Chromium doped Zinc oxide thin films deposited by chemical spray used in photo-catalysis and gas sensing

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Chromium-doped zinc oxide, ZnO:Cr, thin films were deposited onto glass substrates by the chemical spray technique. The effect of both the chromium concentration in the solution and the film thickness on the photocatalytic and gas sensing properties of the films was investigated. All the ZnO films were polycrystalline, fitting well with the hexagonal wurtzite structure, and showing a (002) preferential growth. Grains, with different shape and size cover the film surface. A decrease in the photocatalytic activity was observed with an increase in the Cr concentration in solution. The resistance variation of ZnO:Cr thin films as a function of the operation temperature and propane concentration are reported as well.

Keywords: Zinc oxide; thin films; chemical spray; chemical sensors.

Se depositaron películas delgadas de óxido de zinc, ZnO, impurificadas con cromo, Cr, por medio de la técnica de rocío químico. Se estudió el efecto de la concentración de Cr en solución, así como del espesor de las películas sobre las características fotocalíticas y de sensado de gases de las películas de ZnO. Todas las películas presentaron alta policristalinidad, y los espectros de difracción se ajustan bien a una estructura hexagonal de tipo wurtzita y con crecimiento preferencial (002). Aglomerados de partículas, de diferentes formas, compuestos por partículas de tamaño promedio de 200 nm, cubren la superficie de las películas. Se observó una disminución de la actividad fotocalítica de las películas con el incremento de la concentración de Cr en solución. Se muestra la variación de la resistencia eléctrica con la concentración de gas propano y la temperatura de operación.

Descriptores: Óxido de zinc; películas delgadas; rocío químico; sensores químicos.

1. Introduction

The growing interest in the development of zinc oxide, ZnO, in thin film form is based on the physical characteristics that, under optimal deposition conditions, are attractive for a wide variety of applications in different electronic and optoelectronic devices, such as gas sensors [1], transparent electrodes [2], heat mirrors [3], gamma radiation sensing layers [4], and pressure sensors [5], among others. In ZnO films a high transparency is observed in the visible region, whereas metallic properties lead to a reflectance in the infrared spectrum. In addition, a high conductivity can be simultaneously present [6].

Recently, it is emerging the photocatalytic effect of doped ZnO thin films, in the case of degrading organic pollutants [7,8], in such a way that it can be a good candidate for substituting TiO₂. In fact, the similarity in wide band gap makes ZnO attractive, in addition to their low cost and non-toxicity. Moreover, ZnO in thin film form can be deposited within a wide variety of chemical techniques, most of them with a low cost of equipment and installation. This is the case mainly of sol-gel and chemical spray techniques [9,10], that give rise to deposition of good quality doped ZnO thin films. In this work our interest is centered in films deposited by the chemical spray technique.

The incorporation of Cr as an active impurity into the ZnO lattice can be interesting. As a matter of fact, the work of Shinoda et al. [11] is very interesting, as ZnO:Cr thin films, deposited by sputtering, show an increase in the chemical stability against diluted inorganic acids. Similar results were found out in our laboratory for chemically sprayed ZnO:Cr thin films [12]. In addition, Cr is a good candidate to enhance some others characteristics adequated for different applications, such as chemical sensors, electrically controlled magnetic sensors and actuators, and advanced optical switches, among others [13].

It is worthy of mention the interest in the study of chemical deposition processes, because some aspects, not considered before, can be decisive in the enhancement of the quality of the films [14]. On the other hand, both, the manufacturing
process and the raw materials cost are decisive on the selection of a deposition technique. In this respect, all the Ti compounds are more expensive than those for Zn, which become another advantage of ZnO thin films.

In this work we report the effect of both Cr concentration in the starting solution and film thickness on the chemical sensing and photocatalytic properties of propane gas and degradation of methylene blue (MB), respectively.

