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Doping effects on the response of thin film ZnO gas sensor to ethanol vapour

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A spray pyrolytic system was used to obtain ZnO:X films doped with different elements, X=Al, In, Cu, Fe and Sn. X-ray diffraction, Transmission Electron Microscopy and Scanning Electron Microscopy were used to study the microstructure and surface morphology of the films. From the microstructural analysis, we can conclude that the amount as well as the type of dopant modifies the microstructure and surface morphology. Since it goes from non oriented growth, for undoped films; to strongly (002) oriented, at intermediate (~1 at. %) doping level; and finally again to non-oriented and poor crystallinity, at high (>3 at. %) doping level. The sensitivity of the films was studied in two steps: first of all as a function of their temperature (435-675K) for a fixed ethanol concentration (40ppm) and secondly as a function of ethanol concentration (4-80ppm) for a fixed temperature (675K). It can be observed a better sensitivity for Sn and Al doped films, with a dopant/Zn ratio of 0,4 at. % and 1,8 at. % respectively.

Keywords: Zinc Oxide; Ethanol Gas Sensors; Spray Pyrolysis

1. Introduction

Solid state gas sensor make use of the chemical sensitivity of semiconductor surfaces to different adsorbed gases. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. Doped zinc oxide films have a number of attractive applications, such as: gas sensor devices [1], transparent electrodes [2], piezoelectric devices [3]. Several techniques have been used to produce many distinct zinc oxide films: chemical vapour deposition [4], radio frequency magnetron sputtering [5], Sol-Gel [6], and spray pyrolysis [7-10]. In this work, we have investigated the sensing properties of a spray pyrolytic ZnO-doped films, to ethanol vapour.

2. Experimental

A spray pyrolytic technique was used to obtain doped zinc oxide thin films. The experimental set up was previously described [10, 11]. A 0,1M starting solution of zinc acetate in a mixture of ethanol and deionized water in a volumetric proportion of 3:1 was used. The compound sources of dopants were aluminium chloride, indium acetate, copper acetate, iron chloride and tin tetrachloride. The atomic percentage of dopants in solution were [X/Zn] = 1, 3, 5, 7, 10 and 15 at. % (X=Al, In, Cu, Fe and Sn). X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed to study the microstructure and surface morphology of the films. Details of the microstructural characterisation was reported in a previous work [12]. The films were deposited onto alumina sheets having preprinted gold electrodes and a Pt-heating resistor printed on the reverse side of the substrate. Finally, platinum wires were attached with a drop of low temperature Au paste. A computer-controlled measuring system was used for the gas-response testing. The electrical conductivity of each doped ZnO thin films was measured as a function of temperature, between room temperature and 675 K in air. Also, the sensitivity of the films (G/G_o), i.e. the relation of the conductivity in presence of ethanol vapour (G) to the conductivity in air (G_o), was studied as a function of the sample temperature between 435 and 675K, for a fixed ethanol concentration (40ppm). Finally, the sensitivity was determined as a function of ethanol concentration (4-80 ppm) for a fixed temperature (675K).

3. Results and discussion

3.1 Microstructure

Indium doped films maintains almost the same In/Zn ratio in film as in solution. For the other dopants, their proportion X/Zn in the film is less than that in the solution, nevertheless it can be observed almost a linear correlation between both quantities. From the microstructural analysis, we can conclude that the amount of dopant modifies the film growth process and by consequence the microstructure and surface morphology [12], showing the same behaviour for all the dopants treated in this work. Since it goes from non oriented growth, for undoped films; to strongly (002) oriented, at intermediate (~1 at. %) doping level; and finally again to non-oriented and poor crystallinity, at high (>3 at. %) doping level. Figure 1 shows SEM secondary electron images of the different doped ZnO films onto alumina, it can be observed that the surface morphology of the films is strongly dependent on the type and concentration of the dopant atoms.

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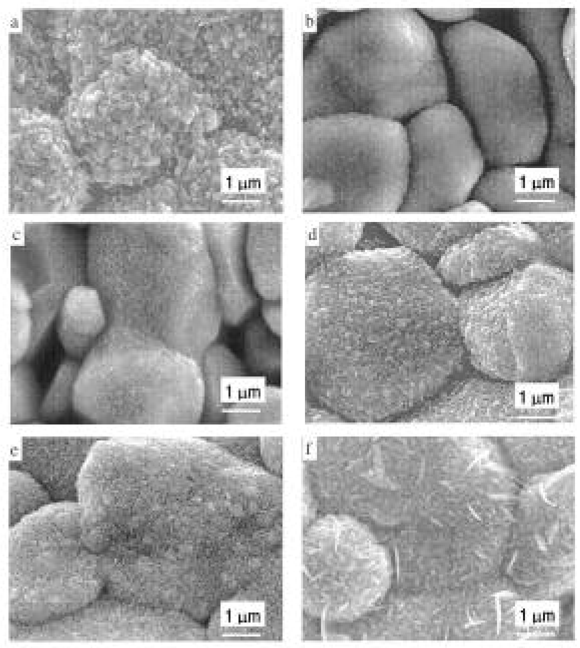

Fig. 1 SEM Secondary electron images of the different doped ZnO films onto alumina substrates. a) undoped, b)In/Zn 5 at %, c) Al/Zn 1.8 at %, d) Sn/Zn 0.4 at %, e) Fe/Zn 1.1 at %, f) Cu/Zn 3.6 at %

