C), as a function of formaldehyde concentration (Fig. 5), one can see, first, a sharp increase in the sensitivity till around 1000 ppm, then the sensitivity remains almost constant, with a slight increase tendency, till 3000 ppm.

#### 4. Discussion

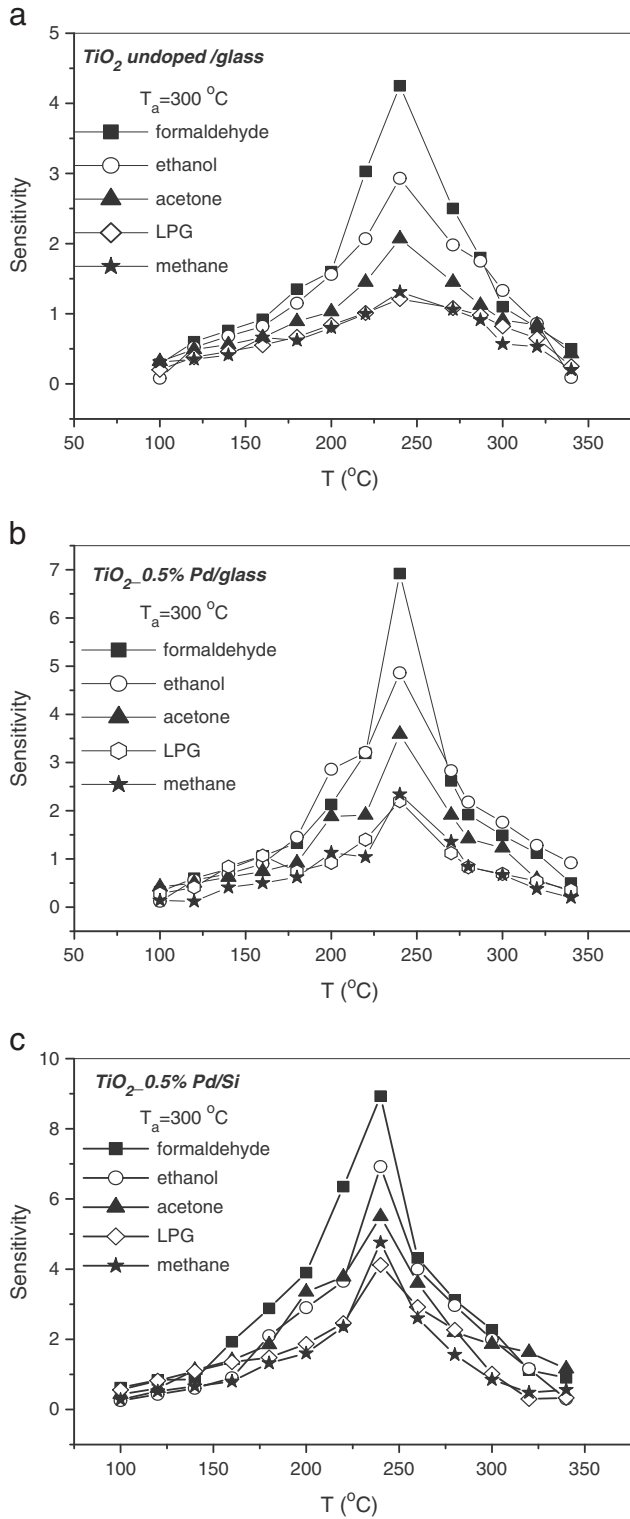
The interplanar distances are correlated with the unit cell volume. In the case of a well formed crystalline phase, a change of the interplanar spacing is reflected in modifications of the unit cell parameters. This supposes a reposition of the atoms from the unit cell. The decrease of the interplanar distances shows a densification of the unit cell due to the presence of Pd ions [3]. All the samples thermally-treated at 300 °C are pure anatase, with crystallite size under 20 nm, while by increasing the annealing temperature till 500 °C, the crystallite size almost double their values and small quantities of rutile appear. The decrease in the rutile phase content by doping is accompanied by the decrease in the average-crystallite size of both phases. Pd inhibits the  $TiO_2$  crystallization.

