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Gas sensing materials based on TiO₂ thin films

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TiO₂ thin films were prepared by spray pyrolysis using a solution of titanium tetrachloride and ethyl alcohol. The deposition was performed onto different substrates (silicon, quartz, glass) maintained at the same temperature, 270 °C. After annealing, a predominant rutile structure is obtained for films deposited onto silicon and quartz substrates, as revealed by x-ray diffraction patterns. The TiO₂ films were exposed to different gases, at different temperatures, in order to evaluate their gas sensitivity. The optimum operating temperatures, showing the highest gas sensitivity, were determined for some gases (acetone, ethanol, methane, and liquefied petroleum gas).

I. INTRODUCTION

Every day our environment is polluted with harmful gases originated from industry activities, car engines, etc. For controlling the quality of air, it becomes imperious necessary the development of the gas sensors devices.¹⁻⁷ Solid state gas sensors gain more and more over the spectroscopic devices because of economic reasons (low costs), rapid response, simple implementation in small spaces such as airplane cabin, for example, etc. Semiconductor metal-oxide gas sensors are preferred, and the transition metal oxides (TiO₂, SnO₂, etc.) in thin films appear to be the best candidates.³⁻⁷

In recent years, much effort is made for improving the selectivity and sensitivity of gas sensors. Nanocrystalline films are promising materials for improved sensitivity. Greatly improved sensing properties were reported for grain sizes in the 5–50 nm range.⁸⁻¹⁰ Nanosized grains are preferred for the sensing materials because they increase the specific surface area exposed to gas.⁸ The critical particle size where a substantial improvement is observed depends on oxide material, dopant, and processing method. The sensitivity of these devices is based on the dependence of the conductivity of metal oxides on the surrounding atmosphere.

In this article we have chosen to investigate the sensing properties of titanium oxide thin films because of their attractive properties (durability, high chemical stability in hostile environments, thermal stability in high temperature environment, etc.).

TiO₂ is extensively used in gas sensing because of its desirable sensitivity and mainly because of its good stability in adverse environments. TiO₂ crystallizes in one stable phase, rutile (tetragonal) and two metastable polymorph

phases, brookite (orthorhombic), and anatase (tetragonal). Both metastable phases become rutile (stable) when submitting the material at higher temperatures (in pure state, when no additives have been added).

Different deposition methods are used to obtain these films (sol-gel,¹¹ magnetron sputtering,^{12,13} pyrolysis,¹⁴ etc.), but spray pyrolysis is preferred here because it allows the deposition of rougher films, onto larger surface area, at lower costs than other methods. The deposition is made at atmospheric pressure and, by using a wide variety of solution, dopants can easier be incorporated into the matrix of the film. Together with the sensitivity and selectivity, the stability of the sensing gas films is another important characteristic, which can be achieved by submitting the obtained films to thermal treatment at high calcination temperatures (400–1000 °C); the aim being to obtain the rutile phase, the most stable thermodynamic phase of TiO₂. Here we explore the gas sensing properties of the rutile titanium oxide, which are subjected to the substrate nature.

II. EXPERIMENTAL

Titanium oxide thin films were prepared by a spray pyrolysis method. The solution made from a chemical metal precursor (0.48 cm³ TiCl₄) dissolved in ethyl alcohol (5 cm³) is sprayed onto different substrates (Si[100], p, quartz, glass). The deposition consisted in three identical stages repeated from 10 to 10 min. Each stage involved five identical steps (a step: 5 s of spraying followed by 15 s of pause). The substrate holder (heated at 270 °C), placed in front of the sprayer at a distance of 16 cm, was inclined at 55° (with an estimated accuracy of one minute) in respect with the horizontal plane. Our studies have shown that for

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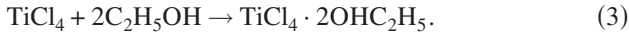
this angle of inclination, the obtained films are more uniform (the impact velocity depends on the substrate inclination angle).

A pyrolytic reaction takes place on the substrates and a nanocrystalline metal oxide is produced. The usual expressions for this reaction are



The TiCl_4 hydrolysis reaction is very fast and exothermic.

In order to obtain dimensions in the nanometric range, it is important to use very low water concentrations. In our case the water source was ethyl alcohol (maximum of 4% water). In water-free ethyl alcohol, TiCl_4 is soluble and forms the following adduct:



The as-deposited thin films were subsequently annealed at 450 °C in air for 4 h. The structure of the thin films was examined by x-ray diffraction technique in the standard θ - 2θ configuration ($\text{Cu } K_\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$).

Film thickness was measured by a stylus profilometer (Dektak) and found to be around 200 nm.

The weight percentage of the rutile phase and the mean grain size values for the anatase phase and for rutile phase were calculated using, respectively, the anatase $A(101)$ and rutile $R(110)$ most intense peaks, the methods being described elsewhere.¹²

For electrical resistance measurements, a two-point method was used. Silver electrodes, placed parallel one to each other at a distance of 0.5 mm, were deposited by thermal evaporation onto the studied titanium oxide films.

