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Original Research Paper

Characterization and sensing properties of ZnO film prepared by single source chemical vapor deposition

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ABSTRACT

A novel deposition technique has been used to grow ZnO films. Good quality films were obtained on glass substrates by single source chemical vapor deposition (SSCVD), for gas sensing applications. The properties of ZnO films were investigated at different deposition temperatures 300, 350 and 400 °C. X-ray diffraction results show that all deposited films were polycrystalline. The morphological, structural, optical and electrical properties of the films have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), cathodoluminescence (CL) and Hall effect techniques. The morphology of the deposited films evolves from columnar grains, to parallel plates as the substrate temperature increases. A significant increase in the relative intensities of the green and red emission with increasing deposition temperature has been observed. Electrical properties, relevant for gas sensing behavior have been investigated as well. In the particular case of CO an operating temperature of 300 °C seems to yield the best sensitivity.

1. Introduction

Gas sensors based on semiconducting metal oxides have gained special importance in the last years. The diversity of applications such as detection of explosive and inflammable gases, environmental monitoring, health care, and air-quality detection has driven relevant studies [1]. Nevertheless, the mechanism of the gas sensing is something complex and still under controversy. There is a general agreement on the preponderant role of the surface properties and surface reactions on these materials, and consequently, on the importance for the sensing performances of the morphology and the microstructure of materials, namely grain size, crystal structure, surface area, porosity, etc. [2]. The gas sensing characteristics of numerous materials such as ZnO, SnO_2, TiO_2, and WO_3 have been reported in the literature [3–6]. Particularly, ZnO offers the advantages of being nontoxic and easily obtained. ZnO is characterized as a wide band gap semiconductor (3.3 eV) with a large exciton binding energy (60 meV) and n-type conductivity [7]. Many techniques have been used to produce ZnO films, such as pulsed laser deposition (PLD) [8], sputtering [9], spray pyrolysis [10] and atmospheric pressure chemical vapor deposition (APCVD) [11]. In the present work, single source chemical vapor deposition (SSCVD) reveals as a useful technique for preparing films, offering the simplicity of having all film components contained within one molecule [12], and some additional advantages as the use of non-severe deposition conditions. This growth method offers then the possibility of producing high-quality films using simple deposition equipment.

The present work is focused on the study of the structural, optical and electrical properties of ZnO films deposited by SSCVD at atmospheric pressure. Also, the study of gas sensing properties of the ZnO film sensor using aluminum electrodes with interdigital structure is reported.

2. Experimental

2.1. Films deposition

ZnO films were deposited on glass substrates using zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) as a single-source precursor. The temperature of the precursor was stabilized at 210 °C during the deposition. The substrates were previously cleaned by 10 min. in a piranha solution (50% sulfuric acid and 50% hydrogen peroxide) [13], rinsed in deionized water (18.2 MΩ cm), and dried. The distance between the source and substrate was 50 mm. For the

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experiments reported in this work, three different substrate temperatures were selected, 300, 350 and 400 °C, while the deposition time was kept in 5 min. An oxygen gas flow was used as oxidant agent and the flow rate was 50 sccm (standard cc/min at 1 atm for 25 °C). Fig. 1a shows a scheme of the deposition system, which has been more extensively described in our previous work [14]. As mentioned, the main advantage of this method, respect to other deposition techniques, is the possibility to work at lower deposition temperatures and the simplicity of the experimental setup, allowing to obtain good quality films faster, cheaper and easier than in more complex reactors.

2.2. Films characterization

X Ray Diffraction (XRD) measurements were carried out by using a Bruker D8 Discover diffractometer with a X-ray source of Cu Kα radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA. The thicknesses of the films deposited were measured by means of a stylus profilometer. Surface morphologies of the films were observed by using a FEI Inspect Scanning Electron Microscope (SEM) and a Nanotec-AFM operated at room temperature. Cathodoluminescence (CL) measurements were carried out at room temperature on a Hitachi 2500 SEM at an operation voltage of 20 kV. CL spectra were obtained with a Hamamatsu PMA-11 CCD camera. The electrical properties of the films were obtained from the Hall effect measurement at room temperature in the van der Pauw configuration using the Ecopia Bridge Technology HMS-5300 system equipped with a permanent magnet yielding a field of 0.55 T.

2.3. Details of gas sensing system and sensor fabrication

Sensing measurements were performed using the gas sensing system described elsewhere [15]. The system consists of a heater fixed on the base plate inside a chamber; a thermocouple and a temperature controller were used to control the heater. The gas is inserted into the chamber from a mass flow controller to control the gas flow. A digital multimeter (Keithley 2001) connected through external leads is used to measure the resistance.