In Table 2 we have introduced the values of the room temperature electrical resistivity. The resistivity distribution may be related to the native defects, such as oxygen vacancies in  $TiO_2$ , which, in turn, depends on the ambient oxygen pressure [10]. Each oxygen vacancy gives two electrons in the titania conduction band, leading to a decrease of the film's electrical resistivity. The film's resistivity can also change, depending on the substrate nature, doping, or thickness of the  $TiO_2$  film [14,15]. From Table 2, one can see that the room temperature resistivities are higher in ambient air than in vacuum, which agrees well with the results presented in ref. [16]. The thin

**Table 2**

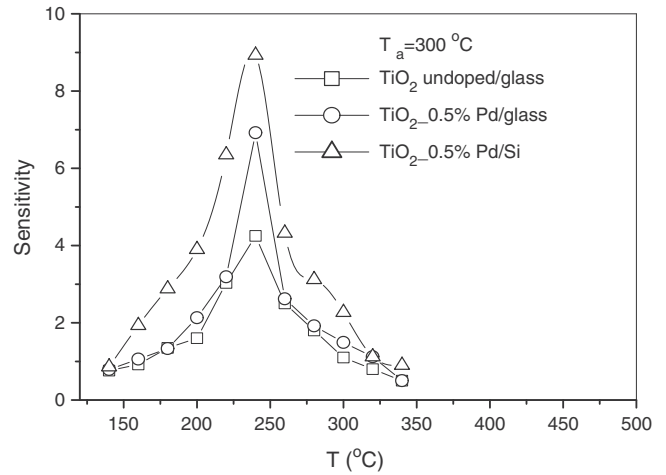
The annealing temperature ( $T_a$ ), the electrical resistivities at room temperature ( $\rho_{RT}$ ), the mean crystallite size ( $L$ ), the barrier height ( $E_b$ ) and the standard errors in determining the barrier height from fitting, the depletion layer ( $l_2$ ), the Debye screening length ( $L_D$ ), the donor concentration ( $N_d$ ) and the correlation coefficients ( $R$ ) for the linear fits presented in Fig. 2 for the studied  $TiO_2$  samples.

| Samples                                     | $T_a$ (°C) | $\rho_{RT}$ ( $\Omega\text{cm}$ ) | $L$ (nm) | $E_b$ (eV)         | $l_2$ (nm) | $L_D$ (nm) | $N_d$ ( $\text{cm}^{-3}$ ) | $R$    |
|---|------------|-----------------------------------|----------|--------------------|------------|------------|----------------------------|--------|
| $TiO_2$ undoped (vacuum, glass substrate)   | 300        | $1.03 \times 10^8$                | 17.3     | $0.817 \pm 0.0051$ | 6.04       | 1.42       | $5.01 \times 10^{19}$      | 0.9993 |
|   | 500        | $5.12 \times 10^8$                | 42.35    | $0.801 \pm 0.0027$ | 14.83      | 3.52       | $8.18 \times 10^{18}$      | 0.9998 |
| $TiO_2$ undoped (air, glass substrate)      | 300        | $1.41 \times 10^8$                | 17.3     | $0.626 \pm 0.0161$ | 6.11       | 1.64       | $3.83 \times 10^{19}$      | 0.9961 |
|   | 500        | $1.11 \times 10^9$                | 42.35    | $0.743 \pm 0.0185$ | 14.97      | 3.69       | $7.58 \times 10^{18}$      | 0.9989 |
| $TiO_{2-0.5\%Pd}$ (vacuum, glass substrate) | 300        | $3.5 \times 10^8$                 | 18.5     | $0.786 \pm 0.0055$ | 6.47       | 1.55       | $4.21 \times 10^{19}$      | 0.9992 |
|   | 500        | $7.1 \times 10^8$                 | 30.1     | $0.824 \pm 0.0051$ | 10.51      | 2.46       | $1.67 \times 10^{19}$      | 0.9994 |
| $TiO_{2-0.5\%Pd}$ (air, glass substrate)    | 300        | $2.65 \times 10^{10}$             | 18.5     | $0.485 \pm 0.0244$ | 6.52       | 1.99       | $2.59 \times 10^{19}$      | 0.9982 |
|   | 500        | $7.19 \times 10^{10}$             | 30.1     | $0.516 \pm 0.0212$ | 10.62      | 3.14       | $1.04 \times 10^{19}$      | 0.9929 |
| $TiO_{2-0.5\%Pd}$ (air, Si substrate)       | 300        | $3.48 \times 10^{12}$             | 18.5     | $0.425 \pm 0.038$  | 6.54       | 2.13       | $2.27 \times 10^{19}$      | 0.9967 |
|   | 500        | $2.91 \times 10^{13}$             | 30.1     | $0.777 \pm 0.048$  | 10.62      | 2.56       | $1.57 \times 10^{19}$      | 0.9912 |



