CO sensitivity of undoped-ZnO, Cr-ZnO and Cu-ZnO thin films obtained by spray pyrolysis

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In this work, we present the gas-sensing properties of chemically sprayed undoped (ZnO), copper-doped (Cu-ZnO), and chromium-doped ZnO thin films (Cr-ZnO), in an atmosphere of carbon monoxide, CO. Films were deposited at 400°C, using zinc acetylacetonate as zinc precursor. Three different atomic concentration ratios of the dopant were tested. A maximum sensitivity of the order of four orders of magnitude was obtained at measurement temperatures of 200 and 300°C in an atmosphere containing 100 ppm of CO. It was found that chromium doping favors a higher sensitivity at lower measurement temperatures (200°C), whereas the best sensitivity appears in copper-doped ZnO films at higher measurement temperatures (300°C). The thinnest films exhibited higher sensitivities.

Keywords: Zinc oxide; thin films; gas sensor; carbon monoxide.

En este trabajo presentamos las propiedades sensoras de películas delgadas de óxido de zinc sin dopar (ZnO) y dopadas con cromo (Cr-ZnO) o cobre (Cu-ZnO) en una atmósfera de monóxido de carbono, CO. Las películas fueron depositadas a 400°C, usando acetyl-acetonato de zinc como fuente del zinc. Tres diferentes concentraciones de dopante fueron utilizadas. Una sensibilidad máxima del orden de cuatro ordenes de magnitud fue obtenida a temperaturas de medición de 200 y 300°C, para las películas dopadas con Cr y Cu, respectivamente, en una atmósfera de CO a una concentración de 100 ppm. Las películas impurificadas con Cr mostraron su máxima sensibilidad a temperaturas más bajas (200°C) respecto a las películas impurificadas con Cu, las cuales presentaron su máxima sensibilidad a 300°C. Las películas más delgadas siempre mostraron mayor sensibilidad.

Descriptores: Oxido de zinc; películas delgadas; sensor de gases; monóxido de carbono.

PACS: 68.55.-a; 68.55.Jk; 82.65.-I; 82.65.My

1. Introduction

Gas sensors based on semiconducting metal oxides in thin film form are being used to cover a wide range of applications, such as sensing of automobile exhaust gases, sensing of air for toxic and explosive gases, odor-source localizer systems, and as a detector of leakage of several inflammable gases. The gas sensing characteristics of numerous materials, such as SnO_2, ZnO, WO_3, TiO_2, CoO, CdO, Ga_2O_3, In_2O_3, among others [1-5], have been reported in the literature. Particularly, ZnO offers the advantages of being abundant, nontoxic, and easily prepared. It has a wide band gap (3.3 eV) and an n-type conductivity. Moreover, when a chemical technique of deposition such as chemical spray is used to obtain ZnO in thin film form, then we can manufacture economical, reproducible and reliable gas sensors [6,7]. Promising ZnO-based thin film gas sensors have been obtained using chemical deposition techniques [8]. In the review work of Patil [6], it was stated that the most common reagent used to deposit chemically sprayed ZnO thin films is zinc acetate, despite the well known fact that not only reagents, but additives, affect the physical characteristics of thin film. The gas sensor principle is based on the following physical phenomenon: under certain atmospheric conditions, a decrease is produced in the concentration of the chemisorbed intrinsic oxygen on the surface of the film, when it interacts with a reducing gas. This fact leads to an increase in the free-electron density on the surface region exposed, which witnesses to a decreasing of the surface electrical resistance of the material. On the other hand, it is a well-known fact that the dispersion of noble metals, Pt, Ag, Sb, Rh or Pd, onto the semiconductor oxide films modifies and enhances the sensor properties, and consequently a higher sensitivity to the reducing gases is obtained [9-13]. In addition, a careful control of the sensor operating temperature, as well as an adequate selection of specific impurities, is concerned with an optimum sensitivity in a specific gas. When such conditions have been achieved, it is said that we have a selective sensor. In this work, the sensitivity was calculated by the ratio between the numerical difference of the electrical resistance measured in

air (R_a: reference value) and the resistance measured in CO (R_g), with respect to the reference value, (s= (R_a-R_g)/ R_a).

