

On the sensing gas properties of titanium dioxide films

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In this paper we investigate the gas sensing properties of undoped and Pd-doped TiO₂ thin films obtained by a sol-gel method onto glass and silicon substrates. The sensitivity of these films and the optimum operating temperature were studied for some reducing gases (methane, acetone, ethanol, formaldehyde and liquefied petroleum gas - LPG). Pd-doping (0.5wt.%) induces an increase of the weight percentage of the anatase phase from 74% to 94% and a decrease of both anatase and rutile crystallinity. Films deposited onto glass substrates are almost three times rougher than their counterparts deposited onto silicon substrates. All the studied films are most sensitive to formaldehyde, with a special remark for the Pd-doped ones deposited onto silicon substrates.

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1. Introduction

A lot of harmful gases affect day by day our environment in the detriment of the quality of our life. That is why, it becomes imperious necessary the development of gas sensors devices. Solid state gas sensors are more advantageous than other gas sensors devices (optical or spectroscopic systems), due to their low costs, rapid answer, simple implementation in small spaces (car motors, airplane cabin, etc.). TiO₂ is extensively used as a gas sensing material because of its desirable sensitivity and mainly because of its good stability in adverse environments [1,2].

Among other deposition methods (magnetron sputtering [3-5], pyrolysis [6], etc.), the sol-gel method, based on hydrolysis and polycondensation of metallorganic precursors, allows the obtaining of TiO₂ nanostructured thin films with an excellent compositional control, by simply varying the experimental conditions during the gel formation stage [7,8]. The sol-gel method is adequate for high purity and homogeneous film preparation. It is very well known that the alkoxides are certainly the most common and well-established precursors used in the sol-gel route. The reaction of hydrolysis-condensation with small water content lead to linear polymers from which thin films can be deposited, before gelation of the sol, by common processes such as dipping and spinning. The formation of such networks can be very important for microstructure and crystalline phase development when the coatings are heat treated to obtain the crystalline ceramics. TiO₂ doped by metals (Ce, Nb, Fe) have been already reported by one of us [9]. There are few literature data regarding the use of Pd as cation dopant in a sol-gel TiO₂ matrix. So, we proposed in this paper, a

study of the structural, morphological and gas sensing properties of undoped and Pd-doped TiO₂ sol-gel films.

2. Experimental

Sol-gel method was used to prepare undoped and Pd-doped TiO₂ thin films. The reagents employed were tetraethylorthotitanate, Ti(OC₂H₅)₄ as TiO₂ source, palladium acetylacetonate, Pd(acac)₂ as palladium source (Pd²⁺ = 0.5%), absolute ethyl alcohol as solvent, nitric acid as catalyst and H₂O for hydrolysis. The hydrolysis reaction was carried out in a closed system in nitrogen atmosphere, under vigorous stirring. Supported TiO₂ films (mono and bi-layers) have been obtained by dip coating onto glass and silicon wafer substrates.

The unsupported porous materials, resulted from the gelling of the starting solutions at room temperature, were dried at 80°C and then thermally treated at 500°C, for an hour, with a heating rate of 1°C/min. The densification of the films was realized at the same temperature. The deposition of the second layer was realized after the densification of the first one at 300°C.

The structure of the thin films and unsupported gels was examined by X-ray diffraction technique (Bruker-AXS, D8 Advance type with copper radiation) using an XRAY5.0 program [10].

The thin film morphology was investigated by using a home made AFM equipment.

The thickness of thin films was measured by using an ellipsometric method and found to be 37-53 nm for one coating and 69-95 nm for two coatings.

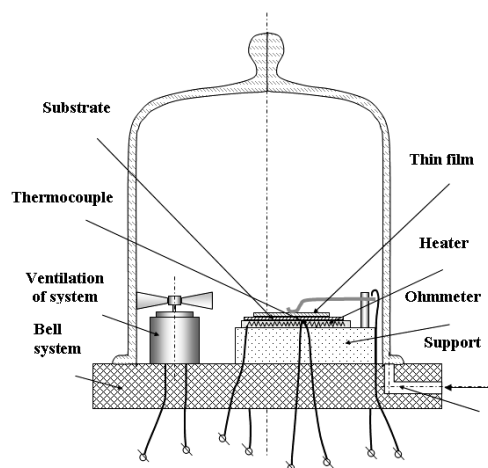


Fig.1. Experimental setup

For gas sensing measurements, the sample was mounted on a heater and placed in a glass enclosure capable of controlling the different gas concentrations (Fig. 1) [11,12]. The gas sensing was performed in the temperature range from 100°C to 340°C. A chromel - alumel thermocouple placed in the glass chamber indicates the working temperature. Acetone, ethanol, methane, formaldehyde and LPG were used as test gases, their concentration being maintained constant (1000ppm). During the cooling process, the samples continued to be exposed to test gases.

