DOI 10.5162/IMCS2012/8.3.5

Gas sensitivity of different metal oxide nanostructured thin films

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Abtract

Two different techniques were used for manufacturing thin films of SnO_2: RGTO [1] and pore wetting [2-4]. The former produces a microstructure formed by nanograins obtained and the latter a microstructure consisting of nanotubes. The film of SnO_2 nanotubes shows good sensitivity to volatile gases and an unusual sensitivity even at room temperature. SnO_2 microrods exhibited an ultra-fast photo-response when light of 402-940 nm wavelength was switched on and off. Furthermore, TiO_2 gas sensors were prepared by anodic oxidation method. The morphology of the TiO_2 nanostructures were characterized by scanning electron microscopy (SEM), Xray diffraction (XRD) and Raman spectroscopy. At room temperature, the sensors exhibited highly sensitive and fast response-recovery (less than 2 min) to NH_3 gas of concentrations ranging from 50 to 200 ppm.

Key words: gas sensor, nanograins, nanotubes, microrods, SnO_2, TiO_2

Introduction

Sensors based on SnO_2 are widely used to detect very low concentration of different gases. There are a lot of techniques to obtain SnO_2 films such as physical vapor deposition, magnetron sputtering [5], thermal evaporation [6], spray pyrolisis [7], laser pulses deposition [8] and chemical vapor deposition [9] .

A new generation of SnO_2 nanostructures has been produced recently, such as nanowires, nanobelts, nanorods, nanotubes and nanowhiskers [10, 11]. One of the main features of these nanostructures is the surface/volume relationship that makes them attractive to use as sensitive film gas sensors. The present challenge now is to achieve a manufacturing process of nanostructures compatible with micromachining processes.

Throughout this process we used two different manufacturing techniques to develop thin films of SnO_2: RGTO and pore wetting. From the first one, microstructures formed by nanograins were obtained and from the second microstructures consisting of nanotubes were obtained. A comparison of the electrical response for the sensitive films obtained from different volatile gases.

Experimental

SnO_2 thin films were obtained by Rheotaxial Growth and Thermal Oxidation (RGTO) [1] and pore wetting [2-4]:

a) The RGTO technique is carried out in two steps. In first step Sn was deposited over silicon nitride for physical vapor deposition. In the second step the samples underwent a thermal treatment at 873 K in wet air. The surface morphology of the films was examined with X-Ray Diffraction, Scanning Electron Microscope and Atomic Force Microscopy. Figure 1 show a typical morphology of the film where a microstructure formed by nanograins can be observed.

The film shows a high specific surface area, which is a prerequisite for gas sensing applications.

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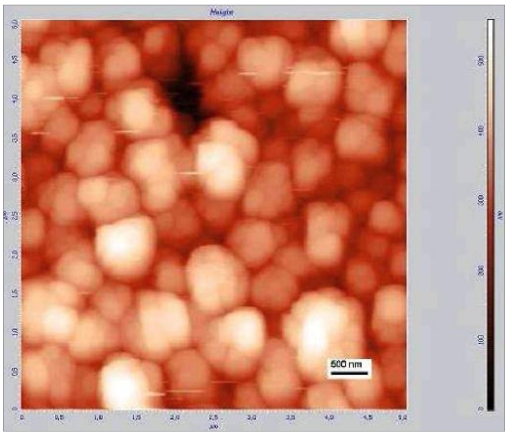

Fig. 1. AFM micrograph obtained by RGTO techniques, spherical structure typical of SnO_2 is evident.

b) The porous polycarbonate film was fixed to the silicon nitride surface and a thermal treatment at 873 K in air was performed. The resulting materials were nanotubes sintered onto the surface; no contamination was observed due to the total decomposition of the porous polycarbonate film and the electrical contacts were print during this treatment (see Figure 2).

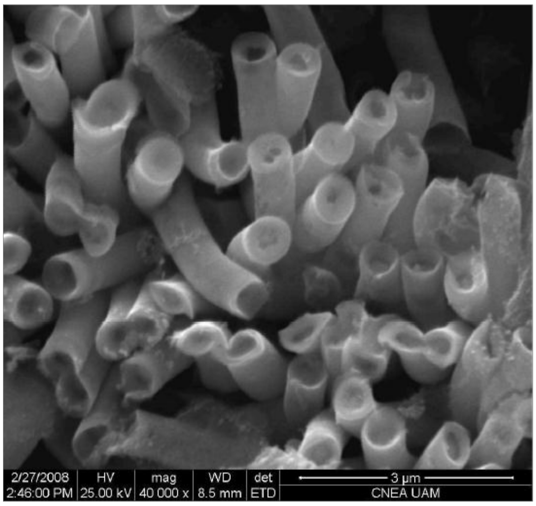

Fig. 2. SEM micrograph obtained by pore wetting techniques.

For electrical measurement, sensors were located in a chamber (volume 3500 cc) where gases flow at a total and constant rate of 300 sccm. Changes in sensor electrical resistance were measured by voltmeter (Keithley 2000) and impedance analyzer (Solartron 1260A). these measurements were performed at different temperatures, in presence of air and vapor isopropyl alcohol.