2. Experimental

Zinc oxide thin films were deposited starting from a 0.1 M solution of zinc acetate, \([\text{CH}_3\text{COO}]_2\text{Zn} \ 2\text{H}_2\text{O}\) (Merck), dissolved in a mix of water, acetic acid, and methanol (with a volume proportion of 250:50:700). A 0.1 M prepared solution of chromium acetylacetonate (Merck) in acetic acid was used as doping source. The relative atomic concentration of Cr with respect to Zn, \([\text{Cr}]/[\text{Zn}]\), was taken as the reference for doping; the \([\text{Cr}]/[\text{Zn}]\) ratios used in this work were 1, 3, 5 and 8 at.%. The selection of these values was based on a previous work [12]. In fact, we have noted that optimal properties of ZnO:Cr thin films deposited by chemical spray are located around this doping ratios, more precisely, in the narrow range of 1 to 3 at.%. Sodalime glass plates, \(2 \times 1 \ \text{cm}^2\) area, were used as substrates, after a standard cleaning process. For the films deposition only one substrate temperature was tried, namely, 500°C. Nitrogen was used as carrier gas with a flow of 8 L/min. The solution flow was kept constant at 8 ml/min. In order to observe the effect of the film thickness on the performance as chemical sensor and photocatalyst, films with thicknesses around of 100 and 550 nm, were deposited.

The film structure was obtained by means of X-ray diffraction spectra, in a Siemens-Kristalloflex equipment based on Cu-K\(_\alpha\) radiation (\(\lambda=1.5405 \ \text{Å}\)). Surface morphology was observed directly by scanning electron microscopy (SEM), using a JEOL 35C equipment. The films thickness was measured, after a step was made, by a KLA Tencor P15 profilometer.

The sensing characteristics of the films were analyzed thorough a home-made system, based on the registration of the electrical resistance change of the films as a function of the operation temperature and propane concentration. ZnO:Cr thin films were placed in thermal contact with a cooper plate, which is heated in a controlled way by an electrical resistance. In this way the temperature of the ZnO:Cr thin films, termed as the operation temperature, was varied from ambient, 100, 200, and 300°C. Propane gas was used in this case, and the concentrations were varied at values of 5, 50, 100, 200, 300, 400, and 500 ppm. More details on the experimental procedure are listed in Ref. 15.

The photocatalytic activity was quantified by means of bleaching of methylene blue (MB) in aqueous solution. Three milliliters of MB solution at an initial concentration of 25 \(\mu\text{M/L}\) was put in a quartz cell of \(1 \ \text{cm} \times 1 \ \text{cm} \times 4 \ \text{cm}\). A sample of rectangular geometry (area=2cm\(^2\)) was immersed into the cell and this arrangement (cell+solution+sample) was exposed to UV radiation. A 15W-G15T8 germicidal lamp was used as UV-vis illumination source. The cell-lamp distance was kept constant at 4 cm, and the exposure times were 1, 2, 3, 4, and 5 h. The MB residual normalized concentration (MB) was determined in the same UV-vis range.

3. Results and Discussion

3.1. Structure

Figure 1 shows the X-ray diffraction patterns of 500-nm-thick ZnO thin films deposited at 500°C as a function of the doping concentration in solution. All the samples were polycrystalline, fitting well with the ZnO hexagonal-wurtzite structure, with a preferential crystalline orientation along the c-axis perpendicular to the film surface, \(i.e.\) along the (002) planes, irrespective of the doping concentration and substrate temperature. No significant contribution of other planes was observed. The similar high intensity of the (002) peak in all the spectra is a fact indicative of the good quality of the films, and the constant position and the width-mean of these peaks corroborate that, the crystalline size is almost invariable.

![Figure 1. X-ray spectra of ZnO:Cr thin films as a function of the Cr content in the starting solution.](image-url)
It should be noted that the variation of grain size here shown does not coincide with that reported previously [12]. In fact, the surface of the films reported in this work is smoother than those shown previously. This is attributed to the effect of the acetic acid added in the solution. In fact, in this work we added a lower quantity as compared with the previous work. This difference raises the role of acetic acid in the morphology of the films, and probably, in the sensing and photo-catalytic properties.

