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Effect of different dopant elements (Al, Mg and Ni) on microstructural, optical and electrochemical properties of ZnO thin films deposited by spray pyrolysis (SP)

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ABSTRACT

In the present work we studied the influence of the dopant elements and concentration on the microstructural and electrochemical properties of ZnO thin films deposited by spray pyrolysis. Transparent conductive thin films of zinc oxide (ZnO) were prepared by the spray pyrolysis process using an aqueous solution of zinc acetate dehydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] on soda glass substrate heated at 400 ± 5 °C. $AlCl_3$, $MgCl_2$ and $NiCl_2$ were used as dopant. The effect of doping percentage (2–4%) has been investigated. Afterwards the samples were thermally annealed in an ambient air during one hour at 500 °C. X-ray diffraction showed that films have a wurtzite structure with a preferential orientation along the (002) direction for doped ZnO. The lattice parameters *a* and *c* are estimated to be 3.24 and 5.20 Å, respectively. Transmission allowed to estimate the band gaps of ZnO layers. The electrochemical studies revealed that the corrosion resistance of the films depended on the concentration of dopants.

1. Introduction

Zinc oxide is a material that belongs to the family of transparent conductive oxides (TCO). Its non-toxicity, abundant availability in the earth [1,2], easy fabrication, good electrical, optical and

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piezoelectronic behavior compared with other possible materials such as ITO, Cd_2SnO_4, In_2O_3 and SnO_2 make this material favorable for applications [3,4]. Additionally ZnO is a semiconductor [5], with a hexagonal wurtzite structure [6], a large band gap (3.3 eV) and a large exciton binding energy 60 meV [7]. It has a high stability [8] and transparency in the visible long waves region. Its resistivity varies in the range $(10^{-3}, 10^5)\,\Omega$ cm [9]. The electrical conductivity of ZnO is controlled by intrinsic defects namely oxygen vacancies and/or zinc interstitials. The resistivity is lowered further by extrinsic doping with group III elements (B, Al, Ga, and In) [10] and IV elements (Pb, Sn) [3] of the periodic table. Thin films of ZnO can be used as a window layer and electrodes on hydrogenated amorphous silicon based solar cells [3]. In addition ZnO thin films offer a variety of applications in integrated piezoelectronic optics, gas sensitive devices [8], transparent electrodes [11] and Light Emitting Diodes (LEDs) [6]. These materials have been prepared by a variety of techniques and are described in the literature (R.F magnetron sputtring, Pulsed Laser Deposition (PLD) [12], reactive evaporation, electron beam evaporation, Chemical Vapor Deposition (CVD), Chemical Bath Deposition (CBD) [9,13], Metal Organic Chemical Vapor Deposition (MOCVD), sol–gel and spray pyrolysis [14–17]).

Many researchers have deposited ZnO thin films by spray pyrolysis technique [16,17]. In this deposition technique, a starting solution containing the Zn and the dopant precursors is sprayed over a hot substrate by means of a nozzle and assisted by a carrier gas. When the fine droplets reach the substrate, the solid compounds react to become a new chemical compound. The quality and the physical properties of the films depend on the deposition parameters such as substrate temperature, molar concentration of the starting solution [18], post treatment, doped materials [19], spray rate, type and rate of carrier gas and geometric characteristics of the spray system [18]. The Spray Pyrolysis (SP) technique has some advantages compared to other methods. It is simple [13] and non-expensive [20]. It is also easy to include in an industrial production line [21], and the produced films can be controlled step by step (e.g., thickness is sensitive to the number of cycles and the rest time) [4].

2. Experimental procedure

ZnO thin films were grown by using the chemical spray pyrolysis technique onto a glass substrates using zinc acetate dehydrate $[Zn(CH_3COO)_2{\cdot}2H_2O]$ as precursor. The spray solution was prepared from a mixture of 0.2 M $[Zn(CH_3COO)_2{\cdot}2H_2O]$ (Sigma–Aldrich) 99.9% purity dissolved in pure ethanol. It is aimed that to obtain doped ZnO thin films with aluminium, magnesium and nickel were added in solution by using $AlCl_3.6H_2O$, $MgCl_2.6H_2O$ and $NiCl_2.6H_2O$ compounds respectively. The atomic percentages of [Al/Zn], [Mg/Zn], [Ni/Zn] were 2, 3 and 4 at.%, respectively. The initial pH value of solution was measured as 6, and then a small amount of hydrochloric acid (HCl) was added to the solution in order to prevent the formation of zinc hydroxide. The resulting solution was stirred at 60 °C for 20 min for yielding a clear and homogenous solution. Glass slides (2.2×2) cm were used as substrates. Before loading into the system, the substrates were washed with detergent and then completely rinsed in methanol, acetone and deionized water and finally dried in air. Then the substrates were progressively heated up to the required temperature, before being sprayed on. The deposition temperature (Ts) (temperature at the substrate surface) was maintained at 400 °C with an accuracy of ±5°. The latter is measured using a Chrome–Nickel thermocouple. During the pyrolytic process, the following possible reactions take place [12].

$$(Zn(CH_3COO)_2 \cdot 2H_2O) + 2(C_2H_5OH) \rightarrow ZnO + 2(CH_3COC_2H_5) + 3H_2 + \frac{5}{2}O_2 \uparrow \quad (1)$$

The spraying time was 20 min and the spray rate of the solution was maintained at (5 ml/min). The distance between the atomizer and the substrate was kept fixed at 30 cm vertically. The obtained samples were annealed in furnace (Barnsted Termolyne Type 6000) at a temperature of 500 °C during one hour.

The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a (Siemens D-5000) with (CuKα) radiation $\lambda_{K\alpha} = 1.54056$ Å. Surface morphology was examined by a JEOL, JSM 6400 model scanning electron microscope (SEM) operating at 7 kV. The absorption spectra of the films were carried out using spectrophotometer with double beam "UV–visible" in a wavelength range of 300–1100 nm. The thickness of the films was determined with a profilometer Dektek [3].