Finally, the TiO_2 gas sensors were fabricated on a (100) p-type Si wafer with 300 nm layer of SiO2. A Titanium layer of 600 nm thickness was deposited by RF magnetron sputtering. scanning electron microscope was employed for the morphological characterization of the TiO_2 nanostructured samples (Fig. 3); what we see there can be nanotubes with a diameter less than 50 nm.

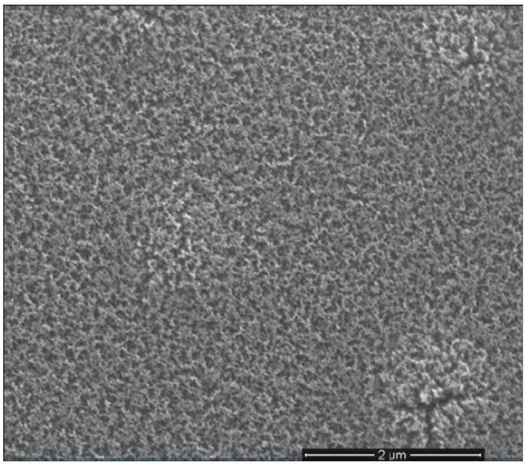

Fig. 3. SEM images of TiO2 thin film.

Results

Electrical measurement of resistance

Typical electrical response to isopropyl alcohol vapor, for both RGTO and pore wetting SnO_2 films, is shown in Figure 4 (at temperature higher than room temperature) and Figure 5 at room temperature.

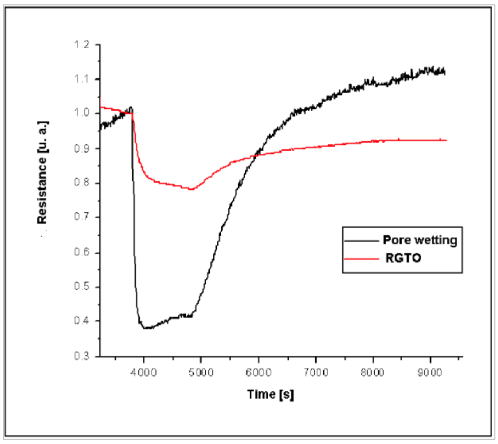

Fig. 4. Comparison of responses from SnO2 film obtained by RGTO and pore wetting at 482 K.

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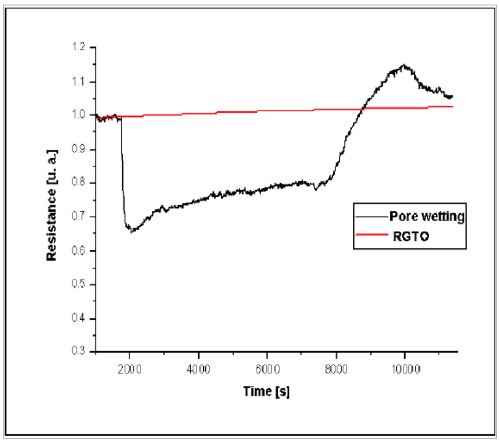

Fig. 5. Comparison of responses from SnO2 film obtained by RGTO and pore wetting at room temperature.

Figure 4 shows that the sensitivity of the vapor isopropyl alcohol nanotubes film is greater than the RGTO film. Figure 5 shows that the nanotubes film is sensitive to isopropylic gas even at room temperature.
In the case of the TiO2 gas sensors the response is showed in Fig. 6.

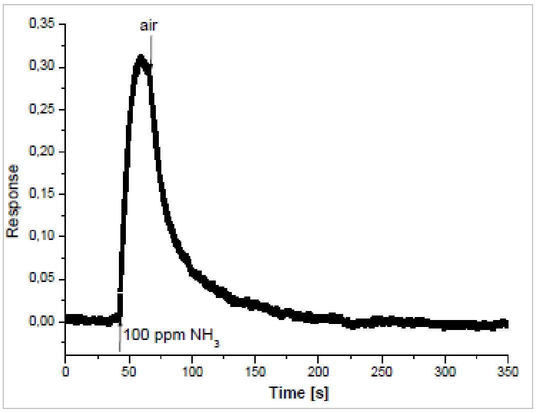

Fig. 6. Electrical response of TiO2 thin film to 100 ppm NH3 at room temperature.

Electrical measurement of impedance

The frequency dependent properties of a material are generally described by complex impedance plots, where the impedance Z is given by:
Z = Z' – i Z''.
Z' and Z'' being the real and imaginary parts of the impedance, respectively.
Figures 7 and 8 show measurements of complex impedance in air and isopropyl alcohol vapor from both films at room temperature.
Relating to the complex impedance spectra in Fig. 7, a semi-circular arc corresponds to a distributed R-C element and these figures are practically the same for both air and isopropyl alcohol vapor. The equivalent circuit for complex impedance plots in Fig. 7can be explained by a resistance (Rgb) and capacitance (Cgb) in parallel where Rgb is the grain boundary resistance and Cgb is the grain boundary capacitance. The optimum values for Rgb and Cgb are ~ 54 kW and 50 pF respectively.