3.3. Optical properties

Figure 3 shows the transmittance spectra of ZnO:Cr thin films as a function of the Cr content in the starting solution.

Figure 2. SEM images of 550-nm-thick ZnO:Cr thin films deposited from solutions with different [Cr]/[Zn] concentrations; (a) 1 at.%, (b) 3 at.%, (c) 5 at.%, and (d) 8 at.%.

Figure 3. Transmittance spectra of 550-nm-thick ZnO:Cr thin films deposited from solutions with different [Cr]/[Zn] concentrations.

3.2. Morphology

Figure 2 shows the SEM micrographs of typical surfaces of the ZnO thin films deposited at 500°C as a function of the Cr content in the starting solution. From a closer view the images show that secondary grains, approximately rounded, cover the surface; however at higher Cr concentrations the grains present an irregular geometry. A general observation is that, the primary grains have a size that decreases as the [Cr]/[Zn] ratio in the solution increases. In fact, in the case of films deposited with a [Cr]/[Zn] of 1, 3, and 5 at.%, it is found that the grain size is in the order of 125, 80, and 60 nm, respectively. Hence more compact films, that is to say less porous, are formed as the doping content in solution increases up to 5 at.%. However, at the highest [Cr]/[Zn] concentration used, of 8 at.%, the surface presents a high porosity with a grain size around of 100 nm.

Figure 4. Electrical resistance variation as a function of the propane concentration of 100 nm ZnO:Cr thin films deposited from starting solutions with different [Cr]/[Zn] concentrations, 1 and 3 at.%, measured at different operating temperatures.
the optimum operation temperature was 200°C for four operating temperatures. In both cases, the resistance of the ZnO:Cr thin films as a function of the propane concentration is shown. In the case of the films with a thickness of 100 nm, only the resistance variation was observed. In the case of thicker films, the variation with the Cr doping shows no significant variation with the Cr doping. Probably this trend is due to the electrical stabilization of the surface as the Cr content in solution increases. In the case of thicker films, the variation in electrical conductance observed was lower than in the case of the films with a thickness of 100 nm. Hence, only the resistance variation as a function of the Cr content in the starting solution was studied. The results show that the variation in the electrical resistance was about one order of magnitude, and even constant, according to a variation in the photocatalytic performance. In fact, Quintana et al. [8] have shown the role of the porosity of the ZnO thin films on the degradation performance. Accordingly, in our case the variation in the electrical resistance and the degradation of MB can be limited by the nature of the surface. Hence, more work on the characteristic of the surface of ZnO:Cr thin films is still needed.

4. Discussion and conclusions
According to the results, the ZnO:Cr thin films show good sensing and photocatalytic responses. However, from the results it seems that the performance level is still far from being acceptable for device applications as compared with other materials. This can be due to a wide variety of factors. Particularly, the way the doping is made can be very crucial in the performance of the films, as a sensor or as a photocatalyst. In our case, the films present an excellent Cr incorporation, as was expected, as the Cr content into the film is dependent on the Cr content in the starting solution. However, the sensing mechanisms in both referred applications (chemical sensors and photocatalyst) occur mainly on the surface, making the effect of some deposition variables crucial. This is the case of the starting solution. In fact, it has been reported that the solution pH, modified by the addition of acetic acid for example, strongly affects the surface morphology, leading to a variation in the photocatalytic performance [8]. In fact, Quintana et al. [8] have shown the role of the porosity of the ZnO thin films on the degradation performance. Accordingly, in our case the variation in the electrical resistance and the degradation of MB can be limited by the nature of the surface. Hence, more work on the characteristic of the surface of ZnO:Cr thin films is still needed.

In conclusion, ZnO:Cr thin films, with sensing and photocatalytic properties were deposited by the chemical spray pyrolysis technique. The doping [Cr]/[Zn] concentration in solution affects mainly the sensing properties, as the best results were observed in the films doped either with 1 or 3 at.%. The thinnest films, in the order of 100 nm, show the best performance as sensing and photocatalytic materials.
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