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Electrostatic spray deposited zinc oxide films for gas sensor applications

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Abstract

In this work, thin films of zinc oxide (ZnO) for gas-sensor applications were deposited on platinum coated alumina substrate, using electrostatic spray deposition (ESD) technique. As precursor solution zinc acetate in ethanol was used. Scanning electron microscopy (SEM) evaluation showed a porous and homogeneous film morphology and the energy dispersive X-ray analysis (EDX) confirmed the composition of the films with no presence of other impurities. The microstructure studied with X-ray diffraction (XRD) and Raman spectroscopy indicated that the ZnO oxide films are crystallized in a hexagonal wurtzite phase. The films showed good sensitivity to 1 ppm nitrogen dioxide (NO_2) at 300 °C while a much lower sensitivity to 12 ppm hydrogen sulphide (H_2S).

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1. Introduction

Monitoring the air quality especially in urban areas has become a priority due to the great amounts of pollutants released in the atmosphere, which have a noxious effect on the human and animal's health and also on the vegetation. To detect pollutant gases different kinds of sensor have been developed, i.e. electrochemical sensors [1], polymer sensors [2], surface acoustic waves (SAW) sensors [3] and metal oxide semiconductor (MOS) sensors [4]. The last ones are preferred mainly employed because of their simplicity, small dimensions and low cost.

So, because of its semiconducting, optical, piezoelectrical properties, ZnO have been used as gas sensor [5] and in different applications such as: solar cells electrodes [6,7], optical waveguide device [8], light emitting device [9], catalyst [10], etc.

Until now, different physical and chemical techniques have been used to prepare ZnO which are more or less sophisticated and expensive [11–16]. From our knowledge, there is no paper in the literature describing the gas sensing properties of ZnO deposited by electrostatic spray deposition technique. The ESD method was selected for the deposition of ZnO films taking into account the advantage such as: simple and cost-effective set-up, high deposition efficiency, large choice of precursors and ambient atmosphere operation. It provides an easy [13–16] control of the surface morphology, from dense to fractal-like porous and reticular structure morphologies [17], by tuning the deposition parameters such as: temperature, time, flow rate, etc. The control of the surface morphology is of particular interest for gas sensor application where a porous morphology is desired for increasing the adsorption and implicitly the sensor response to a certain gas [18].

The ESD technique was used so far to deposit thin films of functional metal oxide with application in different fields, i.e. rechargeable lithium batteries [19], solid oxide fuel cells [20], heat exchange reactors [21], biomedical implants [22] and sensors [23,24].

ZnO is one of the earliest materials used as chemoresistive sensor [25], to detect different pollutant gases including: CO [26], C_2H_5OH [27], H_2 [28], O_2 [29] and O_3 [30]. There are only few papers in the literature, which describe the gas sensing properties of ZnO to NO_2 and H_2S [31–35]. The aim of this work is to present the deposition of porous ZnO films using ESD

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method, their structural and morphological characterization and their application as gas sensors for the detection of NO_2 and H_2S.

2. Experimental aspects

2.1. ESD set-up

For the deposition of the films a vertical ESD set-up working under ambient atmosphere was used [36]. The liquid precursor solution was pumped by a syringe pump through a flexible tube of plastic material to the tip of a stainless steel nozzle (outside diameter, 0.9 mm). When a high voltage is applied by a DC voltage power supply between the nozzle and the substrate the precursor solution is atomized at the tip of the nozzle into an aerosol of very fine droplets. This aerosol of highly charged droplets is directed to the heated substrate under the electrostatic force. At the impact the droplets are loosing their charge and spreading, drying and decomposition of the precursor solution occur. In this way, a thin layer is formed on the substrate surface.

The temperature of the substrate was maintained at a constant value using a temperature control unit, which includes a heating element and a temperature controller.

