Response enhancement of sprayed ZnO thin film-based NO_2 sensor by indium-doping

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The development of a sprayed ZnO thin film-based NO_2 sensor is reported. The effect of In-doping on the sensor performance is studied. With the addition of 3 wt % of indium nitrate to the spraying solution, a good sensor response to 5 ppm of NO_2at 275°C and an important decrease in the device electrical resistance is obtained. The dependence of the electrical resistance on temperature in several gas atmospheres is also considered. A possible sensitization mechanism is discussed.
Keywords: Gas sensor; spray pyrolysis; ZnO.

Se reporta el desarrollo de un sensor de NO_2 basado en capas delgadas de ZnO obtenidas por spray. Se estudia el efecto del dopamiento con In sobre las características del sensor. La adición de un 3% de nitrato de indio a la solución de partida conduce a una buena respuesta ante 5 ppm de NO_2 a 275°C y una reducción importante de la resistencia eléctrica. Se estudia también el comportamiento de este parámetro con la temperatura. Finalmente se discute un posible mecanismo de sensibilización.

Descriptores: Sensores de gas; rocío químico pirolítico; ZnO.

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1 Introduction

Resistive-type gas sensors based on thin films of metal oxides have been intensively investigated in the last few years. The sensor performance can be improved by the incorporation of different additives to the films. They can participate directly in the gas–solid interaction by means of a chemical or electronic mechanism [1], thus favoring the adsorption of gas molecules on the surface. As a consequence, the gas surface coverage increases and the electrical conductivity changes. In addition, a decrease of the working temperature for the highest sensitivity is generally observed. Moreover, the additives can increase the material porosity, thus increasing the specific surface area suitable for gas adsorption and, consequently, the sensor response.

Despite the mentioned positive effect, the use of additives might provoke an increase in the electrical resistance of the metal oxide films. In fact, NO_2 is an oxidizing gas and it induces a resistance increase on an n-type semiconductor. The increase of sensor impedance is a non-desired effect, since a complicated associated electronic circuitry is required when it exceeds about 10 MΩ. Therefore, the sensitization of sensors by using additives which decrease the electrical resistivity of films via a doping mechanism may be a good solution. However, the increase of the carrier concentration associated to doping would decrease the fractional change of the resistance in the target gas and air, which would also decrease the sensor response [2]. In the present work, the enhancement of the response of sprayed ZnO thin film-based sensor with a simultaneous decrease in the sensor impedance, via the addition of indium (In), is reported.

2 Experimental

The spraying solution (0.1M) was prepared, starting from zinc acetate (Merk) diluted in distilled water. A small amount of acetic acid was added to obtain a total dissociation of the zinc acetate. Different concentrations of the doping element were examined by adding different proportions in weight of indium nitrate. The resulting solution was sprayed onto alumina substrates having interdigitated Pt-electrodes on the front side and Pt-heating resistors on the bottom side. Films about 60 nm thick were prepared. The technological parameters used were: substrate temperature 350°C, solution flow 3 ml/min, carrier gas flow (nitrogen) 5 l/min, nozzle height 0.3m. All as-deposited films were subsequently annealed in static air at 400°C for 3 hours in order to stabilize the sensing properties. The layer thickness was estimated by ellipsometry with a maximum deviation through the sample area of ± 5 nm. The XPS measurements were performed with a SSX-probe (SSX-100 model 206) photoelectron spectrometer. Gas sensing tests were carried out in a stainless steel chamber under a dynamic regimen. The gas composition was regulated by mixing the target gas (NO_2) and synthetic air.

3 Results

Figure 1 depicts the dependence of the sensor response, S, to 5 ppm of NO_2 at 275°C (S= R_g/R_a, R_g and R_a being the sensor resistance in the target gas and air respectively) and ZnO film resistivity on the content of indium salt in the spraying

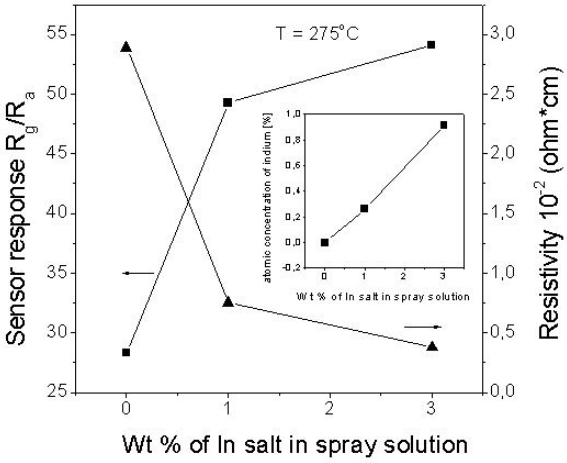

FIGURE 1. Dependence of the response to 5 ppm of NO_2 at 275°C and ZnO film resistivity on the content of indium salt in the solution. The inset shows the variation of the atomic concentration of indium in the film with the indium salt content in the spraying solution.

