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Modification of morphological and optical properties of ZnO thin film

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Abstract

Zink oxide thin films were prepared using different wet-processing techniques to study the morphological and optoelectronic properties. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) have been utilized to study the effect of technique and preparation procedure on the morphology of the films. The spin coated ZnO layers have exhibited ripple-shaped morphological features. Using the growth process with $ZnCl_2$ and $Al(NO_3)_3$ doping at different time has shown a change in surface morphology. UV–Visible absorption spectroscopy was used to understand the absorption behaviour and so to calculate the energy gap (E_g) for the films produced. It has been revealed that E_g of the ZnO thin film increases with the increasing of the number of layers spun onto the substrate. $ZnCl_2$ doping has no quite big change in E_g values, however, $Al(NO_3)_3$ has resulted in a higher E_g value.

Keywords: ZnO; Spin coating; Sol–gel; SEM; AFM

1. Introduction

Zinc oxide is well-known as a wide direct band gap of 3.3 eV semiconductor at room temperature [1]. Even though physical techniques such as molecular-beam epitaxy, sputtering [2–4] and spray pyrolysis [5] have been widely used, sol–gel method is mainly modified to produce ZnO colloids and films in simple, low-cost and highly-controlled method [6]. Sol–gel ZnO is normally deposited from a zinc precursor dissolved in water or an alcohol controlled by an additive acting as a chelating agent [6,7]. The sol–gel procedure is permitted producing a solid material from a solution by the means of a sol or a gel as a transitional step, and at lower temperatures than traditional methods of preparation [8,9]. Currently, two sol–gel methods are used based on the type of the molecular precursors; metal alkoxides in organic solvents or metal salts in aqueous solutions [8]. The explanation of ZnO film's preparation is included several steps and a combination of the two sol–gel methods. ZnO films are prepared using inorganic salts such as nitrates, chlorides, perchlorates or organic salts like acetates and acetylacetonates, dissolved in alcoholic solvents. Generally, this process consists of two steps: the first

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one includes in situ formation of alkoxide or alkoxy-complexes. In the second step, the oxide is formed when these complexes undergo transformation through hydrolysis and polymerization [9]. Several authors have reported different structural, optical, morphological, electrical and physical properties of ZnO thin films deposited by different methods [10–12]. ZnO nanostructures can be acquired in different geometries such as nanorods, nanoflowers, nanodots, nanowires, nanopyramids, and nanohexagons [13–18]. In the current study, the variations in the morphological and optical properties were determined using scanning electron microscopy (SEM) and UV–visible absorption spectroscopy. Different spin coating parameters as well as spray coating methods were employed. Additionally, different growth time was used to investigate the effect of the latter on the optical and morphological properties for ZnO thin film for applications in opto-electronic devices.

2. Experimental procedure

2.1. Preparation methods of ZnO solution

Sol–gel method was used to prepare the 1% Mole of ZnO precursor which was prepared by the following procedure: (1) Monoethanolamine (MEA) (0.17 ml) was dissolved in 5 ml 2-Methoxy ethanol (2ME) under stirring without heat for 10 min. Afterward, zinc acetate dehydrated (0.6 g) was added slowly to the solution under stirrer; small amount of HCL (37%) was wisely dropped to the final solution to increase the reaction. The final solution was stirred for another 10 min at room temperature, and then aged in a desiccator in dark overnight; the resulted solution was used for spin coating processes. (2) Similar procedure and concentrations were used to prepare the precursor solution for spray coating method based water instead of 2ME:MEA co-solvent. Furthermore, another solution was prepared for the growth step using (1:1) molar ratio of MEA to zinc acetate, which were dissolved in 20 ml water and stirred for 20 min at room temperature.

2.2. ZnO thin film preparations

ZnO thin films were prepared using different conditions and preparation methods as shown in Fig. 1. Spin coating method was employed to prepare the reference ZnO layer as in Fig. 1(a); ZnO films were spin coated on a cleaned glass substrates at 4000 rpm/30 s, the films were left to dry in air for 30–35 min before hot plate annealing at 100 °C for 10 min (Reference layer). This layer was then used to the second step which is the grow process as demonstrated in Fig. 1(b); the latter was done with different dopants ($Al(NO_3)_3.9H_2O$ and $ZnCl_2$) and different substrates (glass and Al sheet). The molar ratio of the dopant was kept constant for the two types of dopants with the ratio of 1:0.1 of ZnO: dopant, respectively. Furthermore, spray coating method was also used to prepare ZnO thin film as shown in Fig. 1(c) under controlled condition such as stable pressure and fixed distance between the gun and the substrate. ZnO films were spray coated on the cleaned glass for 2 times with a distance 20 cm and the final films were left to dry in air for 30–35 min before hot plate annealing at 100 °C for 10 min. All the layers were subjected to further annealing in a furnace under controlled temperature; the temperature steps have been increased gradually from room temperature to 250 for 2 h and then kept at this temperature for 2 h,

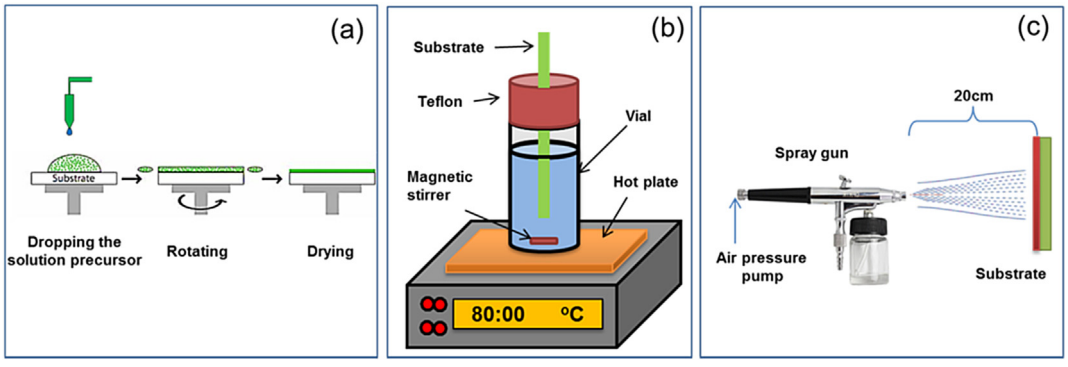

Fig. 1. The preparation methods of ZnO thin films; (a) spin coating method to prepare the reference ZnO layer; (b) the growth process after the reference layer preparation; (c) spray coating method using hand held spray gun.