A semiconducting gas sensor change its electrical conductivity when exposed to different gas atmosphere. The mechanism usually depends on the operating temperature, which is optimal depending on the sensor material properties and on the selected gas atmosphere. The electric resistance of the thin film sensor in test gases (R_g) and in pure air (R_a) was measured, and the gas sensitivity (S) was determined as:

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a} \quad (1)$$

3. Results and discussion

Because the films are very thin (under 100nm), their diffraction pattern are covered by the substrate diffraction pattern (amorphous for the glass substrate and polycrystalline for silicon). For this reason, the crystallization study was accomplished on un-supported gels resulted from the gelation of the starting solutions used for the films preparation. From Fig. 2 one can observe that Pd-doping (0.5wt.%) induces an increase of the weight percentage of the anatase phase from 74% to 94%. Our calculations showed that the mean crystallite size decreases from a value of 44 nm to 31nm for the anatase phase and from 41 nm to 30nm for the rutile phase.

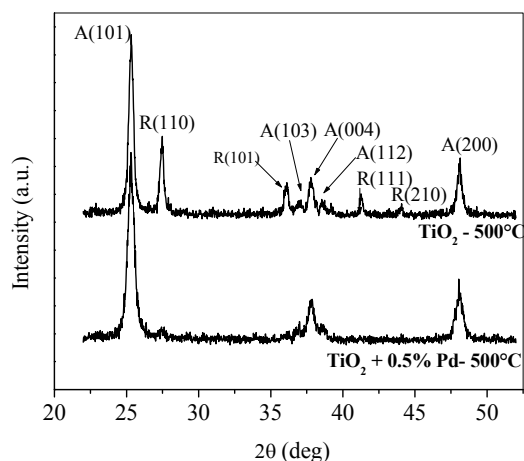


Fig. 2. XRD pattern of corresponding un-supported gels.

All the studied sol-gel films have smooth nanometer granular structures, but the films obtained onto glass substrates are almost three times rougher (the root mean square roughness (R_{rms}) of about 6.4 nm) than their counterparts deposited onto silicon substrates (the root mean square roughness of about 2.2 nm). From Fig. 3 it can be observed an improvement in the crystallization for the two-layered films deposited onto silicon.

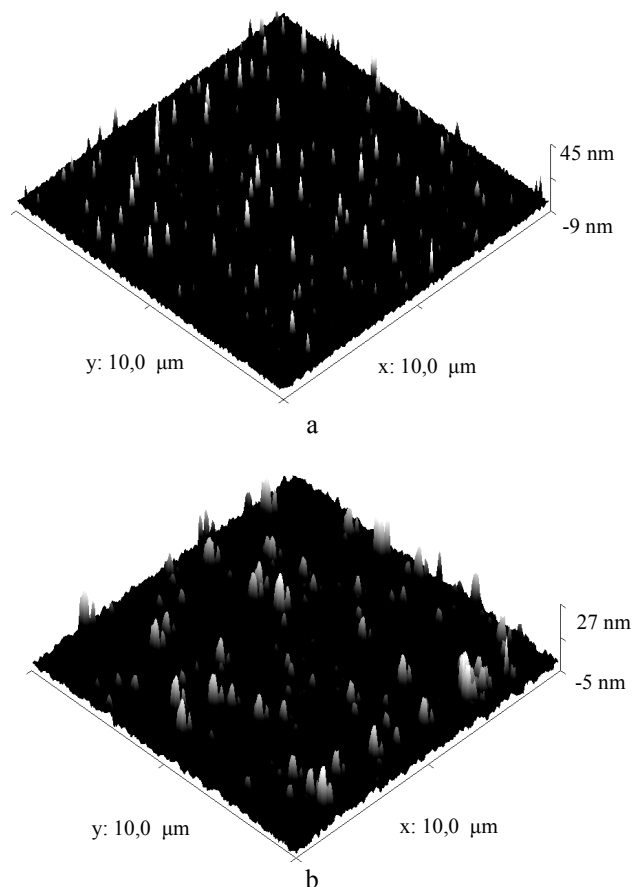


Fig. 3. 3D-AFM images of thin films
(a) $\text{TiO}_2/\text{Si}_{0.5\% \text{Pd}_1}$ coating ($R_{rms}=2.26\text{nm}$);
(b) $\text{TiO}_2/\text{Si}_{0.5\% \text{Pd}_2}$ coatings ($R_{rms}=2.20\text{nm}$).