2.2. Films deposition

As precursor solution a 0.05 M zinkacetat–dehydrate (99.5% purity) in ethanol (99.9% purity) was used. Few drops of hydrochloric acid (37–38%) were added to the solution in order to dissolve any precipitate of zinc hydroxide formed due to the reaction of the ethanol with zinc acetate. The as-obtained precursor solution was pumped through the metal nozzle using a flow rate ranging from 1 to 2 ml h^{-1}. The substrate is alumina pellets, with dimensions of 10 mm × 20 mm and thickness 1 mm. The substrate was coated partially with a layer (1–5 μm) of platinum paste and fired at 800 °C for 2 h in air. The distance between electrodes was 1 mm. The as-made substrate was fixed in a stainless steel substrate holder, in order to allow a circular deposition surface of 10 mm in diameter (Fig. 1). The temperature of the substrate was 350 °C and the deposition time was varied between 1 and 2 h. A distance of 20 mm was kept between the nozzle and the substrate. A positive voltage between 7.5 and 8.0 kV was applied to the nozzle, breaking the liquid at the tip of the nozzle in an aerosol composed of very small droplets.

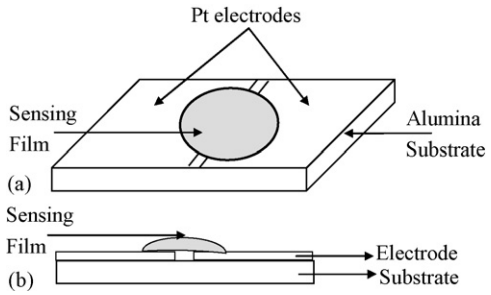

Fig. 1. Schematic representation of the films deposited on Pt-coated alumina substrate: (a) top view and (b) cross-sectional view.

The as-deposited films were annealed at 600 °C in air for 2 h to remove any possible organic rests remained from the precursor solution and also to improve the crystallinity and to sinter the layer. For this study, we have prepared and analysed about 20 films.

2.3. Structure characterization techniques

The surface morphology of the coatings was investigated using a JOEL JSM 580 LV scanning electron microscope. The film thickness was determined from the SEM cross-section image. For the determination of the film thicknesses a thin film of gold was sputtered on the surface in order to avoid charging.

The chemical analysis of the thin films was investigated using an energy dispersive X-ray analyzer (Oxford Instruments). The samples are placed on Quantifoil carbon polymer supported on a copper grid by applying a few droplets of ground sample with ethanol, followed by drying in air.

The crystal structure of the films was studied with a BRUKER D8 ADVANCE X-ray diffractometer using monochromatic Cu Kα radiation (λ = 1.5406 Å, 40 kV and 40 mA).

Raman measurements were performed at room temperature using a home-built set-up described in more details elsewhere [37].

2.4. Gas sensing measurements

The gas sensor measurements were carried out in a closed quartz tube furnace. The temperature was measured using a type K thermocouple and was controlled by a PID temperature regulator. Prior to the measurements the films were allowed to age 14 days at 300 °C. Repeated heating/cooling cycles in the temperature range 200–450 °C were made in order to provide stability of the resistance in the studied temperature range. The resistance measurements were performed using the two-point probe method with an electrometer (KEITHLEY 6514).

To determine the optimum operating temperature the gas sensor was exposed to a fixed concentration of NO_2 (1 ppm) or to H_2S (12 ppm) and the temperature was changed between 200 and 450 °C with a step of 50 °C. The time of exposure to the gas was 20 min and the regeneration was made with synthetic air during 1 h. The relation between the sensitivity and the gas concentration was evaluated at a fixed temperature (i.e. optimum operating temperature) by changing the NO_2 and H_2S concentration between 1–5 and 1–12 ppm, respectively.

The concentration of the gases was fixed by adjusting the flow rates of the target gas and the carrier gas (synthetic air) in the way to maintain a constant total flow rate of 100 ml/min. The concentration of the gases was controlled using mass flow controllers.

3. Results and discussion

3.1. Structure characterization techniques

The morphology of the films was studied by SEM and the micrographs of the ZnO films deposited at $T = 350$ °C for 1 h