The gas sensing was performed in the temperature range of 100–350 °C; each sample being mounted on a heater placed in a glass enclosure capable of controlling the different gas concentrations.^{15,16} During the cooling process, the samples continued to be exposed to test gases.

A thermocouple, fixed on the sample surface, allowed to measure the working temperature with a sensitivity of $\pm 3 \text{ }^\circ\text{C}$. Some gases such as acetone, ethanol, methane, and liquefied petroleum gas (LPG) were used to test the response of the studied films, at a concentration of 1000 ppm of analyte.

The electric resistances of the thin film sensor were measured in test gases (R_g) and in pure air (R_a), and the gas sensitivity (S) was determined as

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a}. \quad (4)$$

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analyses showed that the as-deposited thin films have an amorphous structure. After a subsequent annealing at 450 °C, in air, for 4 h, they become polycrystalline, an exception occurring for the films deposited onto glass substrates, which remain amorphous even af-

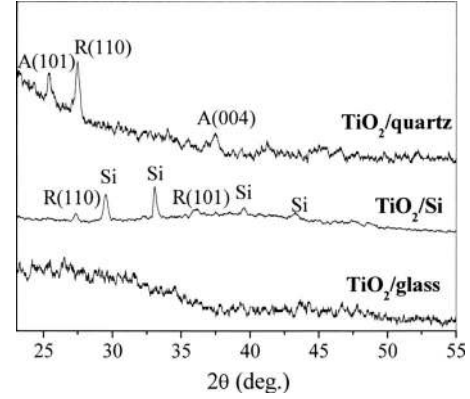


FIG. 1. XRD patterns ($\text{Cu } K_\alpha$) plotted for the studied samples.

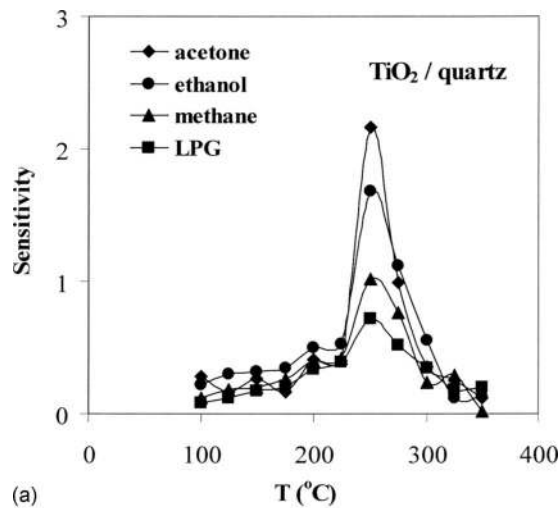
ter annealing. In our previous work we have established how the deposition parameters influence the structure of titanium oxide films and, as a consequence, their electrical, optical, and hydrophilic properties.^{12,13,17–20} One of the most important parameter, as established in Refs. ^{12,20}, is the substrate nature. The mobility of the adatoms on the substrate surface, which is responsible for the degree and type of nucleation on the substrate, depends on its nature. Polycrystalline thin films with pure rutile structure, as shown by x-ray diffraction patterns (Fig. 1), were obtained, after annealing, for films deposited onto $\text{Si}[100]p$ substrate. On the quartz substrates, the weight percentage of the rutile phase is in proportion of 72%, with a major reflexion along $R(110)$. The polycrystalline thin film $\text{TiO}_2/\text{quartz}$ contains a mixture of anatase and rutile crystallites, both having the average size of 34 nm, as calculated¹² using the $A(101)$ and rutile $R(110)$ peaks. These grains are considerably larger than those of rutile in the TiO_2/Si sample (average value of 23 nm).

The surface conductivity of semiconducting titanium oxide films depends on electron concentration near the surface and may be affected by the nature of the chemisorbed species.

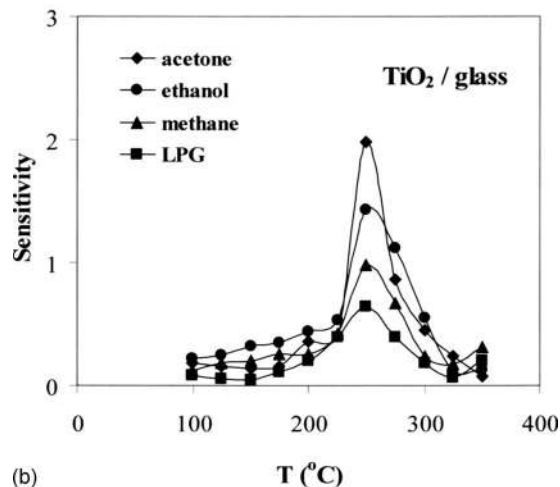
By measuring the electrical resistance of each sample in air and in different gas atmospheres at a certain gas concentration, the sensitivity of each film was determined for each test gas, using the relation (3).