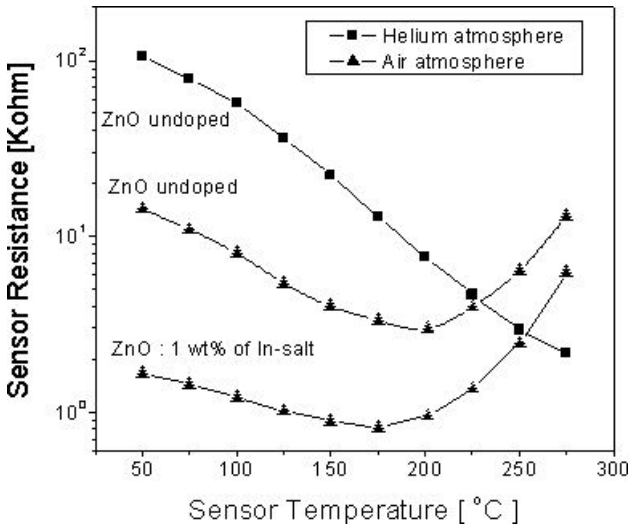

FIGURE 2. Variation of the sensor resistance in air and helium atmospheres with temperature.

solution. At this temperature a good compromise between the sensor dynamic and sensor response was found. The inset in Fig. 1 shows the variation of the atomic concentration of indium in the film with the indium nitrate content in the solution. The sensor response increases with the indium content. Moreover, a significant reduction of the film resistivity is obtained, probably as a result of a doping process. Indeed, the ion Zn^{2+}on the ZnO lattice can be replaced by the In^{3+} ion with a corresponding increase in the free electron concentration.

Figure 2 shows the sensor resistance as a function of temperature. The measurements were carried out in helium and dry synthetic air atmospheres. Observe that in the inert atmosphere, the sensor resistance decreases monotonically as temperature increases, according to a typical semiconductor behavior; however, when the sensor surface is in contact with an oxidizing agent (oxygen in air), the resistance reaches a minimum at a specific temperature, revealing a typical surface-controlled sensor model. Moreover, in this case, the rate of increase in the sensor resistance after this temperature is higher for the doped film devices than for the undoped ones, thus showing that In-doping favors the adsorption of oxygen species.

Figure 3 shows AFM images for undoped and In-doped ZnO films. An important increase in the film roughness as a result of doping is appreciated. The RMS-values are 3.99 nm and 5.19 nm for undoped and doped films respectively. This fact may be related to a change, produced by doping, of the kinetic of the deposition process, with a corresponding change in the film morphology. This possibility is suggested by the observed decrease in the deposition rate, when adding indium salt to the spraying solution.