The sensitivities to five test gases were determined for each thin film under study, by measuring their electrical resistance in air and in the corresponding gas atmospheres, at a certain gas concentration, using the relation (1). From Fig. 4, a maximum sensitivity value can be observed

around 240°C, which is the optimum operating temperature. Formaldehyde followed by ethanol, acetone, LPG and, at the end, methane, is the test gas that produces the most significant changes in the electrical resistance of all the studied films.

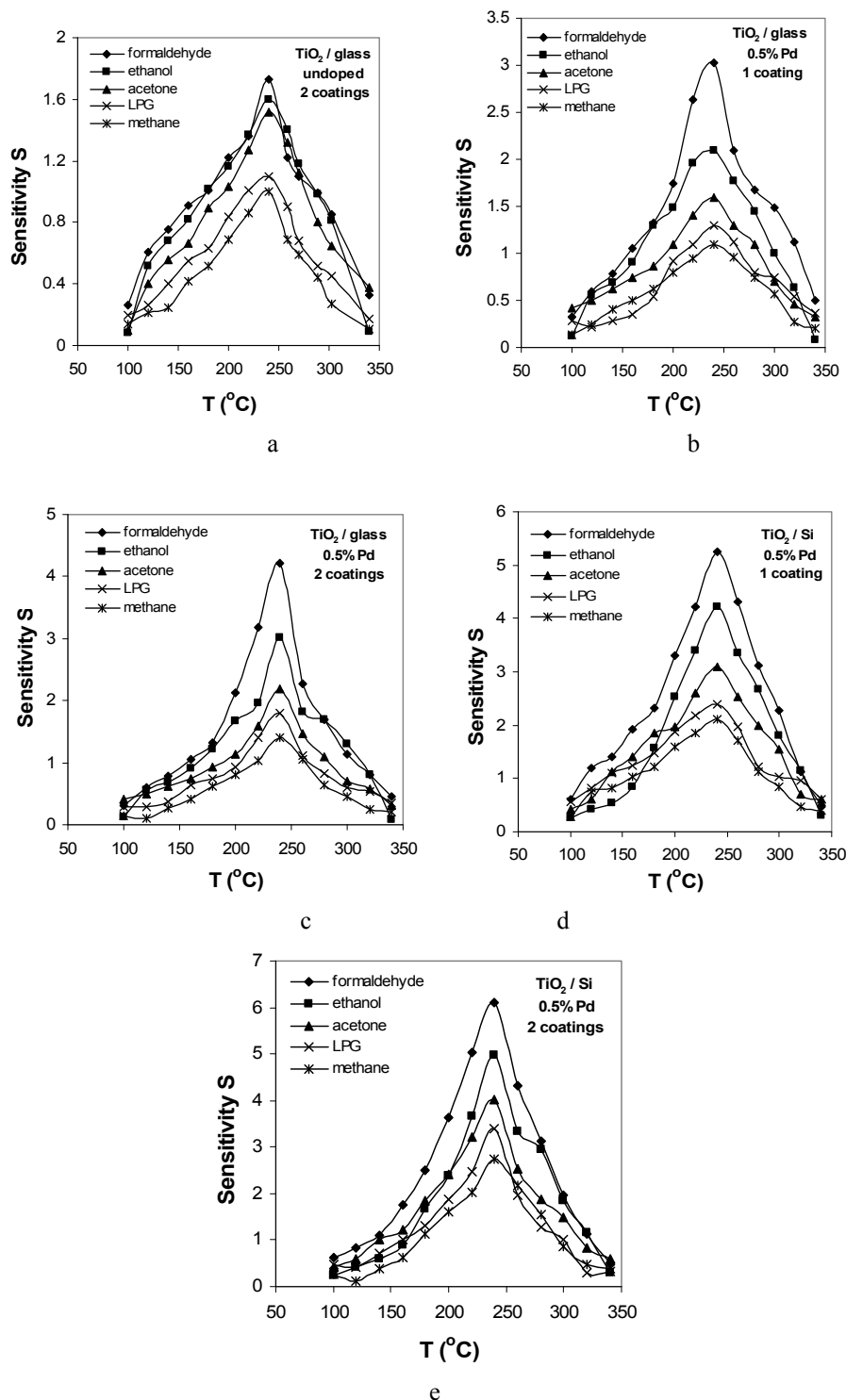


Fig. 4. Sensitivity of the studied samples as a function of operating temperature plotted for different test gases:

- (a) TiO_2 /glass_undoped_2coatings;
- (b) TiO_2 /glass_0.5%Pd_1coating;
- (c) TiO_2 /glass_0.5%Pd_2coatings;
- (d) TiO_2 /Si_0.5%Pd_1coating;
- (e) TiO_2 /Si_0.5%Pd_2coatings.

In Fig. 5(a) there is a comparison between the sensitivities to formaldehyde for all samples, as a function of operating temperature. For a better understanding, Fig. 5(c) gives the corresponding bar diagram, at 240°C, showing the highest sensitivity, of 6.12, to formaldehyde for the 2-layered TiO_2 films deposited onto silicon and doped with 0.5wt.% Pd, and the lowest sensitivity, of 1.73, to the same gas for the 2-layered undoped TiO_2 films deposited onto glass substrate. An explanation may be related to the decrease, observed by doping, in the mean sizes of both anatase and rutile crystallites, knowing that nanosized grains could increase the sensing materials properties [13].

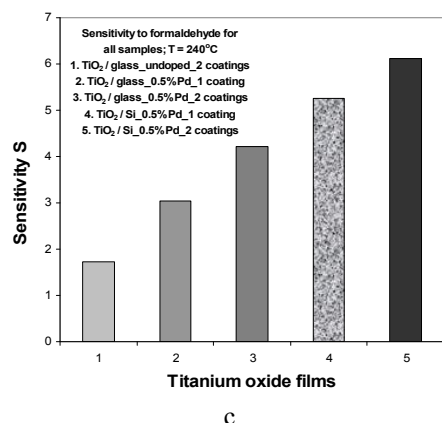
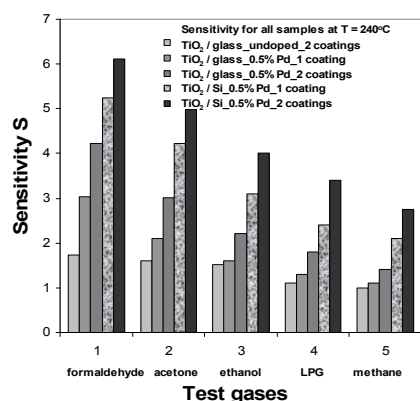
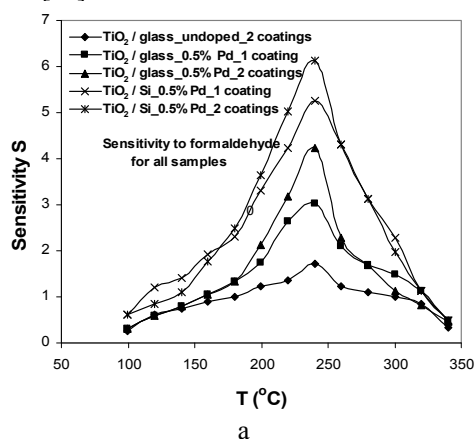


Fig. 5. (a) Sensitivity to formaldehyde for all samples; (b) bar diagram for all samples for different test gases, at 240°C; (c) bar diagram for all samples for formaldehyde at 240°C.

4. Conclusions

Gas sensitivity studies were performed on undoped and 0.5 wt.% Pd doped TiO_2 thin films obtained by a sol-gel method onto glass and silicon substrates (1 coating and 2 coatings). Pd-doping determined an increase in the weight percentage of the anatase phase, together with a decrease in the mean sizes of both anatase and rutile crystallites. Five reducing gases: methane, acetone, ethanol, formaldehyde and LPG were used as test gases. As a general remark, an improvement in the crystallization for the 2-layered films is observed, these films being also more sensitive to all gases under study than the one-layered films. The studied films are very sensitive to formaldehyde, with a special remark for the two layered Pd-doped ones, deposited onto silicon substrates.

Acknowledgements

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