Sensors were fabricated by depositing a ZnO film on glass substrates with an area of 100 mm^2, supplied with interdigital aluminum electrodes on top of the film as shown in Fig. 1b.

The gas sensing properties were evaluated for three different operating temperatures 100, 200 and 300 °C, by measuring the changes of sensor resistance in presence of air and CO gas, respectively. The sensor was exposed at different CO concentrations ranging from 0 to 200 ppm. The sensitivity in the experiment was defined as [16]:

$$S = \frac{R_a - R_g}{R_a} \times 100\% \qquad (1)$$

where R_a is the resistance in air and R_g is the resistance in the test gas.

3. Results and discussion

3.1. Morphological characterization

The morphological characteristics of the ZnO films were investigated by SEM and AFM. The morphology of the deposited films evolves from columnar grains, to parallel plates as the substrate temperature increases. Fig. 2 shows SEM images of the ZnO films deposited on glass substrates; at the three different temperatures used. The film deposited at 300 °C (Fig. 2a) shows columnar grains growing perpendicular to substrate. The columnar structures are common for low thermal mobility species, for which, the initial

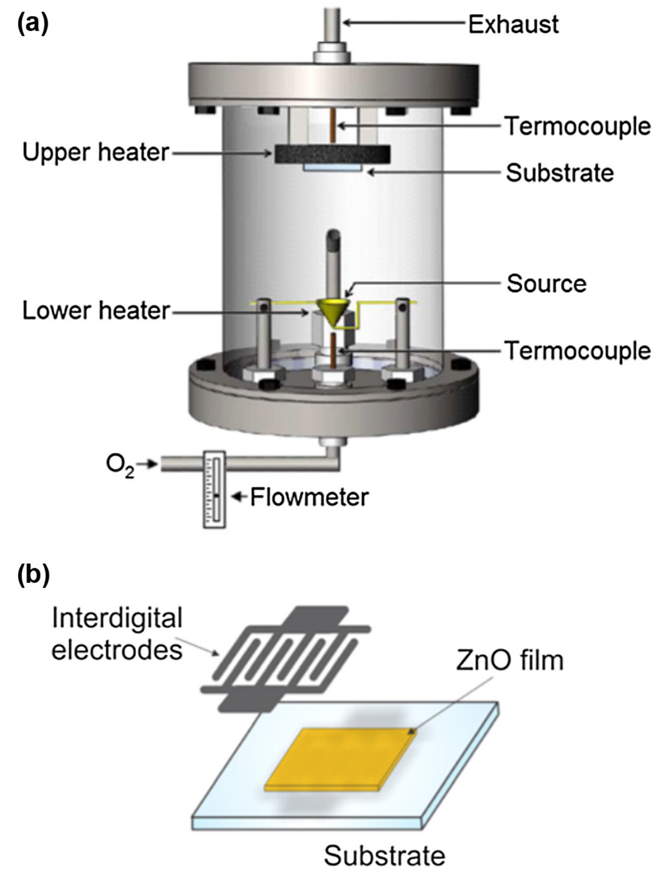

Fig. 1. (a) Schematic drawing of the SSCVD system; (b) Schematic illustration of the sensor fabrication.

stages of film formation result in a random distribution of small crystallites, acting as a nucleus for further growth [17]. By increasing the deposition temperature to 350 °C, a higher densification in the film is observed (Fig. 2b), this can be attributed to enhanced surface diffusion, resulting in more homogeneous grains. Regarding the film thickness, it increases from 540 nm, 650 nm to 790 nm for deposition temperatures of 300, 350 and 400 °C, respectively.

In the particular case of a deposition temperature of 400 °C (Fig. 2c), plate-like ZnO structures are uniformly distributed over the surface of the film with lateral dimensions of 200–600 nm and thicknesses of 50 nm. At this temperature, the higher ZnO volatility, and the subsequent high vapor pressure, would prevent the nucleation and growth of crystal orientations different from those with the lower energy [18]. Consequently, the plates are preferentially oriented along (0001) directions. Kaneti et al. demonstrated that (0001) planes of ZnO plates exposed to the gas species, show higher sensitivity in the detection due to higher surface area over other planes [19].

Surface roughness determines the effective surface area of the films and hence it is an important parameter for sensor applications, playing a major role on sensitivity. In the present work, Atomic Force Microscopy (AFM) was used to investigate the surface roughness of the films over an area of 100 μm^2. Fig. 3 shows the AFM surface images of the ZnO films deposited at different temperatures. The root-mean square (RMS) surface roughness of the ZnO films deposited at different deposition temperatures is determined from the AFM measurements shown in Table 1. This increase in surface roughness is consistent with an adherence increase from particles in the gas phase, which would render a higher deposition ratio.