In this work, the gas sensor behavior of undoped ZnO, Cu-ZnO and Cr-ZnO films deposited on soda-lime glass substrates by the spray pyrolysis technique, starting from zinc acetylacetonate is presented. The aim of this work is the experimental study of the influence of Cu and Cr as dopants on the sensitivity properties of zinc oxide thin films deposited on glass substrates, when a controlled atmosphere containing CO is present. Sensitivity calculations of the films were made on this basis. In addition, the surface morphology of the films is correlated with the sensitivity properties.

2. Experimental procedure

The reactants used to prepare the starting solution in this experiment were zinc pentanedionate (Alfa Aesar), copper chloride (Baker), chromium pentanedionate (Merck), methanol (Baker), acetic acid (Baker) and deionized water. The instruments required were a stirring plate with variable velocity control, a home-made spraying system in a fume hood. The ZnO thin films were deposited on glass substrates starting from zinc pentanedionate dissolved in a mixture of deionized water (25% in vol.), methanol (72.5% in vol.) and acetic acid (2.5% in vol.), for a final molarity of 0.05 M of zinc pentanedionate. Doping of the films was achieved by adding the corresponding amount of either copper chloride or chromium pentanedionate to the starting solution. The atomic ratio of Cu/Zn or Cr/Zn, (taken as the number of atoms of Cu with respect to Zn or the number of atoms of Cr with respect to Zn, contained in a liter of solution) was used to refer the doping in the starting solution. The substrate temperature was electronically controlled within an accuracy of $\pm 1°$C. The solution and carrier flow rates were held constant at 12 ml/min and 8 l/min, respectively. For the deposition process, the spraying time selected was less than two minutes, taking into account the fact that thinner films show a higher sensitivity to reducing gases. Film thicknesses were measured by a DEKTAK IIA profilometer. Atomic force microscopy was use to analyze the surface of the samples.

3. Results and discussion

Figure 1 shows the resistivity variation as a function of the CO concentration for undoped ZnO thin films. Three different measurement temperatures were used. From this figure we can see that at room temperature there is no significant variation of the surface resistance for all of CO concentrations used. However, an evident surface resistance change is observed when the measurement temperature is increased to 100°C, becoming more marked as the measurement temperature increases.

Maximum resistance variation is registered at low CO concentration values on the order of 5 ppm. Beyond this value, we can observe a saturation behavior as the CO concentration is increased. The variation of the surface resistance values ranged between one and two orders of magnitude and a maximum variation is observed at 300°C, which corresponds to the highest temperature used. These results show that undoped ZnO thin films are a good starting point in the design of more efficient gas sensors, as the sensor sensitivity is directly proportional to the resistance change. This behavior is explained by the surface oxygen desorption, which occurs when the film is exposed to a reducing atmosphere, as is the case of the CO gas. As a consequence of this process, the barrier height on the grain boundaries decreases and consequently two electrons transit to the conduction band leading to a decrease in surface resistance.

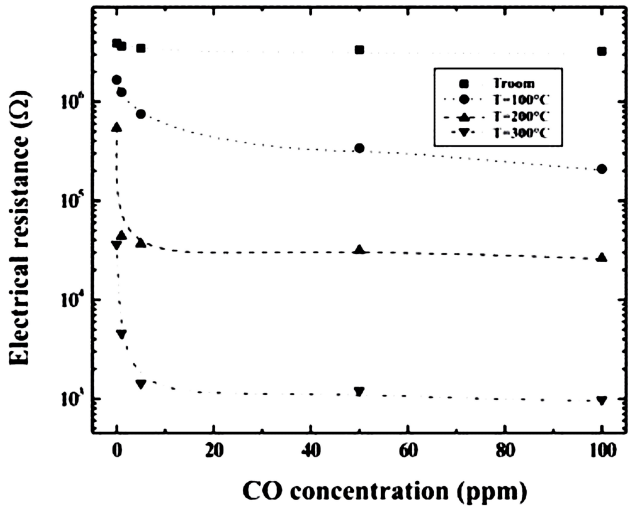

FIGURE 1. Resistance variation as a function of CO concentration for different measurement temperatures for an undoped ZnO film deposited at 400°C.