Vapors of acetone, ethanol, liquefied petroleum gas, and gases, such as methane, react with the chemisorbed oxygen, reducing the resistance of titanium oxide films. Such changes are caused by the formation of a space charge region induced by either gas adsorption or by the formation of oxygen vacancies on the surface.²¹ Improved efficiency and sensing selectivity of these devices require detailed understanding of the surface and interfacial processes at the atomic level and their relationship with material properties.

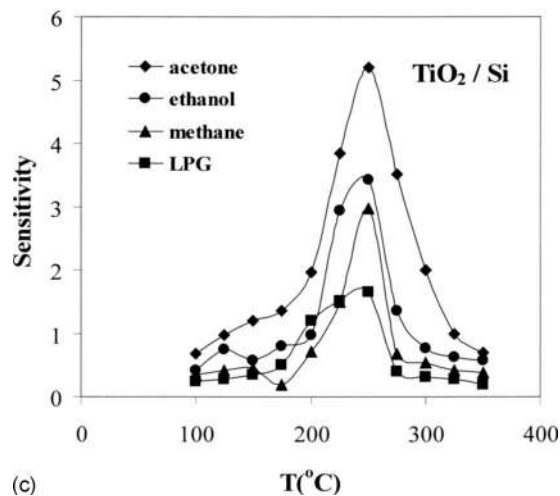
From Fig. 2 it can be seen that, by increasing the operating temperature, the sensitivity of all the studied titanium oxide thin films increases, reaching a maximum value corresponding to an optimum operating temperature. The films are the most sensitive to acetone and less sensitive to LPG. For $\text{TiO}_2/\text{quartz}$ and $\text{TiO}_2/\text{glass}$, there is a small increase in the sensitivity for acetone to the maximum values of 2.16 and



(a)



(b)



(c)

FIG. 2. Sensitivity to different gases plotted as a function of operating temperature for (a) $\text{TiO}_2/\text{quartz}$, (b) $\text{TiO}_2/\text{glass}$, and (c) TiO_2/Si .

1.98, respectively, at optimized operating temperature of 250°C , whereas for TiO_2/Si sample, the sensitivity is significantly higher, having the maximum value of 5.2, at 250°C . Above the optimum operating temperature, the sensitivity decreases; the difference between the resistance in air

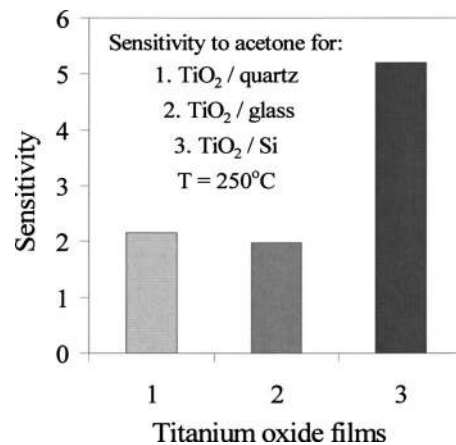


FIG. 3. Sensitivity to acetone at 250°C for all the studied samples (bar diagram).

and in the gas test becomes insignificant at about 350°C . One can observe that the films deposited onto silicon are the most sensitive not only to acetone but also to the other gases, comparing to the TiO_2 films deposited onto quartz and glass substrates. An explanation of the best performances of these films can be related to the fact that they are more fine grained than the others, as observed from the XRD patterns. Moreover, as it is known, the conduction mechanism in polycrystalline metal oxides strongly depends on the morphology of the layer and the grain size of the metal oxides.²² As Rothschild and Komem specified²³ that the effect of the grain size on the sensing performance is still under debate, but it was demonstrated, and our results confirm, that a decreasing grain size enhances the performance of a sensor, namely, its sensitivity. So, the desired operating regime of modern sensors would be the one in which the overall conductivity is determined by nanocrystalline sensing materials.

The electrochemical properties depend not only on the specific surface area exposed to gas but also on the density and type (Ti or O) of surface sites available for gas adsorption, which are different for each plane, in the rutile and anatase phases. So, the response can be also related to the anatase/rutile percentage. The rutile structure of these films offers another desired property for a sensor, namely, its stability.

A bar diagram is presented in Fig. 3 showing the highest sensitivity (at 250°C) to acetone for TiO_2 sample deposited onto silicon substrate.

IV. CONCLUSIONS

Titanium oxide thin films were deposited by spray pyrolysis onto different substrates (quartz, glass and silicon). After subjected the amorphous as-deposited films to an annealing process, we have investigated their sensing properties to four reducing gases: acetone, ethanol, methane, and LPG. All the films are sensitive to acetone, with a special remark for the titanium oxide films deposited onto silicon substrates. In fact, the rutile films, obtained onto silicon, being more fine grained, are the most sensitive to all gases, and they offer the

necessary stability for a sensor due to the fact that the rutile phase is the thermodynamically stable phase in titanium dioxide films.

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