**Fig. 3.** The sensitivity of the studied samples as a function of operating temperature plotted for different test gases: TiO<sub>2</sub> undoped/glass (a); TiO<sub>2</sub>-0.5% Pd/glass (b); TiO<sub>2</sub>-0.5% Pd/Si (c).

film's exposure to ambient air results in oxygen molecule's adsorption at their surface, since in air, the most important reactive gas is oxygen. The adsorbed oxygen gas molecules capture electrons from the conduction band or donor states, leading to the observed increase in the electrical resistivity.

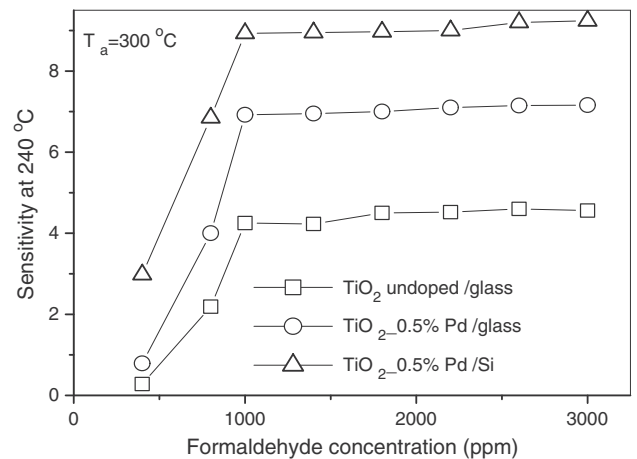


**Fig. 4.** The sensitivity to formaldehyde plotted as a function of operating temperature for the samples thermally-treated at 300 °C.

Two conductivity mechanisms can be considered here [11,12]: the surface trap limited conductivity mechanism, in which the key parameter determining the conductivity is the thickness of the depletion layer ( $l_2$ ), and the barrier-limited conductivity, mechanism in which the key parameter responsible for conductivity is the barrier height at grain boundaries. Either gas adsorption or the formation of oxygen vacancies on the surface leads to the formation of the depletion layer near the surface, which causes changes in electrical conductivity. The electrical properties of the material are influenced by the concentration of chemisorbed molecules. In this process, the adsorbed oxygen molecules may capture electrons from the surface layer of the material. Barrier limited conductivity mechanism is possible only for  $L/2 > L_D$  [11,12] ( $L_D$  is the Debye screening length) and it causes significant changes in the conductivity of the polycrystalline materials. The values of  $L_D$  can be calculated with the following expression [12]:

$$L_D = \sqrt{k_B T \epsilon_0 \epsilon / e^2 N_d} \quad (3)$$

If  $L_D < L/2$ , energy barriers exist at the grain boundary region, due to the surface trap states [12]. If, however,  $L_D$  is larger than  $L/2$ , the conduction band becomes flat, without the energy barrier [12], and



**Fig. 5.** Sensitivity at 240 °C plotted as a function of formaldehyde concentration for the samples thermally-treated at 300 °C.

the electrons are transported without grain boundary scattering. From Table 2, one could notice the very low values for  $L_D$  (less than 4 nm). The fact that the condition  $L_D < L/2$  is fulfilled for the investigated samples, sustain the existence of the energy barriers at the grain boundary region.