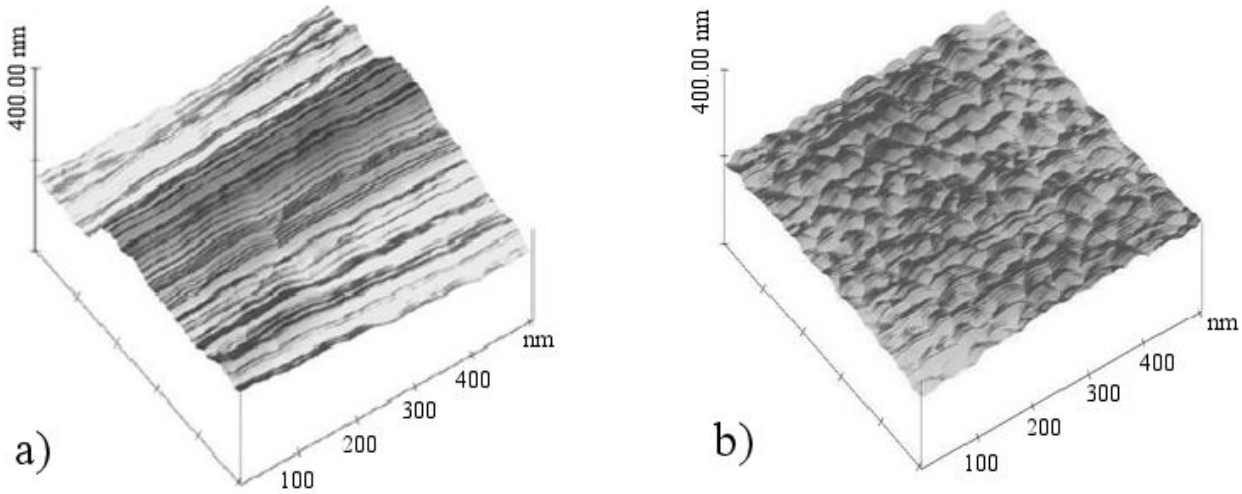

FIGURE 3. Atomic force images of surface morphology of a) undoped film and b) 3 wt % doped film.

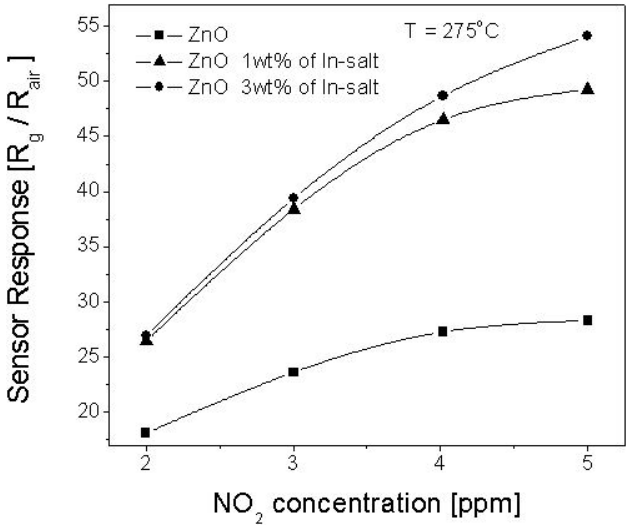

FIGURE 4. Sensor response as a function of concentration of NO_2 (in ppm) at 275°C for undoped and doped films.

Finally, Fig. 4 depicts the variation of the sensor response with NO_2 concentration. It increases with the target gas concentration; however, the sensor response to concentrations as low as 2 ppm is acceptable for sensors with In-doped ZnO films.

4 Discussion

In view of the experimental results, the enhancement of the sensor performance (increase in the sensor response and decrease in the film resistance) with In-doping should be analyzed in the light of the concurrence of several mechanisms or phenomena taking place at the film surface:

a) The first is the increase of the carrier concentration with doping, which leads to a decrease of the oxide resistivity and film resistance. However, this effect induces a decrease in the sensor response, since the fractional change of the resistance due to the decrease of the electron concentration when detecting an oxidising gas is small in this case.

b) The second is the possible creation of the active adsorption sites (In-atoms and oxygen vacancies), which favor the adsorption of oxygen species. These species compete with the NO_2 molecules for the adsorption site. At 275°C, the most possible oxygen specie is O^-. Therefore, the following reaction could take place: $NO_{2\,gas} + O^-_{ads} \rightarrow NO_{gas} + O_{2\,gas} + e^-$, which leads to a decrease in the sensor response.

c) The third is the possible reactions between the NO_2 molecules or nitrogen oxide adsorbed species and oxygen adsorbed species as, for example, $NO^-_{2\,ads} + O^-_{ads} + 2e^- \rightarrow NO_{gas} + 2\,O^{2-}_{ads}$. This reaction, as well as the typical adsorption reaction $NO_{2\,gas} + e^- \rightarrow NO^-_{2\,ads}$, produces an increase of the sensor response.

d) Finally, the increase in active surface area as a consequence of the indicated increase in surface roughness with In-doping should also increase the sensor response.

In our opinion, the last two mechanisms, especially the last one in view of the Fig. 3, are responsible for the enhancement of the sensor response.

5 Conclusions

The sensor performance of sprayed ZnO thin film-based NO_2 sensor is enhanced by In-doping. The increase of sensor response could be mainly related to the increase in the active surface area with doping. However, the occurrence of surface reactions between NO_2 adsorbed species with the adsorbed oxygen species, which are favored by the In-doping, could also increase this parameter.

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