Figure 2 shows the resistance variation of Cr-ZnO thin films versus CO concentration. The Cr/Zn concentration ratios in the starting solution were varied systematically. It is evident from Fig. 2 that the resistance behavior of Cr-ZnO resembles that of undoped ZnO thin films when the temperature is varied. From Fig. 2 it is observed that a maximum resistance variation of more than three orders of magnitude is obtained in films doped with [Cr/Zn]= 2 and 6 at.% in solution and measured at 200°C. However, the optimum measurement temperature is ruled by the chromium incorporated into the ZnO lattice, as in Cr-ZnO thin films doped with higher concentrations, [Cr/Zn] = 10 and 20 at.%; the optimum temperature was 300°C. The catalytic effect of chromium could be understood in two ways; the first one is related to the work function value of the chromium, which leads to an excess of free bonds near the surface region, producing an important oxidation, which favors the subsequent reactions with the CO gas, and consequently an increase in sensitivity is observed. The second is related to the formation of a Cr_2O_3phase close to the surface region, which increases the catalytic activity of this region due to the fact the surface chromium atoms can be easily oxidized and reach an effective valence of 4, so, they can adsorb a complete monolayer of active oxygen [14].

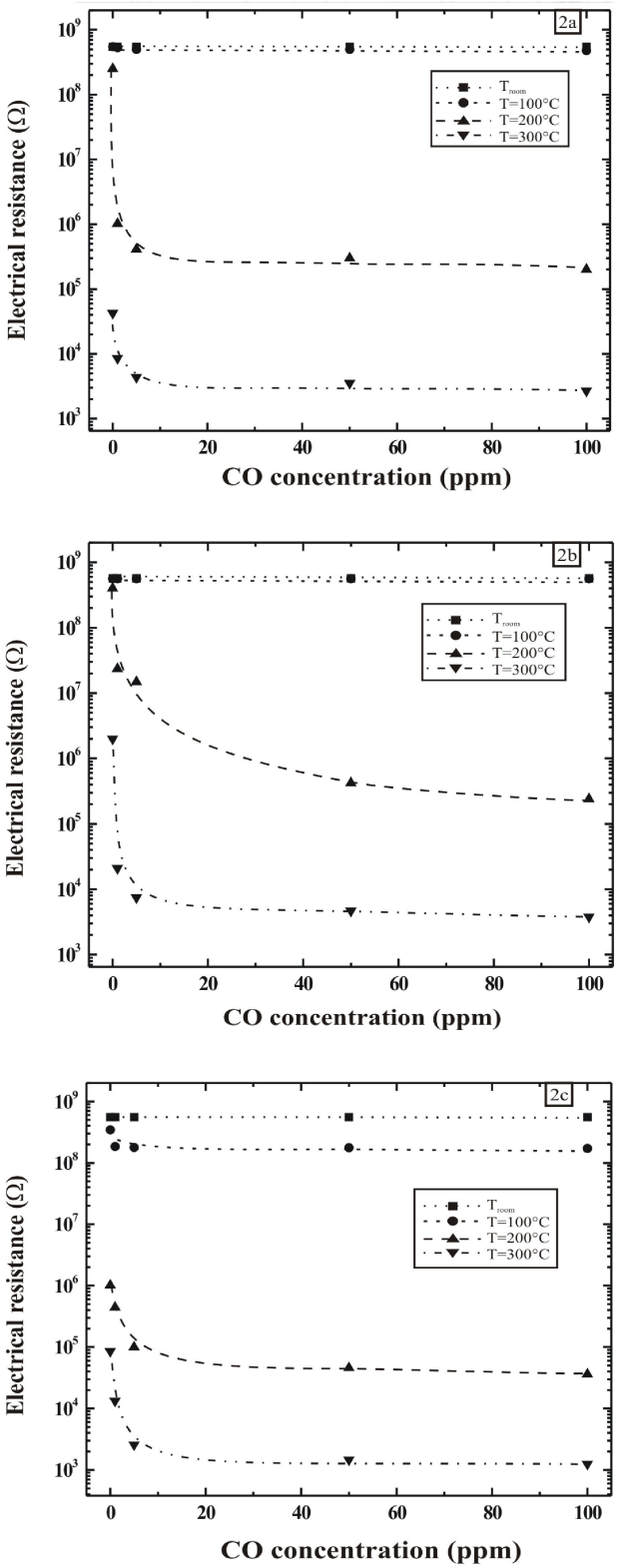

FIGURE 2. Resistance variation as a function of CO concentration, for Cr-ZnO thin films. (a) (Cr/Zn)= 2 at.%; (b) (Cr/Zn)= 6 at.%; (c) (Cr/Zn)= 10 at.%.

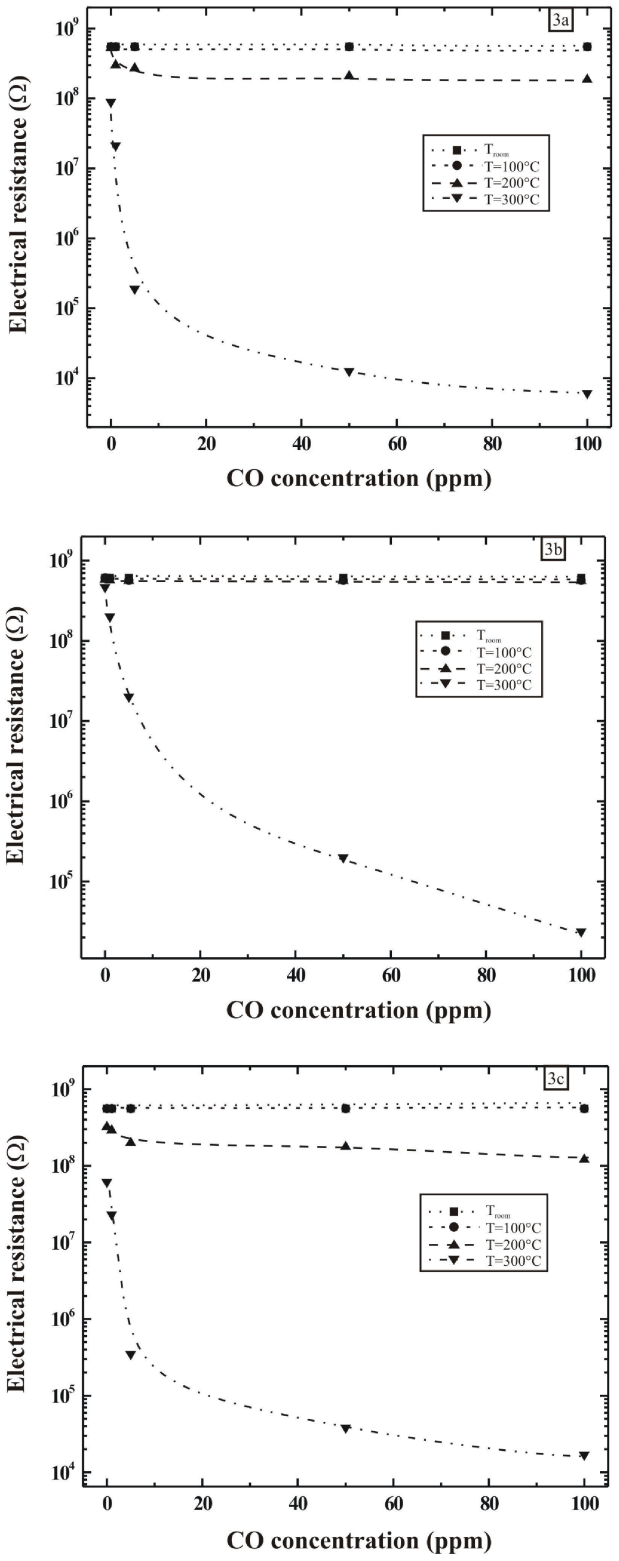

FIGURE 3. Resistance variation versus CO concentration for Cu-ZnO films. (a) (Cu/Zn) = 2 at.%; (b) (Cu/Zn) = 6 at.%; (c) (Cu/Zn) = 10 at.%.