The crystallite size has an important effect on the sensitivity. With decreasing crystallite size, especially when the dimension of the crystallite is on order of the depletion layer width ( $l_2$ ), sensor performance significantly increases. The values of  $l_2$ , listed in Table 2, have been obtained with the relation [11,12]:

$$l_2 = L_D \sqrt{E_b / k_B T} \quad (4)$$

It has been reported that the optimum sensitivity can be obtained for small crystallite size, since the film surface area increases [17]. If the crystallite size is much larger than  $l_2$ , band bending is limited only to the surface region of the crystallite. On the other hand, if  $L$  is reduced to  $l_2$ , the properties of the crystallites change and the sensor performance is improved. In ref. [18] it is reported that the best sensitivity of SnO<sub>2</sub> films was obtained if the condition  $2l_2/L > 1$  was fulfilled. In our case, the ratio of  $2l_2/L$  is about 0.7 for the investigated films. Therefore, band bending is limited only to the surface region of the crystallite. Note that the electrical parameters ( $E_b$ ,  $L_D$ ,  $N_d$  and  $l_2$ ) obtained for the investigated samples, appear to be in reasonable agreement with the previous observations for various polycrystalline systems [14,15,19,20]. Thus, the approach of analyzing the data using the grain boundary model for the thermal activation of conductivity is valid for all the samples. Knowing these parameters, could play an important role in metal-oxide gas sensors applications.

Doping with impurities like, Pt, Ag etc., is an effective way to improve sensitivity of the transitional metal-oxide. These impurities decrease the activation energy of the reaction occurring on the surface, and then raise the adsorption activity of the material. The conductivity response can be determined by the efficiency of the catalytic reactions with detected gas participation, taking place at the surface of the gas-sensing material. Such catalytic reactions can control the electronic properties of the material. So, the sensitivity of the film can be significantly enhanced by the chemical modification of the material surface. In light of the above discussion, the improvement of gas sensitivity in the investigated TiO<sub>2</sub> films is anticipated for samples thermally-treated at 300 °C and doped with Pd impurities. Since the crystallite size ( $L$ ) is smaller for the samples annealed at 300 °C, one can expect that the sensitivity will increase whereas it decreases at 500 °C. Also, one can expect that Pd-doping will raise the adsorption activity of the material, leading to an increase in the sensitivity.

The best sensing performance is attributed to 0.5 wt.% Pd doped films deposited on silicon and thermally-treated at 300 °C, which present the highest sensitivities to all the test gases, with a special remark for formaldehyde, where the sensitivity increases from 6.12 to 8.93, with the increasing annealing temperature ( $T_a$ ) from 300 °C to 500 °C. The comparative study for the films TiO<sub>2</sub>\_0.5% Pd/Si, thermally-treated at 300 °C and 500 °C, clearly shows the superiority of titania films doped with 0.5 wt.% Pd deposited on silicon substrates and thermally-treated at 300 °C (Fig. 6a). The films respond relatively fast (400 s) in front of formaldehyde, to reach the highest sensitivity at the optimum operating temperature (240 °C), and at the recovery time being of 300 s. (Fig. 6b).