3.2. Ethanol vapour response studies

The conductance of the films, with the exception of Cu doped, and for any one concentration show the typical four region behaviour reported by Kwon et. al. [1]. For all Cu doped films, the conductivity monotonically increase as the temperature augment. The results for Indium doped films are shown in Figure 2, we can notice the four regions: electron activation (I), oxygen adsorption (II), equilibrium (III) and oxygen desorption (IV). Figure 3 shows the logarithm of the sensitivity of the different ZnO films as a function of the sample temperature. It was considered only those films with optimal dopant concentration for which the sensitivity is maximal. It is interesting to note the close to linear correlation with the absolute temperature. Figure 4 presents the typical sensitivity performance as a function of time of Tin doped ZnO film (0,4 at. %), for certain ethanol vapour concentration and for a fixed temperature (675 K). It is interesting to note that the reponse time is

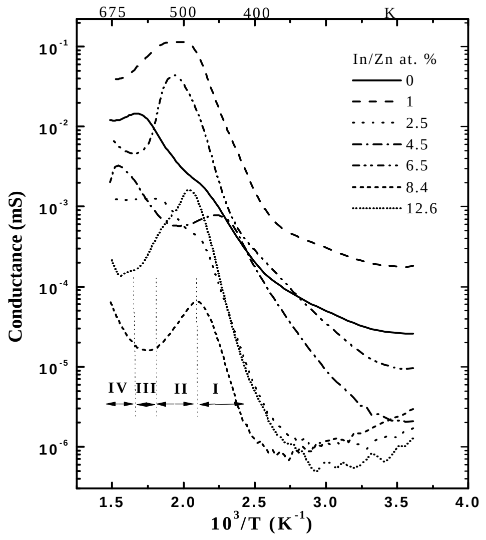

Figure 2.- Semilog plot of conductance of In doped ZnO thin films as a function of inverse temperature.

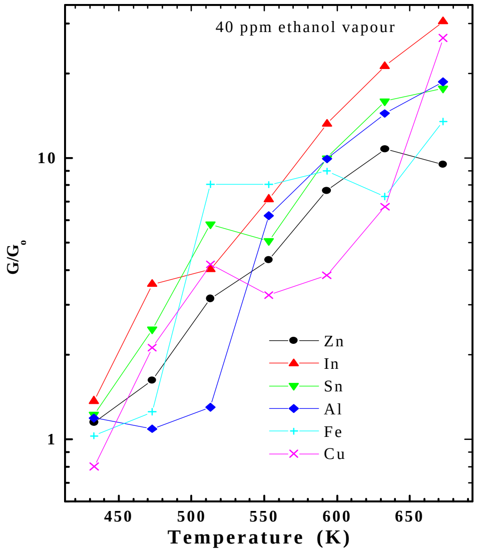

Figure 3.- Sensitivity of the different ZnO films as a function of the sample temperature. For a fixed concentration of ethanol vapour (40 ppm).

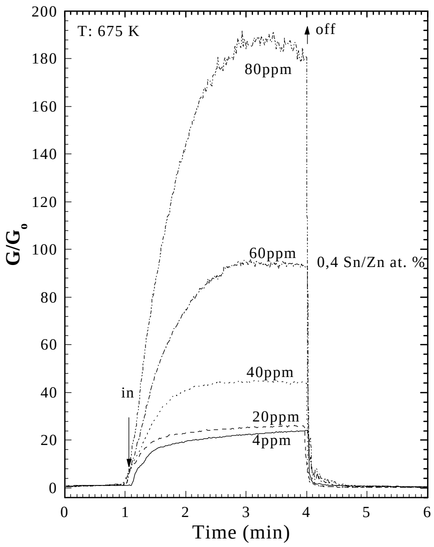

Figure 4.- Typical sensitivity performance as a function of time of Tin doped ZnO film (0,4 at. %). For different concentration pulses of ethanol vapour and for a fixed temperature (675 K).

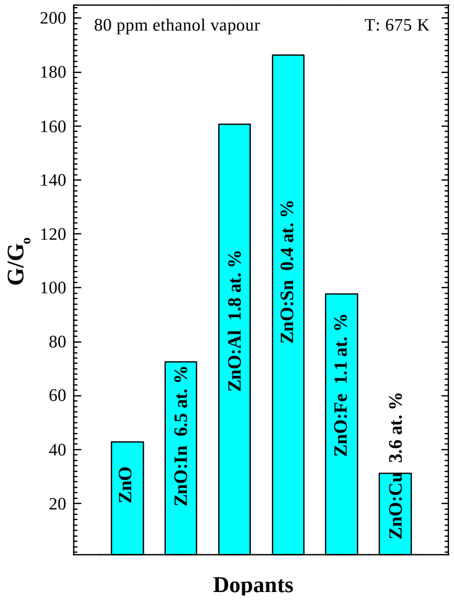

Figure 5.- Maximal sensitivity for optimal dopant concentration of the different ZnO films. It was obtained for 100ppm of ethanol vapour concentration and at 675 K.

of the order of one minute, this attribute was common to all the films treated in this work. In figure 5 it is shown the maximum sensitivity of different doped ZnO thin films, for 80 ppm of ethanol vapour and for a fixed temperature (675 K). Sn and Al doped films with 0,4 at. % and 1,8 at. %, respectively give the highest sensitivity.

Conclusions

Changes in the conductivity as a function of temperature suggest that their magnitude is determined by three basic mechanism: electron activation, oxygen adsorption and oxygen desorption.

It is shown that doped ZnO thin films deposited with a spray pyrolysis system can have high sensitivity to ethanol vapour (as high as 190). Sn and Al dopants gave the highest sensitivity in the working temperature 675 K.

Acknowledgements

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