Figure 3 shows the resistance variation of Cu-ZnO films as a function of CO concentration. Similarly to the Cr case, three different Cu/Zn concentration ratios are reported: 2, 6 and 10 at.%. The resistance measurements taken at room temperature, 100, and 200°C do not show a significant

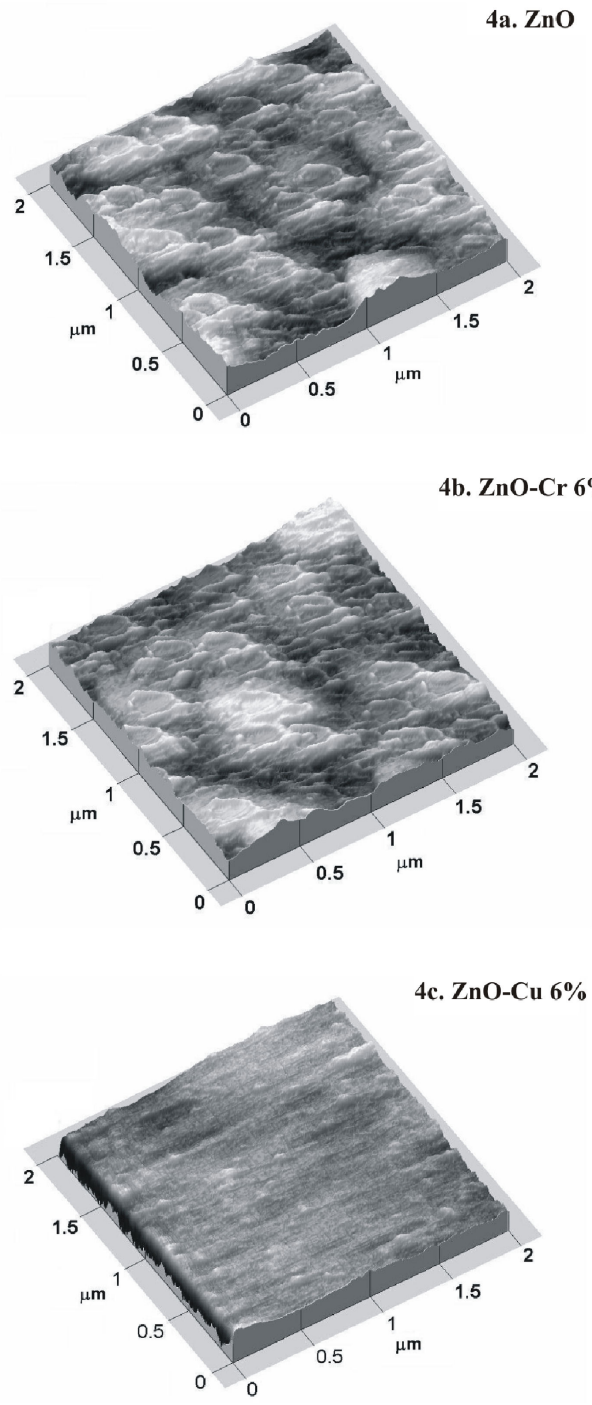

FIGURE 4. AFM micrographs. (a) undoped ZnO; (b) Cr-ZnO with (Cr/Zn) = 2 at.%; (c) Cu-ZnO films, with (Cu/Zn) = 6 at.%.