The sensitivity data could be understood if we take into consideration the adsorption of the oxygen species, present in the air, on the film surface of the films under study. By capturing free electrons, the species are ionized to  $O_{ads}^-$  and  $O_{ads}^{2-}$ . As earlier mentioned, this induces a depletion layer which increases  $E_b$  and the electrical resistance. On the other hand, when the film is exposed to

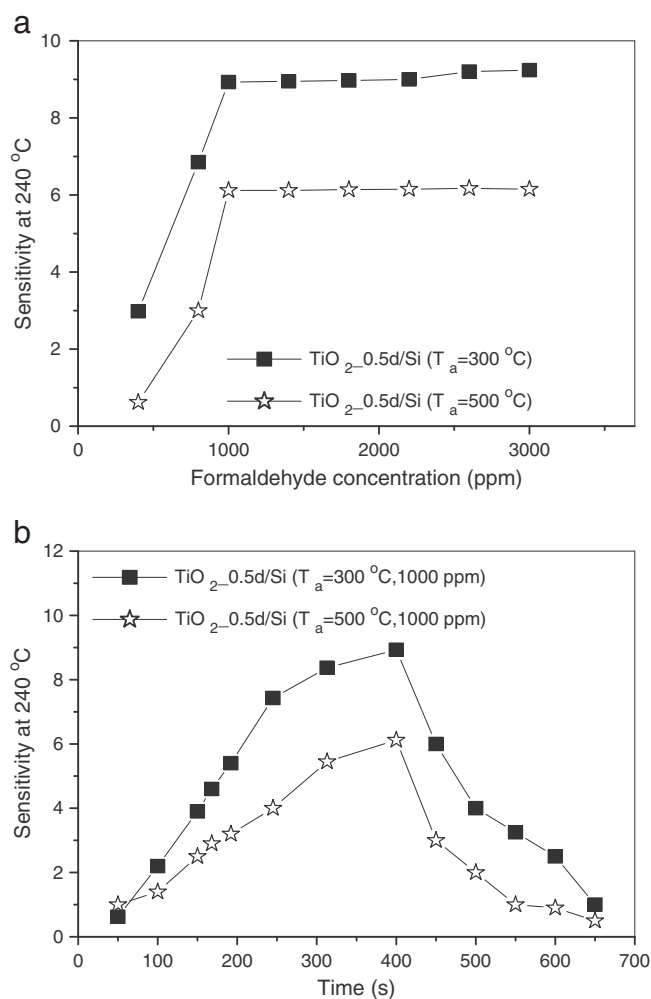
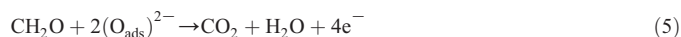


Fig. 6. A comparative study for the films TiO<sub>2</sub>\_0.5% Pd/Si, thermally-treated at 300 °C and 500 °C: (a) The sensitivity at 240 °C, plotted as a function of formaldehyde concentration; (b) Response time in front of formaldehyde, at 240 °C.

formaldehyde (CH<sub>2</sub>O), for instance, the following reaction take place [21]:



This kind of reaction, taking place on the surface area of the film, could release more or less electrons which can affect the decrease in the electrical response, and the increase in the gas response. The maximum sensitivity data (Fig. 3) may be explained by assuming that a maximum in the adsorption equilibrium of oxygen is reached at 240 °C.

## 5. Conclusions

Undoped TiO<sub>2</sub> thin films and palladium-doped (0.5 wt.%) were deposited by the sol-gel method (dip-coating) on glass and silicon substrates. Two sets of samples were investigated: thermally-treated at 300 °C and thermally-treated at 500 °C.

Gas sensitivity studies revealed the superiority of titania films doped with 0.5 wt.% Pd, deposited on silicon substrates, and thermally-treated at 300 °C, that present the highest sensitivities in front of all the test gases, with a special remark for formaldehyde (8.93). In fact, all the sol-gel deposited films are most sensitive to formaldehyde. A significant increase, around 1000 ppm gas

concentration, is observed in the sensitivities of all samples. The film's response is relatively fast—400 s in front of formaldehyde to reach its maximum, while the recovery time is 300 s. At 0.5 wt.% concentration, Pd impurities effectively catalyze the reaction between formaldehyde and adsorbed oxygen, leaving conduction electrons behind and thus increasing the sensitivity of TiO<sub>2</sub> films.

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