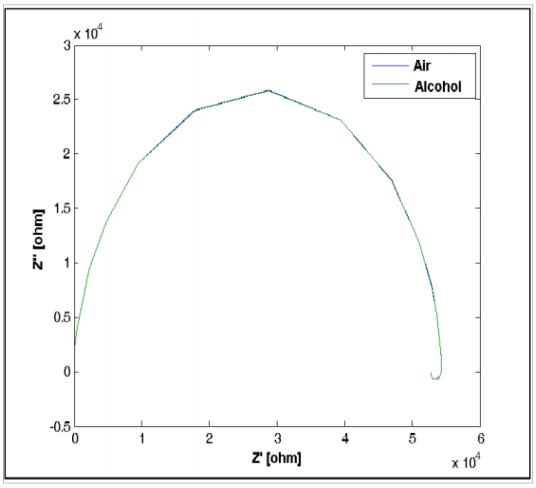

Fig.7. Complex impedance in air and isopropyl alcohol vapor from the RGTO film.

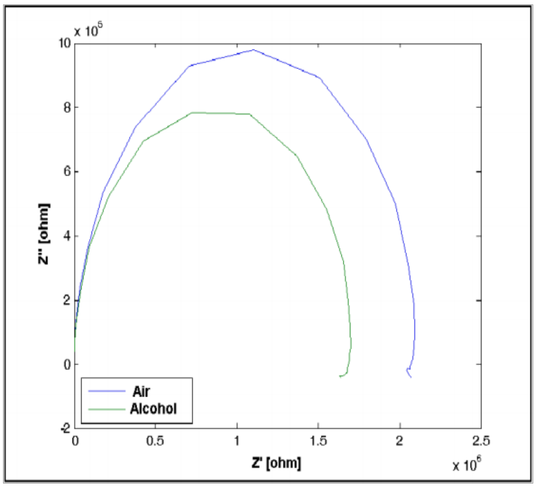

Fig. 8. Complex impedance in air and isopropyl alcohol vapor from the RGTO film.

The impedance spectra in Fig. 8 are also a semi-circular arc corresponding to a distributed R-C element. However, the figures are different for air and isopropyl alcohol vapor. The equivalent circuit for complex impedance plots in Fig. 8 can also be explained by a resistance and capacitance in parallel. The optimum values for Rgb and Cgb in air are ~ 2000 kW and 8 pF respectively. In contrast, isopropyl alcohol vapor the optimum values for Rgb and Cgb are ~ 1700 kW and 10 pF respectively. In presence of isopropyl alcohol vapor, Rgb decreases and at the same time Cgb increases. The increase in the capacitance with exposure gas is attributed to a reduction in the width of the depletion region.

SnO_2 microrods exhibited an ultra-fast photo-response when 402-940 nm light was switched on and off. SnO2 microrods films were prepared with $SnCl_4$ as the starting material.We found that increasing light radiation flux decreases the resistance [12].

Discussion

It is well known that the microstructure of the sensing film depends on grain size among other variables.

Currently, most of the semiconductor gas sensors based on SnO_2, TiO_2, ZnO, etc exhibit gas sensitivity only when these are heated to several hundred degrees.

However, SnO_2 sensors fabricated by the hydrolysis of $SnCl_4$ exhibit sensitivity to the saturated vapor of alcohol at room temperature [13]. This can't be explained solely by the size of the grains, since the SnO_2 sensors obtained from other techniques do not present sensitivity to alcohol vapor at room temperature. One of the possibilities is that a high surface/volume microstructure relationship was obtained by the hydrolysis of $SnCl_4$.

Two different techniques were used to prepare thin films of SnO_2: RGTO and pore wetting. From the first one a microstructure formed by nanograins was obtained and from the second, a microstructure consisting of nanotubes was obtained.

Sensitivity to isopropyl alcohol at room temperature was reached only for the nanotube sensors film, highlighting the central role played by the microstructure of thin-film within its properties. Possibly, microstructures with a high surface/volume relationship would be more adequate for gas sensors. Determining the optimal microstructure in order to enhance sensitivity is a very appealing line for future work.

When the light was switched on, the intensity was increased, the oxygen species (O_2^- and O^- depending on the temperature) were removed from the surface. Finally, when the ligth was switched off, the oxygen species were re-absorbed on the surface.

Conclusions

Thin film of SnO_2 gas sensor with microstructures formed by nanotubes is sensitive to isopropyl alcohol vapor even at room temperature.

The results obtained with ligth show that SnO_2 thin film have an ultra-fast photo-response for wavelength in the range of 402-940 nm. These results indicate that the photoinduced effect has strong dependency of nanostructures.

It is important to highlight that the techniques used in its fabrication, namely pore wetting, are compatible with the sensors microfabrication.

Acknowledgements

This work was supported by CNEA (Comisión Nacional de Energía Atómica), CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and ANPCyT by means of grant PMTIII BID 1728/OC-AR No. 22592.

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