change with the variation of CO concentration, as can be seen from Figs. 3a, 3b, and 3c. However, when the samples were measured at 300 °C a maximum resistance variation, more than four orders of magnitude, was found in all the films, regardless of the Cu/Zn rate. As was mentioned above, the change in the resistivity observed can be explained on the basis of the work function value of the copper, leading to an excess of free bonds near the surface producing then an important oxidation, which in turn favors the later reactions with the CO molecules. In this way, an increase in the sensitivity is observed. So, we can conclude that the use of adequate impurities in the ZnO films can increase their sensitivity. The criteria for the selection of a dopant take into account its work function value, WF, which must be different from the ZnO (WF_{ZnO}= 4.3eV), as in the case of copper and chromium (WF_{Cu}= 4.59eV and WF_{Cr}= 4.44 eV). Thus, in a first step the oxygen is adsorbed on the film surface, later being removed in an atmosphere containing the reducing gas. In this last process, free electrons are generated.

Morphology

Figure 4 shows three atomic force microscope (AFM) micrographs, corresponding to undoped-ZnO, Cr-ZnO and Cu-ZnO thin films. A similar surface morphology for undoped ZnO and Cr-ZnO films can be observed from these images. However, Cu-ZnO films show a smoother and more uniform surface. The irregular surface exhibited is due probably to the intentionally low deposition temperatures used. It is well known that a high roughness of the surface is appropriate for gas sensing applications, because the surface reduction reactions are increased as a consequence of the increase of the effective area, leading to a better sensitivity.

4. Conclusions

Chemically sprayed undoped-ZnO, Cu-ZnO, and Cr-ZnO thin films were successfully tested as gas sensors. In decreasing order of importance, Cu-ZnO, Cr-ZnO, and undoped-ZnO films exhibit a good sensitivity at different measurement temperatures. Thinner films show higher sensitivity values. The highest resistance variations were obtained at 300°C for all tested doped and undoped ZnO films, although for undoped ZnO films resistance variations starting at 100°C were observed. For Cr-ZnO thin films, depending on the Cr ratio, the maximum resistance variation was obtained at 200°C or 300°C. For Cu-ZnO thin films almost no resistance change was registered from room temperature up to 200°C. On the other hand, at 300°C a very significant resistance variation, more than four orders of magnitude, was obtained. Cu-ZnO thin films presented the high resistivity variation or the highest sensitivity. However, resistance variations at lower measurement temperatures than 100 and 200°C are also important. Based on these preliminary results, the ZnO in thin film form is a promising material in the manufacturing of gas sensors.

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1. T. Schwebel, M. Fleicher, H. Meixner, and C.D. Kohl, *Sensors and Actuators B* **49** (1998) 46.
2. Morio Miura, Takahisa Raisen, Geyu Lu, Noburu Yamazoe, *Sensors and Actuators B* **47** (1998) 84.
3. Marta Radecka, Katatzyna Zakrzewska, Mieczyslaw Rekas, *Sensors and Actuators B* **47** (1998) 194.
4. A. Gurlo *et al.*, *Sensors and Actuators B* **44** (1997) 327.
5. L. Delabie *et al.*, *Sensors and Actuators B* **44** (1997) 446.
6. Pramod S. Patil, *Matter. Chem Phys.* **59** (1999) 185.
7. P. Mitra, Ap.P. Chatterjee, and H.S. Maiti, *Matter. Lett.* **35** (1998) 33.
8. P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho, and R. Martins, *Vacuum* **64** (2002) 281.
9. T.B. Fryberguer, J.W. Erickson, and S. Semancik, *Surface and Interface Analysis* **14** (1989) 83.
10. Semancik and T.B. Fryberguer, *Sensors and Actuators B* **1** (1990) 97.
11. D. Briand, M. Labeau, J.F. Currie, and G. Delabouglise, *Sensors and Actuators B* **48** (1998) 395.
12. P.S. More, Y.B. Khollman, S.B. Desphande, S.K. Date, R.N. Karekar, and R.C. Aiyer, *Materials Letters* **58** (2003) 205.
13. Stambolova and K. Konstantinov, *J. of Mater. Sci.* **31** (1996) 6207.
14. D. Baresel, W. Gellert, W. Sarholz, and P. Scharner, *Sensors and Actuators* **6** (1984) 35.